Probing Exotic Superconducting Order Parameters Using Point-Contact Andreev Reflection Spectroscopy

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
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Abstract

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Point-contact Andreev reflection spectroscopy measurements were performed on various unconventional superconducting systems, as a function of temperature and magnetic field, to probe their superconducting order parameter symmetries.

Low-temperature differential conductance measurements on the heavy-fermion system PrOs$_4$Sb$_{12}$ revealed multiple spectral features, including distinct evidence for gap nodes in the superconducting order parameter. A field-driven change in order parameter symmetry was also observed confirming the existence of multiple superconducting phases with different symmetries in PrOs$_4$Sb$_{12}$. The effect of Ru doping in Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ was studied and the spectral evolution is interpreted in terms of multigap pairing. Our data which indicates that the nodal order parameter is rapidly suppressed by the introduction of Ru is consistent with other experimental results.

Point-contact tips were fabricated from the high-$T_c$ superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) and used to form high impedance junctions with CrO$_2$ to determine how the formation of Andreev bound states is effected by spin polarization. Strong suppression of the $d$-wave Andreev reflection characteristics were observed in the YBCO/CrO$_2$ junctions indicating that spin polarization prevents Andreev surface states from forming. The point contacts were estimated to be on the order of several nanometers in size, attesting to their microscopic nature and demonstrate the feasibility of using superconducting high-$T_c$ tips
as spin-sensitive nanoprobes of itinerant ferromagnets.

Point-contact Andreev spectroscopy measurements were performed on single crystal samples of the heavy-fermion superconductor CeCoIn$_5$. The temperature dependence of the differential conductance spectrum, measured down to 150 mK, showed multiple features whose characteristics depended on the junction impedance. Spectral analysis revealed two co-existing order parameters with nodal symmetry indicating a highly unconventional pairing symmetry in CeCoIn$_5$. The magnetic field dependence of the differential conductance spectrum, where the applied field was parallel to the $c$-axis, was measured and the upper critical field observed was consistent with that determined by other experimental studies.

Low-energy peak structures were observed in low-temperature differential conductance measurements performed on the itinerant ferromagnet ZrZn$_2$. The temperature and field dependence of the spectra were measured and discussed within the context of surface superconductivity known to exist in ZrZn$_2$. 

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To my parents
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Chapter 1

Introduction

1.1 Superconductivity

In 1908 H.K. Onnes successfully liquefied helium and three years after this pioneering achievement he discovered superconductivity when he found that on cooling below 4.15 K, the electrical resistivity of mercury abruptly dropped to zero. Several elemental metals and alloys were subsequently found to exhibit superconductivity and after several decades the highest superconducting transition temperature $T_c$ was $\sim 23$ K in Nb$_3$Ge. In 1933 Meissner and Ochsenfeld observed that magnetic flux could not penetrate into a superconductor$^1$ and this phenomena, another signature of superconductivity, is now known as the Meissner effect.

Soon after the discovery of superconductivity much effort was put forth toward constructing a theory to explain the underlying mechanism. Based on Landau’s theory of second order phase transitions, Ginzburg and Landau introduced a complex wavefunction $\psi(r)$ as the superconducting order parameter. While the Ginzburg-Landau theory successfully predicted various macroscopic phenomena observed in superconductors, it was a phenomenological theory and the microscopic origin of superconductivity remained

$^1$To within a penetration depth $\lambda$
unknown. In 1956 L.N. Cooper showed that the entire Fermi sea of electrons become unstable if two electrons experience an arbitrarily weak attractive interaction such that a bound Cooper pair is formed [8]. The Coulomb repulsion between electrons, which would make the formation of a Cooper pair seem unlikely, can be overcome via electron-phonon coupling. Based on Cooper’s work that any attractive interaction between two electrons can lead to the formation of a bound pair, J. Bardeen, L. N. Cooper, and J. R. Schrieffer developed a quantum mechanical description for many Cooper pairs residing in a common ground state [9]. Their theory, now referred to as the BCS theory of superconductivity, demonstrated that a finite, isotropic (s-wave) energy gap exists between the ground state and elementary excitations of a superconductor and they also successfully predicted the temperature dependence of the energy gap. The BCS theory also yielded that superconductivity was a result of a second-order phase transition and correctly predicted the Meissner effect, the isotope effect, the temperature dependence of the specific heat and penetration depth.

However, with the perpetual quest to increase $T_c$ and to elucidate the interplay between superconductivity and magnetism, superconductors with extremely unusual properties began to emerge. Superconductivity in a heavy-fermion metal\textsuperscript{2}, CeCu$_2$Si$_2$, was first reported in 1979 [10]. Soon after, several other heavy-fermion superconductors were discovered and experimental evidence indicated that in some of these materials the superconducting energy gap was not fully isotropic - i.e. the pairing symmetry was not s-wave. In 1986 superconductivity was observed in a Ba-La-Cu-O system where $T_c \sim 30$ K [11], considerably higher than the highest value known at that time. Other copper-oxide based superconductors such as La$_{2-x}$Sr$_x$CuO$_4$, YBa$_2$Cu$_3$O$_{6+x}$ and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+x}$ were soon discovered and $T_c$ was raised above the boiling point of liquid nitrogen (77 K). Such a rapid increase in $T_c$ generated tremendous excitement and renewed interest in the field of superconductivity, particularly since these new superconductors exhibited a host

\textsuperscript{2}Refer to Chapter 1.2.1 for definition
of unconventional properties, including experimental evidence for an anisotropic $d$-wave energy gap. While electron-phonon interactions are responsible for Cooper pairs forming in conventional superconductors, the pairing mechanism in the unconventional heavy-fermion and high-$T_c$ superconductors remains unknown. Conventional superconductors are characterized by spin singlet $S = 0$ pairing and by a $s$-wave $L=0$ energy gap where $S$ and $L$ are the total spin and orbital angular momentum quantum numbers respectively. In unconventional superconductors the pairing may be spin singlet ($S = 0$) or triplet ($S = 1$) and $L > 0^3$. For example the spin singlet $d$-wave pairing state is given by $S = 0$ and $L = 2$. Determining the pairing symmetry in unconventional superconductors is critical to understanding the nature and origin of the superconducting state. This chapter introduces the compounds that were investigated in this study, along with some of their key unconventional superconducting properties.

1.2 Unconventional Superconductors

1.2.1 Heavy Fermion Metals

Many intermetallic compounds that contain an atom which has a partially filled $4f$ or $5f$ electron shell (usually Ce, Pr, Yb or U) are referred to as heavy-fermion systems. These materials are termed heavy-fermion because at low temperatures the conduction electrons are strongly coupled to the localized $f$-electrons, resulting in an effective mass $m^*$ that appears enormously enhanced compared to the bare electron mass $m_e$. The existence of heavy itinerant quasiparticles have been confirmed by the observation of extremely large Sommerfeld coefficients $\gamma$ in the specific heat, highly temperature dependent de-Haas-van-Alphen (dHvA) oscillation amplitudes, a virtually temperature independent Pauli-

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3A strict definition of unconventional superconductivity is given in terms of symmetry breaking on going from the normal to superconducting phase. While all superconductors, conventional and unconventional, break gauge symmetry in the superconducting phase, unconventional superconductors break additional symmetry - orbital, spin, time reversal [12, 13].
like magnetic susceptibility and a $T^2$ low temperature dependence of $\rho$, the electrical resistivity.

The formation of a heavy-fermion electronic state arises from the presence of localized $f$-electrons and can be explained by an extension of the single impurity Kondo model. In the Kondo model a dilute concentration of magnetic impurities embedded in a non-magnetic host will display local-moment behaviour at high temperatures. At lower temperatures, the conduction electrons begin to screen the magnetic impurities resulting in a non-magnetic ground state. This effective screening which results in the demagnetization of the local moment causes a logarithmic increase in the electrical resistivity at low temperatures, which eventually saturates as the temperature approaches zero. In heavy-fermion systems however the $f$-electrons form a periodic lattice of magnetic moments and are not strictly a dilute concentration of randomly scattered magnetic impurities as assumed in the Kondo model for an isolated impurity. In the lattice-Kondo model, where the local moments have the lattice periodicity, coherence effects arise at low temperatures resulting in a decrease in scattering and the formation of a heavy-electron band. While Kondo screening results in a spin compensated ground state, many heavy-fermion metals exhibit magnetic order at low temperatures. The Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction allows coupling between local moments through the conduction electrons and this leads to the formation of an antiferromagnetic or ferromagnetic ground state. The competition between Kondo screening and the RKKY interaction determines the magnetic nature of the ground state in heavy-fermion systems [14, 15, 16, 17, 18].

In conventional superconductors, the addition of magnetic impurities rapidly destroys the superconducting state [19] and so the discovery of superconductivity in the heavy-fermion compound CeCu$_2$Si$_2$, where the $f$-electrons form a lattice of local magnetic moments, was remarkably surprising [10]. Soon after, superconductivity was observed in several other heavy-fermion materials such as UBe$_{13}$ [20] and UPt$_3$ [21] and many other systems. Heavy-fermion superconductors are generally classified as being uncon-
ventional because many of them exhibit properties which deviate from that predicted by BCS theory. An extremely large jump in the specific heat is observed at $T_c$ in these compounds confirming that it is indeed the heavy-electrons that partake in the superconducting pairing. Also, experimental evidence has indicated the presence of $k$-space nodes in the superconducting gap function for many heavy-fermion superconductors. In fact in UPt$_3$ it has been shown that multiple superconducting phases exist and that a spin triplet $S = 1$ pairing state might be favoured [22]. Although the electron pairing mechanism in heavy-fermion superconductors remains unknown, it appears unlikely that simple electron-phonon interactions are responsible and it is widely speculated that spin fluctuations play a prominent role in the formation of Cooper pairs [23].

The superconducting transition temperature for most heavy-fermion superconductors is quite low - $T_c \leq 1$ K. Two notable exceptions are the recently discovered compounds PrOs$_4$Sb$_{12}$ and CeCoIn$_5$ which have $T_c = 1.85$ and $T_c = 2.1$ K respectively\footnote{The heavy fermion compound PuCoGa$_5$ also has an unusually large superconducting transition temperature with $T_c \sim 18.5$ K.}. Although evidence for an unconventional superconducting state has been observed in both compounds, the pairing symmetries remain unknown.

**PrOs$_4$Sb$_{12}$**

PrOs$_4$Sb$_{12}$ belongs to the family of compounds known as the filled skutterudites. Figure 1.1 illustrates the cubic crystal structure of PrOs$_4$Sb$_{12}$ and shows that the central Pr atom is surrounded by eight canted OsSb$_3$ octahedra\footnote{Image provided by W. M. Yuhasz and M.B. Maple.}. The filled skutterudite compounds, whose chemical composition is given by RM$_4$X$_{12}$ where $R$ is a rare earth element, $M$ is Fe,Ru or Os and $X$ is P, As or Sb, exhibit a rich variety of exotic phenomena which include superconductivity, heavy-fermion behaviour, antiferromagnetic and ferromagnetic ordering, quadrupolar ordering and non-Fermi liquid behaviour.

Although superconductivity has been observed in several heavy-fermion metals, al-
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most all of these materials contain either Ce or U. The discovery of superconductivity in
PrOs$_4$Sb$_{12}$ was quite remarkable as it is neither Ce nor U based [24]. Specific heat mea-
surements were amongst the first to characterize the heavy-fermion nature of PrOs$_4$Sb$_{12}$
and found that the effective electron mass was approximately 50 times larger than the
bare electron mass$^6$[24]. Specific heat measurements which observed a double supercon-
ducting transition at $T_{c1} \sim 1.85$ K and $T_{c2} \sim 1.7$ K provided early indication that the
superconducting state of PrOs$_4$Sb$_{12}$ may be unconventional[25, 26, 27].

Double superconducting transitions have been observed in the specific heat for both
U$_{1-x}$Th$_x$Be$_{13}$ for $0.02 \leq x \leq 0.04$ [28] and UPt$_3$ [29], two heavy-fermion superconductors
which exhibit multiple superconducting phases [22, 30, 31]. Angular magnetothermal
conductivity $\kappa(H, \phi)$ measurements made to map out the superconducting magnetic field

$^6$Although heavy-fermion behaviour and superconductivity have been observed in the filled skutterudite family of compounds before, PrOs$_4$Sb$_{12}$ is the first instance where both occur in the same material.
versus temperature \((H - T)\) phase diagram of PrOs\(_4\)Sb\(_{12}\) found that for a magnetic field rotated within the \(ab\) plane, the angular variation of the \(c\)-axis thermal conductivity changed modulation depending on the strength of the applied field [1]. The data indicated that the order parameter symmetry undergoes a field-induced phase transition from two point nodes at low fields to six point nodes at high fields. Specific heat [2, 32] and ac magnetic susceptibility \(\chi\) [33] measurements however have not observed this transition.

Figure 1.2 compares the \(H - T\) phase diagrams obtained by (a) \(\kappa(H, \phi)\) [1] and (b) specific heat measurements [2]. The specific heat data shows that the \(H_{c2}(T)\) and \(H'(T)\) curves run parallel to each other and their temperature dependence is identical with the exception that the \(H_{c2}\) curve terminates at \(T_{c1}\) while the \(H'(T)\) curve terminates at \(T_{c2}\). The \(\kappa(H, \phi)\) measurements on the other hand show that the temperature dependence of the \(H_{c2}(T)\) and \(H'(T)\) curves is different and that \(H'(T)\) separates the low-field (B) and high-field (A) superconducting phases which have different order parameter symmetries.

![Magnetic field vs temperature phase diagram](image)

Figure 1.2: Magnetic field vs temperature phase diagram obtained from (a) angular magnetothermal conductivity and (b) specific heat measurements. The \(H'\) and \(H_{c2}\) curves in (a) are non-parallel and the separate low-field (B) phase where the order parameter symmetry contains two point nodes from the high-field (A) phase where it contains six point nodes. The \(H_{c2}\) and \(H'\) curves in (b) run parallel with each other and terminate at \(T_{c1}\) and \(T_{c2}\) respectively. Reprinted with permission from (a) Ref [1] and (b) adapted from Ref [2]. Copyright by the American Physical Society (a) 2003 and (b) 2004.
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After superconductivity in a material is discovered, a flurry of experiments are usually performed in an attempt to determine the structure of the superconducting gap function. In the case of PrOs$_4$Sb$_{12}$, despite numerous experimental and theoretical studies, its superconducting gap topology has still not been established. Muon-spin resonance ($\mu$SR) [34], Sb-nuclear quadrupolar resonance [35], scanning tunnelling spectroscopy [36], and thermal conductivity $\kappa(T,H)$ [37] measurements have shown the Fermi surface to be fully gapped in the superconducting state. On the other hand, penetration depth [38] and specific heat [25, 39] measurements, which exhibit a low temperature power-law dependence, suggest the presence of nodes in the superconducting energy gap. Small angle neutron scattering results which indicated a strongly distorted flux-line lattice due to an anisotropic superconducting gap [40] and $\kappa(H,\phi)$ measurements [1] have also provided evidence for a nodal gap structure. Zero-field $\mu$SR measurements have revealed the spontaneous appearance of an internal magnetic field below $T_c$ associated with broken time reversal symmetry [41], providing further evidence for an unconventional superconducting state in PrOs$_4$Sb$_{12}$.

dHvA measurements and band structure calculations performed on PrOs$_4$Sb$_{12}$ showed that multiple bands cross the Fermi surface. Two separate $\kappa(T,H)$ studies have indicated that multiple bands are superconducting in PrOs$_4$Sb$_{12}$ [37, 42] and a theoretical proposal based on multiple superconducting bands has been put forth to reconcile the difference between experiments that observe a nodal gap structure and those that observe fully gapped ones[43]. One of the $\kappa(T,H)$ studies, which reported that while one band was fully gapped the other contained nodes [42], would be consistent with the theoretical proposal. However, bulk thermal transport across a sample could potentially be susceptible to sample inhomogeneities, making it desirable to investigate the superconducting order parameter of PrOs$_4$Sb$_{12}$ using a highly local probe such as point-contact Andreev spectroscopy.

Chemical doping is commonly used to provide further insight about the supercon-
ducting state of a material. In PrOs$_4$Sb$_{12}$ replacing Os with Ru dramatically alters the superconducting properties. PrRu$_4$Sb$_{12}$ which has $T_c \sim 1.0$ K, does not appear to be a heavy-fermion metal [44] and several experiments have indicated that the superconducting energy gap is isotropic [45, 46]. $\kappa(T, H)$ measurements however have suggested that multiple superconducting bands, both fully gapped, exist in PrRu$_4$Sb$_{12}$ [42]. Figure 1.3 shows the dependence of $T_c$ on the Ru concentration in Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ as measured by electrical resistivity and magnetic susceptibility [3]. A minimum in $T_c$ is observed for $x \sim 0.6$, indicating that there may be a competition between the superconducting orders of PrOs$_4$Sb$_{12}$ and PrRu$_4$Sb$_{12}$.

![Figure 1.3](image.png)

Figure 1.3: Superconducting transition temperature $T_c$ as a function of Ru doping $x$ as determined by resistivity and ac susceptibility. Reprinted with permission from Ref. [3]. Copyright 2004 by the American Physical Society.

CeCoIn$_5$

The CeMIn$_5$ (where M = Co, Ir or Rh) family of heavy-fermion compounds have a tetragonal crystal structure and can be viewed as alternating layers of CeIn$_3$ and of MIn$_2$ along the c-axis, as illustrated in Figure 1.4. The parent compound CeIn$_3$ is a heavy
fermion metal [47, 48] with a cubic crystal structure and at ambient pressure an onset of antiferromagnetic ordering occurs at the Neel temperature $T_N \sim 10$ K [49]. On applying pressure $p$, $T_N$ is gradually suppressed and at $p \sim 24$ kbar a superconducting state with $T_c \sim 0.2$ K is realized [50, 51]. Not surprisingly, the tetragonal variants of CeIn$_3$ display a mixture of antiferromagnetic and superconducting order that can be tuned using non-thermal parameters such as pressure and doping.

At ambient pressure CeRhIn$_5$ orders antiferromagnetically, with $T_N = 3.8$ K. Under pressure $T_N$ is suppressed and, similar to CeIn$_3$, eventually gives rise to a superconducting state with $T_c \sim 2$ K at $p \sim 16$ kbar [52]. Very recent experiments have however shown that bulk superconductivity and antiferromagnetism may coexist at ambient pressure [53]. CeIrIn$_5$ and CeCoIn$_5$ do not order antiferromagnetically but both display bulk superconducting transitions $T_c \sim 0.4$ K and $T_c \sim 2.1$ K respectively at ambient pressure [54, 55]. The unique interplay between antiferromagnetism and superconductivity in these compounds strongly suggest that magnetic interactions play a role in electron pairing.
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Thermal conductivity, specific heat and NQR studies have all indicated the presence of nodes in the superconducting gap function of CeCoIn$_5$, consistent with a $d$-wave pairing symmetry[56, 57]. On rotating a magnetic field around the $ab$ plane, a four-fold oscillation was observed in both the $c$-axis $\kappa(H, \phi)$ [58] and $C(H, \phi)$ [59] measurements, consistent with a nodal $d$-wave order parameter. However, the $\kappa(H, \phi)$ study indicates that the nodes occurs along the [110] directions, suggesting a $d_{x^2-y^2}$ symmetry [58], while the $C(H, \phi)$ data indicates nodes along the [100] directions, suggesting a $d_{xy}$ symmetry. dHvA experiments and band structure calculations have confirmed the highly renormalized effective electron mass ($m^* \sim 100\, m_e$) and identified multiple sheets crossing the Fermi energy [60, 61, 62, 63, 64]. With such a complex Fermi topology it is possible that multiple bands, with different pairing symmetries, are involved in superconductivity [65, 66, 42].

Specific heat [67] and dc magnetization [68] measurements were the first to reveal an anisotropic upper critical field in CeCoIn$_5$. For an applied field oriented parallel to the $c$-axis $H_{c2,||c} \sim 5$ T, while for a field perpendicular to the $c$-axis $H_{c2,\perp c} \sim 12$ T. A spin singlet Cooper pair can be destroyed by a magnetic field through either the orbital effect or through Pauli suppression. The orbital limit is realized because a Cooper pair consists of two electrons with opposite momentum and when a field is applied the Lorentz force experienced by each electron acts in opposite directions thereby effectively ripping the pair apart [69]. In the Pauli limit, the Cooper pair which consists of one spin up and one spin down electron is destroyed because both electrons try to align themselves in the same direction as the magnetic field [70, 71]. The upper critical field in a material is therefore determined by the relative strength between the orbital and Pauli limits. In superconductors that are Pauli limited, Fulde-Ferrell and Larkin-Ovchinnikov proposed that the Pauli pair breaking effect could be reduced if electrons formed a new, finite (non-zero) momentum pairing state [72, 73]. Despite being proposed over 40 years ago, experimental observation of the FFLO state has proved to be quite difficult. Extremely clean systems where the upper critical field is Pauli limited are required to observed the FFLO state.
and few materials satisfy these criterion. CeCoIn$_5$ is however a potential candidate and several experiments such as specific heat, thermal conductivity, ultrasound velocity and NMR have suggested the possible existence of the FFLO state at low temperatures and high fields [74, 75, 76, 77, 78, 79].

1.2.2 High-$T_c$ Cuprates

Bednorz and Müller were investigating the Ba-La-Cu-O (LBCO) system when they found that at certain concentrations of La and Ba the system displayed a superconducting transition at $T_c \sim 30$ K. Soon after, several other materials with a lattice structure based on copper oxide planes, which seemed to be essential for superconductivity, were synthesized and the transition temperature was dramatically increased with $T_c \sim 155$ K being observed in the Hg-Ba-Ca-Ca-O system under pressure. The family of copper-oxide based compounds exhibiting extremely high superconducting transition temperatures became known as the high-$T_c$ cuprates. Along with their extraordinarily high $T_c$, the cuprates exhibit a host of fascinating phenomena suggesting that the superconductivity in these materials is more complicated than that given by the simple BCS model. While the generic behaviour of the entire cuprate family is similar, subtle differences do exist from material to material.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Several months after the report of superconductivity in LBCO, the cuprate YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) was found to be superconducting with $T_c \sim 90$ K, making it the first superconductor with a transition temperature above the boiling point of liquid nitrogen [80]. The parent compound YBa$_2$Cu$_3$O$_{6+x}$ where $x = 0$ is an antiferromagnetic insulator with $T_N \sim 400$ K. The crystal structure consists of copper-oxide ($\text{CuO}_2$) layers separated by charge reservoir layers (which serve to dope holes into the copper-oxygen plane) that are stacked along the $c$-axis. According to band theory the $\text{CuO}_2$ layer should be conducting.
The Cu\(^{2+}\) ion has a 3\(d^9\) electronic configuration and the tetragonal environment lifts the degeneracy such that the unpaired electron sits in the \(d_{x^2-y^2}\) orbital. As the filled copper and 2\(p\) oxygen band lie close to the half filled Cu band one would expect electrical conduction. However, the on site Coulomb repulsion between electrons is so large that the CuO\(_2\) plane remains insulating. Such materials where metallic transport is predicted by band theory but Coulomb repulsion results in an insulating state are known as Mott insulators.

As electrons are removed (equivalent to adding holes) from the CuO\(_2\) planes the transport properties change dramatically. Hole doping is achieved by adding oxygen to YBa\(_2\)Cu\(_3\)O\(_{6+x}\). The oxygen is added to the Cu chain layers located between the CuO\(_2\) planes. As oxygen is added, the crystallographic lattice changes from tetragonal to orthorhombic as the \(b\) axis (Cu-O chain) lattice parameter becomes slightly larger than that of the \(a\)-axis. Figure 1.5 shows the crystal structure of YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\).

As the oxygen content \(x\) is increased, \(T_N\) is suppressed and gives way to superconductivity. On further increasing \(x\), \(T_c\) rises to a maximum, known as optimal doping, and then starts to fall back down. When the hole concentration is less than that at optimal doping the system is said to be underdoped while when it is greater it is overdoped. Optimal doping in YBCO occurs at \(x \sim 0.94\). Figure 1.6 shows the effect of hole doping in YBCO. The phase diagram generically shows that as holes are introduced the antiferromagnetic order is suppressed, eventually resulting in superconductivity. Similar to how pressure is used in heavy-fermion materials such as CeIn\(_3\) and CePd\(_2\)Si\(_2\), doping is used in the high-\(T_c\) cuprates to tune the system from an antiferromagnet to a superconductor. This resemblance, where a superconducting phase develops as antiferromagnetic order is suppressed, suggests that magnetism may play a crucial role in pairing mechanism for the cuprates. The superconducting phase is strengthened until optimal doping (dome peak) is reached after which further increasing the hole concentration results in a Fermi-liquid ground state. The pseudogap phase that arises at low doping above the superconducting
dome has been extensively studied with evidence suggesting that in this region electron pairing without phase coherence occurs [81].

After the discovery of superconductivity in the high-$T_c$ cuprates several studies attempted to determine the pairing symmetry, strongly indicating a $d$-wave order parameter. The change in sign across a node expected for a $d$-wave order parameter was confirmed by tri-crystal experiments thereby establishing the pairing symmetry in the cuprates [82, 13]. One of the consequences of an anisotropic $d$-wave order parameter is that a zero-energy peak in the quasiparticle tunnelling conductance spectrum is expected\footnote{Detailed discussion is presented in Chapter 2.} [83, 84]. The observation of these zero-energy peaks, not predicted to exist for...
Figure 1.6: Temperature versus doping phase diagram for YBCO.

isotropic $s$-wave superconductors, in tunnelling measurements on the cuprates provided further evidence supporting a $d$-wave order parameter.

1.2.3 Ferromagnetic Superconductors

In conventional superconductors, the two electrons which form a spin singlet Cooper pair have opposite spin [9]. The ground state of a material that is ferromagnetically ordered consists of electron spins all aligned with each other. Therefore the coexistence of conventional (spin singlet) bulk superconductivity and ferromagnetism seems highly unlikely [85, 86]. It is plausible however that spin triplet Cooper pairs could exist in a ferromagnetic environment [87, 88, 89]. Ferromagnetic superconductivity was first reported in UGe$_2$ which orders ferromagnetically at a Curie temperature $T_{FM} \sim 53$ K. At ambient pressure UGe$_2$ is not superconducting but as pressure is applied $T_{FM}$ is reduced and superconductivity eventually appears [90]. It is important to note that superconductivity
in UGe$_2$ occurs deep in the ferromagnetic state ($T_c \ll T_{FM}$) where both orders coexist$^8$. In fact the temperature versus pressure phase diagram for UGe$_2$ indicates that both the ferromagnetic and superconducting phases terminate at the same pressure, suggesting that ferromagnetic order is necessary for superconductivity. Soon after the discovery of ferromagnetic superconductivity in UGe$_2$, ambient pressure superconductivity was reported in the ferromagnetically ordered states of URhGe [92], ZrZn$_2$ [93] and UCoGe [94].

ZrZn$_2$

ZrZn$_2$ crystallizes in a cubic lattice structure with ferromagnetism developing below $T_{FM} \sim 29$ K. Experimental studies have shown that pressure can be used to drive $T_{FM}$ to zero [95, 96] and since in many materials a superconducting state develops in the vicinity of suppressed magnetic order, ZrZn$_2$ is a potential candidate to display superconductivity. Evidence for superconductivity was eventually observed, at ambient pressure, in high-purity single crystal samples of ZrZn$_2$ [93]. Both the resistivity and magnetic susceptibility showed a superconducting transition at $T_c \sim 0.3$ K but specific heat measurements did not. Initially, it was speculated that this might be due to large parts of the Fermi surface remaining gapless, a plausible scenario given the unconventional nature of the superconducting state expected for ZrZn$_2$ [93]. However, more recent experiments have shown that it appears that the spark-erosion procedure used to cut ZrZn$_2$ crystals changes the chemical composition at the surface, inducing a thin superconducting layer [97]. This inhomogeneous surface layer, which is Zn depleted, is believed to be responsible for the superconducting transition seen in Ref. [93]. The superconducting layer forms on the surface of ZrZn$_2$ and although the stoichiometry of layer varies it is still interesting to study how the ferromagnetic ZrZn$_2$ affects the superconducting layer.

$^8$Superconductivity under pressure has also been observed in iron which is ferromagnetic at ambient pressure. However, iron is non-magnetic at the pressures at which superconductivity was observed and is therefore not a true ferromagnetic superconductor [91].
1.3 Previously Published Content

Some of the content presented in the subsequent chapters has already been published.

Chapter 4 - Part of the work detailed in this chapter has been published in:


Chapter 6 - Part of the work detailed in this chapter has been published in:

Chapter 7 - Part of the work detailed in this chapter has been published in:
Chapter 2

Electron Transmission Across a Metal-Superconductor Interface

The conductance across a junction formed between two normal metals is ohmic regardless of whether they are directly in contact with each other or if they are separated by an thin insulating barrier. However, because of the gapped excitation spectrum of a superconductor, the current-voltage \((I - V)\) characteristics of a normal metal-superconductor \((N - S)\) junction is markedly different depending on whether or not an insulating barrier is present at the interface. In this chapter the scattering processes at a \(N - S\) interface in the metallic (no barrier \(N/S\)) and tunnelling (insulating barrier \(N/I/S\)) regimes are discussed and the Blonder Tinkham Klapwijk (BTK) [4] theory which predicts the conductance spectrum in both limits is presented. BTK theory, originally formulated for \(s\)-wave superconductors, has since been generalized to enable theoretical predictions of the conductance spectrum for superconductors where the energy gap is anisotropic [83, 84]. The generalized-BTK theory and the manifestation of an anisotropic energy gap in the conductance spectrum will also be detailed in this chapter.
2.1 Scattering Processes at a $N/S$ Interface

2.1.1 Metallic Regime

Before describing a $N/S$ junction in the metallic regime, it is useful to consider a junction where both electrodes are normal metals ($N/N$). At $T = 0$ K, Fermi-Dirac statistics dictate that the electrons in a normal metal occupy states up to the Fermi energy $E_F$. The excitation spectrum of a metal, by definition, has accessible states at energies arbitrarily larger than $E_F$. Therefore, as shown in Figure 2.1, on applying a bias voltage across two metals in contact with each other, electrons simply flow from one metal to the other thus generating a current. The current due to the single particle transmission process is proportional to the bias voltage and linear (ohmic) $I - V$ behaviour is observed across the junction.

![Diagram of current flow in a junction formed between two normal metals subjected to a bias $eV$. As electronic states just above the Fermi energy exist in the normal metal, the electron simply travels from one electrode to the other.]

The excitation spectrum of a superconductor and normal metal are very different and replacing a normal metal electrode by one that is superconducting will change the $I - V$ characteristics of the junction. In superconductors, the elementary excitation spectrum
is separated from the ground state by an energy gap, $\Delta$. As a consequence, Cooper pairs in the ground state must be imparted a minimum energy $\Delta$ for quasiparticle excitations to exist in a superconductor. Figure 2.2 shows an electron propagating from a normal metal to a superconductor. For energies, $eV > \Delta$, electrons from the normal metal enter the superconductor as quasiparticle excitations. For $eV < \Delta$, there are no available states in the superconductor for the incoming electron. However, the incident electron can be retroreflected as a hole, allowing a Cooper pair to enter the superconducting condensate. This process, known as Andreev reflection, causes the net current across the $N/S$ interface for $eV < \Delta$ to be double that of $eV > \Delta$ [102, 103]. It should be noted that while in principle Andreev reflection is theoretically possible for energies $eV > \Delta$, its probability in this regime is greatly suppressed\(^1\).

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\(^1\)This is shown quantitatively in Chapter 2.2.
Figure 2.3 compares the $I - V$ characteristics of a $N/N$ and $N/S$ junction. In a $N/S$ junction, due to the conversion a of normal current to a supercurrent via Andreev Reflection, the sub-gap conductance is double the normal state conductance. The $I - V$ characteristics of a $N/S$ junction therefore show a departure from the linear behaviour observed in a $N/N$ junction.

![Figure 2.3: $I - V$ characteristics of (a) a $N/N$ showing linear behaviour and (b) $N/S$ junction where the conductance (slope of the $I - V$ curve) for $|eV| < \Delta$ is double that of $|eV| > \Delta$.](image)

### 2.1.2 Tunnelling Regime

Tunnelling is a well understood quantum mechanical phenomena that has no classical analogue. Consider an electron with energy $E$ incident upon a barrier with narrow width and strength $U$ such that $E < U$. Classically, as the electron does not have sufficient energy to cross the barrier, it would simply be reflected back. However, quantum mechanically, the amplitude of the electron wavefunction in the barrier is non-zero and hence a finite probability of the electron tunnelling through the barrier exists. The amplitude of the wavefunction exponentially decays inside the barrier and so the probability of tunnelling across the barrier depends upon its thickness.

Electron scattering at a $N/S$ interface is altered by the presence of an insulating barrier, $I$ (e.g. oxide layer, vacuum gap). Before considering a $N/I/S$ junction it is once
again useful to first consider tunnelling across a N/I/N junction. Shown in Figure 2.4 is a free electron with energy $E$ propagating along the $x$ direction toward a barrier with energy $U$ such that $E < U$. There are three distinct regions - region I ($x < 0$) which can be regarded as the normal metal the electron is incident from, region II ($0 < x < l$) the barrier through which the electron tunnels and region III ($x > l$) the normal metal which the transmitted electron propagates through. The electron wavefunction, $\psi$ in each region can be found by solving the Schrödinger equation:

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi = E\psi \quad (2.1)$$

where $\hbar$ is Planck’s constant and $m_e$ is the electron mass.

![Figure 2.4: Electron with energy $E$ (region I) approaching a barrier with energy $U$ (region II). Classically, since $U > E$, the electron would simply be reflected back. Quantum mechanically, however, there is a non-zero probability of the electron wavefunction tunnelling through the barrier and being observed in region III.](image)

The probability of the electron tunnelling through the barrier is obviously dependent upon the thickness of the barrier and transmission probability $T$ is given by [104]:

$$T \simeq e^{-2\kappa l} \quad (2.2)$$

where $\kappa = \sqrt{2m_e(U - E)/\hbar}$. Equation 2.2 shows that the probability of an electron tunnelling through a barrier decreases exponentially as the length $l$ is increased. To observe physically measurable tunnelling currents, $l$ typically needs to be on the order of
a few nanometers. For a fixed $l$, the tunnelling current is proportional to the bias voltage and therefore the $N/I/N$ junction is ohmic\textsuperscript{2}.

Replacing one of the normal metal electrodes by one that is superconducting ($N/I/S$ junction) results in a departure from the linear $I - V$ behaviour observed in $N/I/N$ junctions. Figure 2.5 shows an electron approaching a $N/I/S$ interface. The normal metal has accessible states at energies arbitrarily larger than $E_F$ while an energy gap $\Delta$ separates the ground state and quasiparticle excitation spectrum of the superconductor. For $eV > \Delta$, electrons incident from the normal metal enter the superconductor as quasiparticle excitations. However, for $eV < \Delta$ there are no available states in the superconductor for the incoming electron.

![Diagram of electron propagation at a $N/I/S$ interface](image)

Figure 2.5: Electron propagation at a $N/I/S$ interface. At energy $eV_A < \Delta$ the electron incident from the normal metal can not tunnel through the insulating barrier because energy spectrum of the superconductor is gapped. At energy $eV_B > \Delta$ the electron incident from the normal metal becomes a quasiparticle excitation in the superconductor.

In $N/S$ junctions, electrons with $eV < \Delta$ are converted to Cooper pairs via Andreev reflection. Such a process does not occur, however, in the classic, high-barrier $N/I/S$ junctions. The probability of one electron tunnelling through an insulating barrier is

\textsuperscript{2}Assuming single-electron capacitive charging can be neglected.
exponentially dependent on the barrier length as given by Equation 2.2. Andreev reflection occurs when the electron incident at the interface is retroreflected as a hole with opposite spin thus allowing a Cooper pair to enter the superconducting condensate. The conversion of a normal current to a supercurrent therefore requires that two electrons simultaneously cross the barrier. The probability of an incident electron and an electron of the correct spin and momentum required to form a Cooper pair both tunnelling through the barrier is exponentially smaller than that of just a single electron tunnelling through the barrier. As a result the Andreev reflection process is rapidly suppressed by the presence of an insulating barrier. Electrons with $eV < \Delta$ are therefore simply reflected back at a $N/I/S$ interface because they can neither undergo Andreev reflection nor, since the excitation spectrum is gapped, can they tunnel into the superconductor. Consequently, on applying a bias voltage smaller than the superconducting energy gap, no net current results across the junction. On applying a larger bias electrons are able to tunnel into the superconductor as quasiparticle excitations and linear $I - V$ behaviour is observed. Experimental [105, 106] and theoretical studies [107, 108] confirmed that the $I - V$ characteristics of $N/I/S$ junctions were indeed a measurement of the electronic density of states of a $s$-wave superconductor. Figure 2.6 compares the $I - V$ curve of a $N/I/N$ and $N/I/S$ junction.

Figure 2.6: $I - V$ characteristics of (a) a $N/I/N$ and (b) $N/I/S$ junction. For $|E| < \Delta$ electrons are reflected at the interface as they can not enter the superconductor and no net current results across the junction.
2.2 BTK Formalism

The scattering processes that occur at a $N/S$ and $N/I/S$ interface are very different and while the theory outlined in Chapter 2.1 describes the $I-V$ characteristics in the extreme metallic and tunnelling limits, it fails to describe the conductance in the intermediate regime. The BTK theory uses the Bogoliubov-de Gennes (BdG) equations to directly calculate the transmission and reflection probabilities at the interface. This approach, expanding on earlier work [109, 110, 111, 112], is extremely powerful because it takes into account both the excitation spectrum of a superconductor and it can be applied to barriers of arbitrary strength - not just the classic, high-barrier $N/I/S$ or metallic $N/S$ limits.

Figure 2.7: Energy vs momentum at the N-S interface depicting the reflection and transmission processes an electron, $O$, incident from a normal metal can experience. Reprinted with permission from Ref [4]. Copyright 1982 by the American Physical Society.

Figure 2.7 shows the energy versus momentum dispersion spectrum for a normal metal and superconductor. Consider the electron with energy $E > \Delta$ and momentum $q^+$ in the normal metal (labeled $O$) propagating toward the superconductor. There are four scattering processes that can occur at the interface: (A) The electron is retroreflected as a
hole (Andreev reflection), (B) the electron undergoes normal reflection, (C) the electron is transmitted across the interface and enters the superconductor as a predominantly electron-like excitation and (D) the electron is transmitted across the interface and enters the superconductor as a predominantly hole-like excitation. An implicit assumption is made that the direction of the group velocity \(v_g = dE/\hbar dq\), indicated by the arrows in Figure 2.7, of transmitted particles remains unchanged while that of reflected particles is reversed. The two other transmission cases \((q^+ \rightarrow -k^+\) and \(q^+ \rightarrow k^-)\) have not be considered because they would involve the group velocity reversing as the electron is transmitted across the interface.

Having identified all the scattering processes that occur at the \(N-S\) interface, their respective probabilities can be determined by solving the BdG equations. The BdG equations are given by:

\[
i\hbar \frac{\partial f}{\partial t} = \left( -\frac{\hbar^2 \nabla^2}{2m} - \mu(x) + V(x) \right) f(x,t) + \Delta(x) g(x,t) \tag{2.3}
\]

\[
i\hbar \frac{\partial g}{\partial t} = -\left( -\frac{\hbar^2 \nabla^2}{2m} - \mu(x) + V(x) \right) g(x,t) + \Delta(x) f(x,t) \tag{2.4}
\]

Equations 2.3 and 2.4 are simply the normal Schrödinger equations for electrons (2.3) and holes (2.4), coupled together by \(\Delta(x)\), and show that an elementary quasiparticle excitation in a superconductor exhibits both electron and hole-like properties. By setting \(\Delta(x) = 0\), Equations 2.3 and 2.4 are no longer coupled and, as expected, independently describe electron and hole-like excitations in normal metals.

Taking \(\mu(x)\) and \(\Delta(x)\) as constant and setting \(V(x) = 0\) (free electron approximation is made whereby the effect of positive ion cores of the lattice are neglected), solutions to Equations 2.3 and 2.4 are given by plane waves of the form:

\[
f(x,t) = \tilde{u}e^{i(kx-Et/\hbar)} \tag{2.5}
\]

\[
g(x,t) = \tilde{v}e^{i(kx-Et/\hbar)} \tag{2.6}
\]
Plugging the above trial solutions into Equations 2.3 and 2.4 and solving, the excitation spectrum is easily obtained:

\[ E^2 = \left[ \frac{\hbar^2 k^2}{2m} - \mu \right]^2 + \Delta^2 \]  
\[ (2.7) \]

and the BCS coherence factors can also be found [19]:

\[ \tilde{u}^2 = \frac{1}{2} \left( 1 \pm \frac{(E^2 - \Delta^2)^{1/2}}{E} \right) = 1 - \tilde{v}^2 \]  
\[ (2.8) \]

The wavefunction solutions to the set of coupled BdG equations can be written in the column vector form:

\[ \psi = \begin{bmatrix} f(x, t) \\ g(x, t) \end{bmatrix} \]  
\[ (2.9) \]

Combining Equations 2.5, 2.6 and 2.9 the wavefunctions in the normal metal \( \psi_N \) and superconductor \( \psi_S \) can be found:

\[ \psi_N = \begin{bmatrix} 1 \\ 0 \end{bmatrix} e^{iq^+x} + a \begin{bmatrix} 0 \\ 1 \end{bmatrix} e^{iq^-x} + b \begin{bmatrix} 1 \\ 0 \end{bmatrix} e^{-iq^+x} \]  
\[ \psi_S = c \begin{bmatrix} u_0 \\ v_0 \end{bmatrix} e^{ik^+x} + d \begin{bmatrix} v_0 \\ u_0 \end{bmatrix} e^{-ik^-x} \]  
\[ (2.10, 2.11) \]

where \( a, b, c \) and \( d \) are the coefficients associated with Andreev reflection, normal reflection, predominantly electron-like quasiparticle transmission and predominantly hole-like quasiparticle transmission processes respectively\(^3\). BTK modeled the elastic scattering that occurs at the N-S interface using a \( \delta \)-function potential where \( V(x) = H\delta(x) \). By applying the appropriate boundary conditions\(^4\) to Equations 2.10 and 2.11 for particles traveling from N to S the coefficients \( a, b, c \) and \( d \) can be found [4]:

\(^3\)See Figure 2.7

\(^4\)(i) Continuity of the wavefunction \( \psi \) at \( x = 0 \) such that \( \psi_N(0) = \psi_S(0) \equiv \psi(0) \).

(ii) \( (\hbar/2m)(\psi'_S - \psi'_N) = H\psi(0) \), the derivative boundary condition appropriate for \( \delta \)-functions.
Chapter 2. Electron Transmission Across a N-S Interface

\[ a = \frac{u_0 v_0}{\gamma} \]  
\[ b = -\frac{(u_0^2 - v_0^2)(Z^2 + iZ)}{\gamma} \]  
\[ c = \frac{u_0 (1 - iZ)}{\gamma} \]  
\[ d = \frac{iv_0 Z}{\gamma} \]  

where

\[ \gamma = u_0^2 + (u_0^2 - v_0^2)Z^2 \]  

and

\[ Z = \frac{mH}{\hbar^2 k_F} = \frac{H}{\hbar v_F} \]  

Here \( Z \) is a dimensionless parameter proportional to \( H \), the magnitude of the \( \delta \)-function potential at the N-S interface, describing the barrier strength. By varying \( Z \) any N-S interface can be modeled. The N/S junction, where there is no insulating barrier (i.e. high transparency regime), is given by \( Z = 0 \) whereas the classic high-barrier N/I/S junction (i.e. low transparency regime) is modeled by large \( Z \) (as \( Z \to \infty \)). While the no-barrier and high-barrier regimes are the two extremes that previous theories have addressed, the BTK theory is particularly powerful because, through varying a single parameter \( Z \), it is also equipped to model intermediate junction transparencies.

Probability currents can now be calculated from the scattering coefficients \( a, b, c \) and \( d \). The probability density of finding either an electron or hole at location \( x \) is defined as \( P(x) \). Therefore the probability density is given by:

\[ P(x,t) = |f|^2 + |g|^2 \]  

and the probability current is:

\[ \vec{J}_P = \frac{\hbar}{m} [Im(f^* \nabla f) - Im(g^* \nabla g)] \]
The above equation can now be used calculate the probability currents for Andreev reflection \( A(E) \), normal reflection \( B(E) \), predominantly electron-like transmission \( C(E) \) and predominantly hole-like transmission \( D(E) \) in units of \( v_F \). For example:

\[
C(E) = \frac{\mathbf{J}_P}{v_F} = \frac{\hbar}{mv_F} \left[ \text{Im}(c^* u_0 e^{-ik^+x} \nabla c u_0 c^{ik^+x}) - \text{Im}(c^* v_0 e^{-ik^+x} \nabla c v_0 e^{ik^+x}) \right] \\
= \frac{\hbar}{mv_F} \left[ \text{Im}(c^* u_0^* c u_0 e^{-ik^+x} c^{ik^+x}) - \text{Im}(c^* v_0^* c v_0 e^{-ik^+x} c^{ik^+x}) \right] \\
= \frac{\hbar k^+}{mv_F} c^* c (u_0^2 - v_0^2) = c^* c (u_0^2 - v_0^2) \tag{2.20}
\]

with similar calculations yielding:

\[
A(E) = a^* a \tag{2.21} \\
B(E) = b^* b \tag{2.22} \\
D(E) = d^* d (u_0^2 - v_0^2) \tag{2.23}
\]

The tunnelling current \( I \) can be calculated using these probability currents. On applying a voltage across the interface, the distribution functions of all incoming particles are given by equilibrium Fermi functions, apart from the voltage shift due to the bias. It is assumed that the Fermi distribution function for all incoming particles from the \( N \) side is \( f_0(E - eV) \) and \( f_0(E) \) for the \( S \) side. To determine the current, the difference between the distribution functions \( f_\rightarrow(E) \) and \( f_\leftarrow(E) \) is integrated over \( E \):

\[
I = 2N(0) e v_F \Lambda \int_{-\infty}^{\infty} [f_\rightarrow(E) - f_\leftarrow(E)] dE \tag{2.24}
\]

where \( \Lambda \) is the effective junction area and \( N(0) \) is the one-spin density of states at the Fermi energy. From the description of the incoming particles and using Figure 2.7:

\[
f_\rightarrow(E) = f_0(E - ev) \tag{2.25} \\
f_\leftarrow(E) = A(E) [1 - f_\rightarrow(-E)] + B(E) f_\rightarrow(E) + [C(E) + D(E)] f_0(E) \tag{2.26}
\]
Using \( A(E) + B(E) + C(E) + D(E) = 1 \) from the conservation of probability, \( A(E) = A(-E) \) and \( f_0(-E) = 1 - f_0(E) \) the current is given by:

\[
I = 2N(0)e v_F \Lambda \int_{-\infty}^{\infty} \left( f_0(E - eV) - [A(E)f_0(E + eV) + B(E)f_0(E - eV)] \right) dE
\]

\[
I = 2N(0)e v_F \Lambda \int_{-\infty}^{\infty} \left[ f_0(E - eV) - f_0(E) \right] \left[ 1 + A(E) - B(E) \right] dE \quad (2.27)
\]

At \( T = 0 \) the Fermi distribution function can be treated as a step-function and thus an \( I - V \) curve can be calculated by integrating the kernel \([1 + A(E) - B(E)]\) over \( E \).

The normal state conductance\(^5\) is given by \((1 + Z^2)^{-1}\) and the normalized differential conductance \(\sigma_s/\sigma_n\) can then be defined as:

\[
\frac{\sigma_s}{\sigma_n} \equiv \frac{1}{1 + Z^2} \frac{dI}{dV} \quad (2.28)
\]

Figure 2.8 shows the normalized differential conductance as a function of voltage calculated using the BTK theory for various values of \( Z \), the barrier strength. While the \( Z = 0 \) and \( Z = 10 \) BTK simulations reproduce the conductance characteristics of the extreme metallic and tunnelling regimes\(^6\), the power of the BTK theory is in its ability to calculate the conductance for intermediate transparencies, e.g. \( Z = 0.3 \) and \( Z = 1.0 \), thus showing the conductance evolution as the junction transforms from the Andreev to tunnelling limit.

### 2.3 Generalized BTK Model

The 1D BTK model assumed that the superconducting gap function is isotropic. Theoretical work by Bruder [113], Hu [83] and Tanaka and Kashiwaya [84] generalized the

\(^5\)For \( \Delta = 0 \), \( u_0^2 = 1 \) and \( v_0^2 = 0 \), the transmission coefficient can be calculated as \( C(E) = c^*c(u_0^2 - v_0^2) = (1 + Z^2)^{-1} \), or equivalently using, \([1 + A(E) - B(E)]\) where \( A(E) = 0 \) and \( 1 - b^*b = (1 + Z^2)^{-1} \).

\(^6\)See \( I - V \) curves for a \( N/S \) and a \( N/I/S \) junction in Figure 2.3(b) and 2.6(b) respectively.
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Figure 2.8: Normalized differential conductance versus voltage curves calculated using BTK theory for $Z = (a) 0$, (b) 0.3, (c) 1.0 and (d) 10. The voltage has been normalized relative to the superconducting energy gap $\Delta$.

BTK theory to 2D and calculated the tunnelling conductance for a $d$-wave pairing potential. Since the $d$-wave gap function is anisotropic, the tunnelling conductance will depend upon $\alpha$, defined as the angle formed between the normal vector at the interface and the $d$-wave gap anti-node. Using a formalism similar to that employed by BTK, Tanaka and Kashiwaya calculate the normalized differential conductance $\sigma(E)$:

$$\sigma(E) = \frac{\sigma_S(E)}{\sigma_N(E)}, \quad \sigma_i = \frac{1}{\pi} \int_{-\pi/2}^{\pi/2} d\theta \sigma_i(E, \theta) \quad (i = S, N) \quad (2.29)$$

where

$$\sigma_S(E, \theta) \equiv 1 + |a(E, \theta)|^2 - |b(E, \theta)|^2 = \frac{16(1 + |\Gamma_+|^2) \cos^4 \theta + 4Z^2(1 - |\Gamma_+\Gamma_-|^2) \cos^2 \theta}{4 \cos^2 \theta + Z^2 \{1 - \Gamma_+\Gamma_- e^{i(\phi_+ - \phi_-)}\}^2}$$

$$\sigma_N(E, \theta) \equiv \frac{4 \cos^2 \theta}{4 \cos^2 \theta + Z^2}$$
and
\[ \Gamma_\pm = \frac{E}{|\Delta(\theta_\pm)|} - \sqrt{\left(\frac{E}{|\Delta(\theta_\pm)|}\right)^2 - 1}, \quad e^{i\phi_\pm} = \frac{\Delta(\theta_\pm)}{|\Delta(\theta_\pm)|} \]

Here \( \theta \) is the incident angle of the electron and \( \Delta(\theta_\pm) = \Delta_0 \cos(2\theta \mp 2\alpha) \) is the effective \( d \)-wave pair potential where \( \alpha \) is the angle formed between the anti-node of the \( d \)-wave superconductor and the junction normal\(^7\). Since the \( d \)-wave gap is anisotropic, the magnitude of the pair potential experienced by electrons will depend upon the angle at which they approach the interface and to account for all possible trajectories it is necessary to integrate between \( \theta = \pi/2 \) to \( -\pi/2 \). Furthermore, a superconducting gap with \( d_{x^2-y^2} \) symmetry has nodes in the \( \pm k_x = \pm k_y \) direction, across which the amplitude changes sign and as a consequence it is possible for the transmitted and reflected quasiparticles in the superconductor to experience different effective pair potentials. For the case \( \alpha = 0 \) (where the anti-node is perpendicular to the junction interface), \( \Delta(\theta_+) = \Delta(\theta_-) \) and so \( \theta \) affects only the magnitude of pair potential experienced by the quasiparticle. For the case \( \alpha = \pi/4 \) (where the node is perpendicular to the junction interface), \( \Delta(\theta_+) = -\Delta(\theta_-) \) and so \( \theta \) affects both the magnitude and the sign of the pair potential experienced by the quasiparticle\(^8\). This peculiar feature, unique to anisotropic superconductors, produces a distinct signature in the conductance spectrum. Consider an electron propagating from a normal metal toward a superconductor such that a node is oriented perpendicular to the interface. On entering the superconductor, within the superconducting coherence length \( \xi \), the quasiparticle can undergo an Andreev reflection process. The quasiparticle, now propagating back toward the normal metal, can undergo a normal reflection process at the interface. Due to the sign change in the order parameter at the node, constructive interference between consecutively reflected Andreev and normal quasiparticles occurs, leading to the formation of a zero-energy, surface bound state \([83]\). These Andreev bound

\(^7\)For an isotropic \( s \)-wave superconductor \( \Delta(\theta_\pm) = \Delta_s \), a constant, which when substituted into the generalized BTK theory reproduces, as expected, the original results of the standard BTK theory.

\(^8\)For any \( \alpha \neq 0 \) there will be some values of \( \theta \) where the sign of \( \Delta(\theta_+) \) and \( \Delta(\theta_-) \) are opposite, but the range of \( \theta \) values over which this difference is most pronounced is at \( \alpha = \pi/4 \).
surface states manifest themselves in the conductance spectrum as pronounced zero-bias conductance peaks (ZBCPs) [83, 84].

Figure 2.9 shows the normalized conductance spectrum calculated using the generalized BTK theory for $N$-$S$ junctions where (a) $\alpha = 0$ and (b) $\alpha = \pi/4$. The insets show an incident electron propagating toward the superconductor from the normal metal and the orientation of the node/anti-node of the $d$-wave order parameter relative to the junction interface. In Figure 2.9(a) the electron entering the superconductor, at an angle $\theta$, and the Andreev reflected quasiparticle both experience the same pair potential. In Figure 2.9(b) the sign of the pair potential experienced by the incident electron (+ as indicated by the red lobe) and the Andreev reflected quasiparticle (− as indicated by the yellow lobe) are opposite, resulting in the ZBCP shown in Figure 2.9(b). While the above discussion has pertained to a $d$-wave pairing symmetry, Andreev bound states form when incident and Andreev reflected quasiparticles experience a sign change in the pair potential at a node, and these states would be expected to occur for any pairing symmetry, for example $p$-wave, where the phase changes across a node. Theoretical work has in fact shown that zero-energy surface states occur for a $p$-wave pairing symmetry and that they manifest themselves as a ZBCP in the conductance spectrum [114, 115, 116].

The generalized BTK approach shows that Andreev spectroscopy measurements are a very powerful probe for studying the pairing symmetry of exotic superconductors as the technique is sensitive to both the amplitude and phase of the order parameter. Andreev spectroscopy has in fact been used to identify unconventional pairing symmetry in several materials including the high-$T_c$ cuprates [117], ruthenates [118, 119], borocarbides [120, 121] and heavy-fermion systems [122, 123, 124, 125, 126, 100].
Figure 2.9: Normalized differential conductance versus voltage curves calculated using the generalized BTK theory for (a) $\alpha = 0$ and (b) $\alpha = \pi/4$. Curves for $Z = 0$ (low barrier strength) and $Z=5$ (high barrier strength) are shown. The voltage has been normalized relative to $\Delta$. Insets show the orientation of the $d$-wave order parameter relative to the junction interface.
It should be noted that the BTK theory is formulated on the assumption that electron transmission across the interface is ballistic such that the point-contact radius $a$ is smaller than the electronic mean free path $l$. To confirm whether an experimentally formed junction is ballistic the Wexler formula can be used [127]:

$$R \simeq \frac{4\rho l}{3\pi a^2} + \frac{\rho}{4a} \quad (2.30)$$

where $R$ is junction resistance and $\rho$ is the electrical resistivity. Here the term $4\rho l/3\pi a^2$ corresponds to the Sharvin resistance for ballistic contacts while the term $\rho/4a$ corresponds to the Maxwell resistance for diffusive junctions. While strictly speaking the BTK formalism is only valid in the ballistic limit $a < l$, theoretical work has shown that even in the diffusive regime $a > l$, for both conventional and unconventional superconducting point-contact junctions, the generic spectral features remain largely unchanged [128, 129, 130].
Chapter 3

Experimental Technique

By bringing a sharp tip into contact with a sample and making a 4-point conductance measurement across the resulting junction, as shown in Figure 3.1, point-contact spectroscopy data can be obtained. There are various techniques for both forming a point-contact junction as well as measuring the conductance across it, and the different methods used to obtain the data presented in this thesis are outlined in this chapter.

Figure 3.1: Illustration of a point-contact junction.
3.1 Approach Mechanism

3.1.1 Mechanical Driver

A schematic illustration and picture of the mechanically driven point-contact mechanism used to bring the sample and tip into contact with each other are shown in Figure 3.2 and Figure 3.3 respectively. In this setup, the tip holder is attached to a spring loaded plunger whose vertical movement is controlled by a differential screw micrometer\(^1\). While the entire sample stage sits inside a vacuum sealed probe, the differential screw is manipulated by a rotary feedthrough that resides outside the probe, thereby allowing controllable tip movement at cryogenic temperatures.

![Figure 3.2: Schematic illustration of the mechanical driver used to form point-contact junctions.](image)

As shown in Figure 3.2, the rotary feedthrough is not directly connected to the dif-

\(^1\)Newport Corporation HPS-80.
ferential screw. This is because the manual actuator on the feedthrough produces purely rotational motion whereas the differential screw moves linearly as it rotates. If the two components were attached directly to a rigid rod the differential screw would not turn. Therefore, to accommodate the linear travel of the differential screw, a formed bellow\(^2\) is used.

The tip holder was electrically isolated from ground by attaching it to the plunger via a macor spacer. The differential screw pushes against the plunger and because the plunger sits on top of a mechanical spring, extending or retracting the differential screw causes the tip holder to move forward or backward.

Using silver paint, the sample is mounted on a sapphire disk which in turn is silver painted to the sample holder. The sapphire disk, which is thermally conductive but electrically insulating, allows the sample to be electrically isolated from ground. Two leads are attached to both the sample and tip holder, enabling a 4-point conductance measurement. Point-contact junction resistances are generally quite low, making it necessary to employ a 4-lead configuration.

![Figure 3.3: Picture of the mechanical driver. Shown in (a) is the driver as ready to mount on the probe, while (b) shows the micrometer tip and plunger.](MDC vacuum products - 470000.)
3.1.2 Piezoelectric Driver

Piezoelectric materials distort their shape when subjected to an applied electric field. This phenomenon can be exploited to form point-contact junctions. A schematic illustration and picture of piezoelectric driver can be seen in Figure 3.4. The sample wagon has a spring tensioned screw and sits on the sapphire rods. By applying an appropriate waveform between the inner and outer surfaces of the piezo, the wagon can be made to slide along the sapphire rods. Figure 3.5 shows the waveform used to move the wagon along the sapphire rods. The typical voltage amplitude of the waveform used at cryogenic temperatures is $\sim 150-175$ Vpp. Silver pasted to the sample wagon is a sapphire disk on which the sample is mounted using silver paint. Once again a 4-point measurement is made by attaching two leads to the tip holder and two leads directly on the sample.

![Figure 3.4: Shown on the left is a schematic illustration and on the right a picture of the piezoelectric driver.](image-url)
Figure 3.5: Waveform used to move the sample (a) toward the tip and (b) away from the tip.

3.2 Conductance Measurements

3.2.1 Direct Differential Conductance Measurement

One method to obtain the dynamic conductance of a point-contact junction is to apply a DC bias across it and measure the differential conductance [131]. Shown in Figure 3.6 is an illustration of such a circuit. Using a Keithley 220 DC current source, a current bias is applied between the sample and tip and the resulting DC voltage is measured using a HP 3457A voltmeter. The conductance at each bias is measured using either a Lakeshore 370 or a Stanford Research Systems SIM921 AC resistance bridge. At each DC bias voltage \( V_{dc} \), the AC resistance bridge sources a small current excitation\(^3\) \( \delta I_{ac} \) across the junction and by measuring the resulting voltage drop \( \delta V_{ac} \), the differential conductance \( \frac{1}{R_{ac}} = \frac{\delta I_{ac}}{\delta V_{ac}} \) is obtained. As the conductance spectrum is non-linear, to obtain maximum spectral resolution, \( \delta I_{ac} \) needs to be smaller than the DC current bias increment \( \delta I_{dc} \). In principle, \( \delta I_{ac} \) could be set arbitrarily low making the \( R_{ac} \) measurement noise limited. However, practically this is not possible because of the technique by which resistance bridges measure \( R_{ac} \). Before a phase-sensitive measurement of \( \delta V_{ac} \) is made

\(^3\)Typically excitation frequency was \( \sim 10-15 \) Hz.
by the resistance bridge, the signal is amplified; the smaller $\delta V_{ac}$ the larger the pre-amplification. However, in the measurement setup described above, the signal returning to the resistance bridge is composed of $\delta V_{ac} + \delta V_{dc}$ and since the pre-amplification is done before any filtering, $\delta V_{dc}$ is also amplified. If $\delta V_{ac} \ll \delta V_{dc}$ the amplification process will rail the pre-amplifier rendering it impossible to determine $R_{ac}$. Though an external DC filter could be added just before the resistance bridge, it was found that doing so added additional noise (the signal $\delta V_{ac}$ is very small) making the $R_{ac}$ measurement unreliable. Therefore it was necessary to set $\delta I_{ac}$ to a value low enough ($\delta I_{ac} \leq \delta I_{dc}$) to capture the non-linear features in the conductance spectrum but not so low ($\delta V_{ac} \ll \delta V_{dc}$) to cause the pre-amplifier to rail.

![Diagram of electronic setup](image)

Figure 3.6: Illustration of the electronic setup used to directly measure the differential conductance as a function of bias voltage.

The circuitry described above was tested by forming a normal metal (Cu)/$s$-wave superconductor (Nb) point-contact junction (using the mechanical driver approach mechanism illustrated in Figure 3.2) and measuring $\delta I_{ac}/\delta V_{ac}$ vs $V_{dc}$ at liquid Helium temperatures. Figure 3.7 shows that the point-contact differential conductance data taken on a Cu/Nb junction, which has been normalized relative to the conductance measured above the superconducting energy gap $\Delta$, is in agreement with the spectrum predicted by BTK theory.
Figure 3.7: Normalized conductance vs bias voltage for a Cu/Nb point-contact junction at (a) 4.2 K and (b) 2.5 K. The solid lines are fits to BTK theory.

### 3.2.2 Pulsed I-V Measurement

At dilution fridge temperatures (< 300 mK) Joule heating becomes a concern, particularly for low impedance junctions, and a pulsed $I-V$ technique is preferred over the standard 4-point ac modulation technique outlined in Chapter 3.2.1. Figure 3.8 shows a schematic design of the pulsed $I-V$ setup. A series of pulsed voltage steps are generated by an analogue output channel on a National Instruments (NI) Data AcQuisition card (DAQ)\(^4\) card, capable of sourcing $\pm 10$ V. The voltage pulses are fed to a current output module\(^5\) which is housed inside a Signal Conditioning Enclosure\(^6\). The current output module can source 0-20 mA and is controlled by the output of the DAQ. To obtain a bipolar current source, two modules are used. The relationship between the output current $I_o$ and the input voltage $V_i$ is linear and given by $I_o = \frac{V_i}{500}$. The current pulses are applied across the point-contact junction and the resulting voltage drop is measured on an analogue input channel of the DAQ. However, to utilize the full range of the DAQ ($\pm 10$ V), the differential voltage is first amplified using a low noise Stanford Research

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\(^4\)PCI-6052E.

\(^5\)NI SCC-C020.

\(^6\)NI CA-1000.
Figure 3.8: Schematic of the pulsed $I - V$ technique used to obtain the conductance spectrum as a function of bias voltage.

preamplifier\textsuperscript{7} before it is sent to the Signal Conditioning Enclosure. Variables such as current amplitude, pulse length, duty cycle etc. are software controlled by user-written code in NI LabVIEW 5.1.

Both ohmic and non-ohmic devices were tested using the pulsed technique outlined above. Current-voltage $I - V$ characteristics obtained for various diodes and resistors are shown in Figure 3.9. Linear behaviour following Ohm’s Law, $I = V/R$ where $R$ is the resistance, was observed for resistors while diodes exhibited characteristic non-linear, knee-shape $I - V$ dependence. Forward voltage drops of $\sim 0.65$ V and $\sim 0.4$ V were observed for the silicon and Schottky diode respectively, consistent with their design specifications.

Using the pulsed $I - V$ setup, point-contact conductance measurements were also made on a normal metal (Cu)/$s$-wave superconductor (Nb) junction at 4.2 K. Figure 4.13 shows that the normalized differential conductance spectrum observed for the Cu/Nb junction is consistent with that predicted by BTK theory for high-transparency junctions as discussed in Chapter 2.2.

\textsuperscript{7}SR-560.
Figure 3.9: Current versus voltage characteristics measured using the pulsed $I - V$ technique for (a) silicon and Schottky diodes and (b) resistors.

Figure 3.10: Normalized conductance vs bias voltage for a Cu/Nb point-contact junction obtained using a pulsed $I - V$ technique at 4.2 K.
3.3 Cryogenic Techniques

3.3.1 \textsuperscript{4}He Dipper Probe

Andreev spectroscopy measurements above 2 K were made using a custom built \textsuperscript{4}He dipper probe. The point-contact driver was attached to the top of a 1 K pot which was encased in an indium sealed vacuum can. After the vacuum can was purged using a rotary pump, a very small volume of \textsuperscript{4}He exchange gas was backfilled. The probe was pre-cooled in liquid nitrogen and then slowly inserted into a liquid helium dewar. The sample was cooled to 4.2 K via the \textsuperscript{4}He exchange gas. Once at thermal equilibrium, measurements at 4.2 K can be made. By opening a needle valve and pumping on the 1 K pot, temperatures as low as \(\sim 2\) K could be accessed\textsuperscript{8}. A heater was attached to the 1 K pot, and by passing a current through it temperatures of \(\sim 30\) K could be reached\textsuperscript{9}.

3.3.2 \textsuperscript{3}He-\textsuperscript{4}He Dilution Refrigerator

In continuous cycle mode, a 1 K pot operating optimally can reach \(\sim 1.5\) K. However, several superconductors such as PrOs\textsubscript{4}Sb\textsubscript{12} and CeCoIn\textsubscript{5} have \(T_c\)'s that are comparable with the temperature limit that can be achieved using a 1 K pot. For such superconductors, at \(T \sim 1.5\) K, the ratio \(T/T_c\) is relatively large and therefore the spectral features are not fully formed making an interpretation of the conductance spectrum difficult. Fully developed spectral features are only realized when \(T \ll T_c\) and to access such temperatures a \textsuperscript{3}He-\textsuperscript{4}He dilution refrigerator was used.

A dilution refrigerator utilizes the rather unique properties of a \textsuperscript{3}He-\textsuperscript{4}He mixture to achieve temperatures less than 0.3 K. On cooling the \textsuperscript{3}He-\textsuperscript{4}He mixture below a certain temperature (\(\sim 0.9\) K) the \textsuperscript{3}He and \textsuperscript{4}He isotopes separate into two phases. One of these phases will be rich in \textsuperscript{3}He which, as the temperature approaches zero, becomes a pure

\textsuperscript{8}For sub 4.2 K operation the exchange gas in the vacuum can must first be pumped out.

\textsuperscript{9}Temperature stability is maintained using the PID controller on a Lakeshore AC 370 resistance bridge.
He phase. However, for the other phase, which is primarily $^4\text{He}$, even at $T = 0 \text{ K}$ a finite concentration of $^3\text{He}$ exists (i.e. it does not become a pure $^4\text{He}$ phase). The finite solubility of $^3\text{He}$ in a $^4\text{He}$ rich phase is critical for the operation of a dilution refrigerator. In the dilution unit the $^3\text{He}$-$^4\text{He}$ mixture is initially condensed by a 1 K pot and allowed to enter the mixing chamber. On cooling sufficiently, the mixture separates into two phases and due to its lower density the $^3\text{He}$ rich phase floats above the dilute $^3\text{He}$-$^4\text{He}$ phase. The dilute phase is connected to the still chamber which when pumped upon primarily removes $^3\text{He}$. Since $^3\text{He}$ has been removed from the dilute phase, to restore the equilibrium concentration, $^3\text{He}$ from the rich phase crosses the phase boundary into the dilute phase and the latent heat associated with this transfer provides the cooling power. Closed cycle operation is achieved by circulating the $^3\text{He}$ vapour pumped from the still chamber back (through a series of heat exchangers and flow constrictions to reliquefy) to the $^3\text{He}$ rich phase in the mixing chamber.

Samples are attached to the mixing chamber via a copper tail in intimate contact with the bottom of the mixing chamber. In principle either a mechanical or piezoelectric point-contact driver could be attached to the tail. However, as cooling down and warming up the dilution refrigerator is time-consuming and expensive it is beneficial to maximize the number of samples attached to the tail for every cooldown and in this regard the piezoelectric driver approach mechanism is advantageous. Each mechanical driver requires its own rotary feedthrough and as there is very limited space inside the fridge it is not feasible to install multiple rotation mechanisms. However, the piezoelectric driver approach mechanism is based on applying a voltage across the inner and outer surfaces and so adding multiple drivers simply involves running additional wiring down the fridge. A total of four piezoelectric drivers were attached to the tail.
Chapter 4

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

4.1 Introduction

Since being reported as a heavy-fermion superconductor [24], the filled skutterudite compound PrOs$_4$Sb$_{12}$ has attracted much interest, particularly because of its unconventional properties. It is the first Pr-based superconductor and as the ground state of PrOs$_4$Sb$_{12}$ is non-magnetic it is unlikely that magnetic fluctuations govern superconductivity. In fact it has been conjectured that the electron pairing is due to quadrupolar fluctuations [132, 133] and as such PrOs$_4$Sb$_{12}$ would be the first superconductor where the pairing mechanism is neither electron-phonon nor magnetically mediated.

A double superconducting transition at $T_{c1} \sim 1.8$ K and $T_{c2} \sim 1.7$ K [25, 26, 27] has been observed suggesting that there may be multiple superconducting phases. Different experiments have however reported different magnetic field-vs-temperature phase diagrams. For example, angular magneto-thermal conductivity $\kappa(H, \phi)$ data indicates that a superconducting order parameter undergoes a field-induced phase transition from two point nodes at low fields to six point nodes at high fields [1]. Specific heat [2, 32, 134, 33]
measurements on the other hand have not observed this transition.

Despite numerous experimental and theoretical studies, the superconducting gap topology of PrOs₄Sb₁₂ has still not been established. Penetration depth [38], \( \kappa(H, \phi) [1] \), small angle neutron scattering [40] and specific heat \( C(T) [25, 39] \) experiments have all indicated the presence of point nodes. In contrast, muon-spin resonance [34], Sb-nuclear quadrupolar resonance [35], scanning tunnelling spectroscopy [36], and \( \kappa(T, H) [37] \) measurements have shown the Fermi surface to be fully gapped in the superconducting state. PrOs₄Sb₁₂ has a complex Fermi topology with multiple sheets on the Fermi surface [44], and recent \( \kappa(T, H) \) have indicated that it is a multiband superconductor [37, 42]. Recently, MacLaughlin et al. have proposed that the discrepancy between experiments that see gap nodes and those that do not could be explained by a scenario where a nodal gap exists on the small-mass band and the large-mass band is fully gapped [43]. Recent \( C(T) \) measurements on Pr(Os₁−ₓRuₓ)₄Sb₁₂ showing fully gapped behaviour for \( x \) as low as 0.01 would be consistent with this picture [39]. However, direct microscopic evidence, obtained using a highly local experimental probe, showing co-existing OPs with different symmetries in PrOs₄Sb₁₂ is still lacking.

Point-contact Andreev spectroscopy is a powerful microscopic technique sensitive to both the amplitude and phase of the superconducting OP making it ideally suited for studying unconventional superconductors. For junctions in the high transparency limit, the differential conductance \( dI/dV \) versus voltage \( V \) spectrum is primarily determined by Andreev reflection - the process by which electrons are converted into Cooper pairs [4]. The conductance for voltages within the superconducting energy gap is double that of the normal state thus Andreev bulk states cause a hump like feature in the \( dI/dV \) spectrum, resulting in excess spectral area. For junctions in the low transparency limit the \( dI/dV \) is primarily determined by quasiparticle tunnelling. For a superconductor with gap nodes, due to a sign change in the OP at the node, consecutively reflected quasiparticles can constructively interfere forming an Andreev bound state.
Chapter 4. Andreev Spectroscopy Study of PrOs$_4$Sb$_{12}$

These surface states manifest themselves in the $dI/dV$ spectrum as a zero-bias conductance peak (ZBCP) where spectral area is conserved. Andreev spectroscopy has been used to identify unconventional pairing symmetry in several materials including high-$T_c$ cuprates [117], ruthenates [118, 119], borocarbides [120, 121] and heavy-fermion systems [122, 123, 124, 125, 126, 100] as well as reveal evidence for multiband superconductivity in MgB$_2$ and CeCoIn$_5$ [100].

In this chapter Andreev spectroscopy measurements performed on single crystal samples of PrOs$_4$Sb$_{12}$ and Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ at low doping are presented. For the undoped sample, multiple features were observed in the conductance spectrum, including evidence for a nodal order parameter. Different spectral features converged to different temperatures $T_{c1}$ and $T_{c2}$ confirming the intrinsic nature of the double superconducting transition using a highly local probe. Spectral dependencies on both temperature and magnetic field were studied and indicated a field-induced change in the OP symmetry. These results suggest that the $H$-$T$ phase diagram for PrOs$_4$Sb$_{12}$ consists of multiple superconducting phases with different symmetries. On increasing the Ru concentration the conduction spectrum was consistent with a suppression of the nodal order parameter.

4.2 Sample Characterization

Single crystal samples of PrOs$_4$Sb$_{12}$ were grown, via a molten-metal-flux growth technique using Sb flux, at the University of California at San Diego. Prior to making measurements, the samples were etched in a 1:1 HCl-HN$_O_3$ mixture and rinsed in ethanol to remove any excess Sb flux. Utilizing a standard four-point technique, electrical resistivity $\rho(T, H)$ was measured using a LR-700 AC resistance bridge in a $^3$He-$^4$He dilution refrigerator. A current modulation with amplitude 0.5 mA and frequency 15.9 Hz was used. Figure 4.1 shows that at $H = 0$ T a single, sharp ($\Delta T_c \sim 0.05$ K) superconducting transition was measured at $T_{c1} \sim 1.85$ K. At $T = 0.2$ K the upper critical field $H_{c2} \sim 2.25$
T was determined. The large residual resistivity ratio of the crystals, \( \rho_{300K}/\rho_{2K} \sim 28 \), reflect their high quality. Figure 4.2 plots the \( H - T \) phase diagram obtained from \( \rho(T, H) \) measurements. The linear variation of \( H_{c2}(T) \) near \( T_{c1} \) given by \(- (dH_{c2}/dT)_{T_c} \sim 2.0 \text{TK}^{-1} \) is in agreement with previous studies [24]. The orbital limited critical field at zero-temperature is given by \( H_{c2}^{orb}(0) = -0.693(dH_{c2}/dT)_{T_c} T_c \) [135]. From Figure 4.2 a value of \( H_{c2}^{orb}(0) \sim 2.5 \text{T} \) is obtained, showing that the upper critical field in PrOs\(_4\)Sb\(_{12}\) is indeed orbitally limited.

Figure 4.1: Electrical resistivity \( \rho \) of a single crystal of PrOs\(_4\)Sb\(_{12}\) vs (a) temperature and (b) magnetic field.

Despite experimental observation of the double superconducting transition in several studies [26, 2, 134, 39], some doubt still exists over its intrinsic nature [32]. While Figure 4.1 shows a sharp superconducting transition in \( \rho(T, 0) \), it does necessarily indicate the absence of a double transition. Resistivity measurements are made by placing current leads on opposite ends of the sample and measuring the voltage drop between them. As soon as one path between the two current leads becomes superconducting, the sample resistance drops to zero. However, other paths that remain normal may still exist but since all the current flows through the superconducting channel (as it is the path of least resistance), it may appear that the entire sample is superconducting. ac susceptibility
Figure 4.2: Evolution of the upper critical field vs temperature as measured by electrical resistivity. Inset shows the resistivity as function of magnetic field and temperature.

χ_{ac} measurements were therefore also performed to determine whether or not a double superconducting transition exists. Figure 4.3 shows that two superconducting transitions at $T_{c1} \sim 1.85$ K and $T_{c2} \sim 1.65$ K were observed in the $\chi_{ac}(T)$ data\textsuperscript{1}.

4.3 Temperature Dependence

Andreev spectroscopy measurements on the c-axis faces of the PrOs$_4$Sb$_{12}$ crystals were made using etched Pt-Ir tips. The measurements were performed in a $^3$He-$^4$He dilution refrigerator between 90 mK and 2 K. Junction impedances were typically $\sim 0.2$ - 1 Ω. To minimize Joule heating the pulsed $I - V$ technique, discussed in Chapter 3.2.2, 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 $dI/dV$ conductance spectrum as a function of $V$.

\textsuperscript{1}$\chi_{ac}(T)$ measurements performed by W.M. Yuhasz at University of California at San Diego.
Chapter 4. Andreev Spectroscopy Study of PrOs\textsubscript{4}Sb\textsubscript{12}

Figure 4.3: ac magnetic susceptibility of PrOs\textsubscript{4}Sb\textsubscript{12} as a function of temperature.

Using the Wexler formula [127]:

$$ R \simeq \frac{4 \rho l}{3 \pi a^2} + \frac{\rho}{4a} \quad (4.1) $$

with $\rho \sim 2 \mu\Omega \text{ cm}$, the mean free path $l \sim 3500 \, \text{Å}$, and $R$ the junction impedance, the Sharvin radius, $a$ is estimated to be $\sim 80\text{nm}$ thus satisfying the ballistic criterion $a < l$.

Figure 4.4 shows the temperature evolution of point-contact $dI/dV$ data taken on PrOs\textsubscript{4}Sb\textsubscript{12} in zero magnetic field. At 90 mK there is a pronounced zero-bias conductance peak (ZBCP), flanked by symmetric dip structures located at $\sim \pm 0.4 \, \text{mV}$. Additional satellite features are also observed at $\sim \pm 0.3 \, \text{mV}$ and $\sim \pm 0.2 \, \text{mV}$. As the temperature is increased the height of the ZBCP is reduced and the position of the dips and satellite features move inward. Above $T \sim 1.8 \, \text{K}$ the $dI/dV$ flattens out, showing no voltage dependence, consistent with the sample no longer being superconducting.

The observation of a ZBCP in the $dI/dV$ conductance spectrum provides microscopic evidence for gap nodes in the superconducting order parameter (OP) of PrOs\textsubscript{4}Sb\textsubscript{12}. Recent theoretical work had calculated the $dI/dV$ spectra [5] for various spin singlet and
Figure 4.4: Differential conductance spectrum as a function of temperature for a Pt-Ir/PrOs$_4$Sb$_{12}$ junction at zero magnetic field.

spin triplet OPs proposed for PrOs$_4$Sb$_{12}$ [136, 137, 138, 139, 140]. Figure 4.5 shows the theoretical $dI/dV$ spectrum for one of the candidate spin triplet pair potentials with two point nodes. The transmission probability $T_B$ represents the junction transparency. At low junction transparencies the theoretical $dI/dV$ conductance shows a ZBCP and satellite features resembling that observed in the experimental data seen in Figure 4.4.

Figure 4.6 shows the temperature evolution of the excess spectral area, defined for the $dI/dV$ spectrum at each temperature by subtracting out the normal-state conductance and then numerically integrating between $\pm$ 1.8 mV, the height of the ZBCP and the features in the $dI/dV$ occurring at $\delta_1$ and $\delta_2$ as indicated in Figure 4.4. To facilitate a quantitative comparison, each spectral feature was normalized to its respective value at 90 mK. ZBCPs are a manifestation of Andreev surface states and as such spectral area should remain conserved. However, as the temperature is decreased an increase in the spectral area was observed, indicating that Andreev bulk states also contribute to the $dI/dV$ spectrum. The observation of the excess spectral area indicates that an OP
Figure 4.5: Theoretical conductance spectrum for a spin triplet order parameter proposed for PrOs$_4$Sb$_{12}$. $T_B$ corresponds to the transmission probability across the junction. Reprinted with permission from Ref [5]. Copyright 2003 by the American Physical Society.

Figure 4.6: Temperature dependence of the normalized spectral features seen in the conductance spectrum for a Pt-Ir/PrOs$_4$Sb$_{12}$ point-contact junction. Shown in the inset are the features corresponding to the symbols.
in addition to the one responsible for the ZBCP contributes to the $dI/dV$ conductance spectrum. In fact, the temperature evolution of the excess spectral weight and the ZBCP coincide with that of the structures observed in the $dI/dV$ at $\delta_1$ and $\delta_2$ respectively, providing evidence for multiple superconducting OPs. Furthermore, the ZBCP appears to terminate at a temperature $T \sim 1.65$ K while the excess spectral area persists up to $T \sim 1.8$ K. Using a highly local probe we observed that the two OP components terminate at different temperatures, coinciding with $T_{c2}$ and $T_{c1}$ as measured by $\chi_{ac}$ in Figure 4.3, providing microscopic evidence for the intrinsic nature of the double superconducting transition in PrOs$_4$Sb$_{12}$. Our spectroscopic results indicating a nodal OP component are consistent with the multigap and multisymmetry scenario proposed by $\kappa(T, H)$ measurements in Ref. [42] which showed that the OP on one band was nodal while the OP on the other band was fully gapped.

Although a ZBCP was observed in the experimental data, as shown in Figure 4.4, and predicted by theory, as shown in Figure 4.5, it should be noted that in a previous STM study no peak at zero-bias was observed [36]. A possible explanation to reconcile the point-contact and STM experiments could be that in point-contact measurements the sample and tip are in direct contact with each other while in STM they are separated by a vacuum barrier. The probability of a quasiparticle tunnelling across an insulating barrier decreases rapidly as the incident angle formed between the quasiparticle and contact normal is increased. To model the directional dependence of quasiparticle tunnelling at the junction interface a phenomenological tunnelling cone is incorporated [141, 118]. In the point-contact regime, as there is no tunnelling barrier, quasiparticles incident from all angles are equally likely to transfer across the junction interface and so a wide tunnelling cone is appropriate. In STM, however, incident quasiparticles with momentum parallel to the contact normal are most likely tunnel across the barrier and so a narrow tunnelling cone is more appropriate. Several theoretical and experimental studies have indicated the presence of point nodes in the superconducting OP [136, 137, 38, 1, 42] of PrOs$_4$Sb$_{12}$
and it is conceivable that in this scenario a narrow tunnelling cone would inhibit the formation of Andreev bound states. Furthermore, recent Fermi surface calculations for PrOs$_4$Sb$_{12}$ have shown that some parts of the Fermi surface may vanish at certain points [142]. A narrow tunnelling cone would therefore only be sensitive to the parts of the Fermi surface that were missing and so again a ZBCP, the signature of Andreev surface states, would not be observed in the STM conductance spectrum.

For conventional electron-phonon mediated weak-coupling BCS superconductors, the ratio of the superconducting energy gap-to-$T_c$ is given by:

$$\frac{2\Delta_0}{k_b T_c} = 3.53$$  \hspace{1cm} (4.2)

where $\Delta_0$ is gap amplitude at $T = 0$ K, $T_c$ is the superconducting transition temperature and $k_b$ is the Boltzmann constant. Assigning the two spectral features seen at $\sim \pm 0.4$ mV and $\sim \pm 0.2$ mV as the magnitude of the superconducting OP components $\Delta_1$ and $\Delta_2$, the gap-to-$T_c$ ratios are $5.0 \pm 0.3$ and $2.8 \pm 0.3$ respectively. The deviation from the BCS prediction of 3.53 indicates PrOs$_4$Sb$_{12}$ is a strong coupling superconductor. Several other studies have determined gap-to-$T_c$ ratios, as summarized in Table 4.1, and the values obtained from point-contact measurements fall within the range of published values.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>$\frac{\Delta}{T_c}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
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<td>This work</td>
</tr>
<tr>
<td>PCS $\Delta_2$</td>
<td>$2.8 \pm 0.3$</td>
<td></td>
</tr>
<tr>
<td>$\mu$SR</td>
<td>4.2</td>
<td>[34]</td>
</tr>
<tr>
<td>Sb-NQR</td>
<td>5.4</td>
<td>[35]</td>
</tr>
<tr>
<td>$C(T)$</td>
<td>5.2 - 7.4</td>
<td>[26, 143, 134]</td>
</tr>
<tr>
<td>$\lambda(T)$</td>
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<td>[38]</td>
</tr>
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<td>STM</td>
<td>1.5 - 4.1</td>
<td>[36]</td>
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<td>[37]</td>
</tr>
<tr>
<td></td>
<td>$\Delta_2$ 1.15</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Table summarizing gap-to-$T_c$ ratios obtained from different experimental studies.

### 4.4 Magnetic Field Dependence

Figure 4.7 shows the field evolution of the $dI/dV$ spectrum measured at 90 mK. As the field is increased, the position of the dips and sub-gap features move inward and the height of the ZBCP shrinks, eventually vanishing at $H^* \sim 1.5$ T. Shown in the inset is the magnetic field evolution of the excess spectral weight and the ZBCP height, each normalized to their respective values at $H = 0$ T. Above 1.5 T there is no discernible ZBCP, indicating that Andreev surface states no longer contribute to the overall $dI/dV$, but excess spectral weight persists up to 2.2 T, the upper critical field measured by $\rho(T, H)$.

The field evolution data which shows that above $H \sim 1.5$ T the OP component responsible for the ZBCP has been suppressed is qualitatively similar with $\kappa(H, \phi)$ measurements that indicated a field-induced change in the superconducting OP pairing symmetry [1]. The magnetic field dependence of different pair potentials in a multiband superconductor was calculated in Ref. [144] and showed behaviour resembling the field dependence seen in the inset of Figure 4.7, indicating that the ZBCP and excess spectral
area correspond to different OPs on different superconducting bands. The \( dI/dV \) spectrum between \( H^* \) and \( H_{c2} \) spectra should reflect the OP symmetry. Theoretical work has calculated the conductance spectrum for several pair potentials proposed for PrOs\(_4\)Sb\(_{12}\) [5]. For some of the high-temperature spin triplet pair potentials, the \( dI/dV \) spectra showed virtually no dependence on bias voltage consistent with our data. Furthermore, in a multiband scenario two conductance channels contribute to the total conductance and if one channel becomes normal while the other remains superconducting, spectral features in the \( dI/dV \) spectrum arising from the superconducting channel will be suppressed by the transport also occurring across the normal channel. Point-contact spectroscopy data taken at low temperatures on UPt\(_3\) [145], another heavy-fermion metal where multiple superconducting phases are known to exist [22], also showed a similar field dependence where spectral features vanished at a phase boundary lower than \( H_{c2} \). Therefore, while it is difficult to determine the exact OP symmetry in the high-field region between \( H^* \) and \( H_{c2} \) without a full study of the spectral dependence on junction direction and impedance.

Figure 4.7: Differential conductance spectrum as function of applied magnetic field for a Pt-Ir/PrOs\(_4\)Sb\(_{12}\) point-contact junction at 90 mK. Shown in the inset is the magnetic field dependence evolution of the excess spectral area and ZBCP height.
[124, 146], the disappearance of the ZBCP at $H^*$ provides strong evidence that the OP symmetry is different between the low-field and high-field phases.

By combining the temperature and field evolutions we determined the magnetic field at which the ZBCP vanishes, $H^*$, and the magnetic field up to which the excess spectral area persists, $H'$, as a function of temperature. Figure 4.8 shows the resulting $H - T$ phase diagram as well as $H_{c2}(T)$ data as determined by $\rho(T,H)$. $H^*(T)$ and $H_{c2}(T)$ clearly emerge from different low-temperature asymptotes and gradually approach each other as the temperature is increased. The $H_{c2}(T)$ and $H'(T)$ data coincide with each other indicating that while the OP component responsible for the ZBCP persists only to $H^*(T)$, the OP component responsible for the excess spectral area in the $dI/dV$ persists up to $H_{c2}$, above which the sample is no longer superconducting.

The non-parallel behaviour of the $H^*(T)$ and $H_{c2}(T)$ curves resembles the $H - T$ phase diagram determined by $\kappa(H,\phi)$ data [1] and should be contrasted with that obtained by
C(H, T) measurements showing two parallel phase boundaries [2]. The $H^*(T)$ and $H_{c2}(T)$ curves also appear to converge to different temperatures at $H = 0$ T. $H_{c2}(T)$ appears to converge to $T \sim 1.85$ K while $H^*(T)$ appears to converge to $T \sim 1.65$ K. The two temperatures coincide with the double superconducting transition $T_{c1}$ and $T_{c2}$ that was measured by $\chi_{ac}(T)$ thus appearing that $H_{c2}(T)$ converges to $T_{c1}$ while $H^*(T)$ converges to $T_{c2}$. The intrinsic nature of the double superconducting transition has been debated [32] but our results obtained using a highly local, microscopic probe, suggests that two different OPs terminate at $T_{c1}$ and $T_{c2}$ thus arguing against sample inhomogeneity, at least down to the length scale of the estimated point-contact radius $a \sim 80$ nm, producing multiple $T_{c}$s.

Figure 4.9 compares the $H - T$ phase diagrams obtained from $\kappa(H, \phi)$, $C(H, T)$ and surface impedance measurements with that obtained from point-contact and $\rho(T, H)$ measurements in this study. Although the phase diagram shown in Figure 4.8 is qualitatively consistent with that obtained by $\kappa(H, \phi)$, there is some minor quantitative discrepancy in the low-temperature asymptote of $H^*$. Surface impedance measurements however have also indicated a second phase boundary below $H_{c2}(T)$ with a low temperature asymptote of $\sim 1.5$ T [6], which would be consistent with $H^*(T)$ as determined by our Andreev spectroscopy data. Our results showing multiple superconducting phases with different $T_c$s are reminiscent to that of UPt$_3$ which also exhibits a complex $H$-$T$ phase diagram [22].

A possible explanation for the discrepancy in the $H - T$ phase diagram between the specific heat and thermal conductivity might be related to the heavy-fermion nature of PrOs$_4$Sb$_{12}$. While the Sommerfeld coefficient $\gamma$ in low temperature specific heat is proportional to the effective mass $\gamma \propto m^*$, the thermal conductivity is inversely proportional to the effective mass $\kappa \propto 1/m^*$. PrOs$_4$Sb$_{12}$ has multiple bands crossing the Fermi energy and recalling the proposal put forth by MacLaughlin et al. whereby the small-mass band is nodal while the large-mass band is fully gapped [43], it is plausible that $C(H, T)$
measurements primarily detect the contribution of the heavy quasiparticles while \( \kappa(H, \phi) \) measurements detect the light quasiparticles.

![Graph showing phase diagram](image)

**Figure 4.9:** \( H - T \) phase diagram comparing results from various studies. Data corresponding to \( \kappa(H, \phi) \) (squares)[1], \( C(T, H) \)[2], surface impedance (green triangles) [6], \( \rho(T, H) \) (diamonds) and PCS (blue triangles) are shown. Dashed lines are a guide to the eye.

### 4.5 Doping Dependence

Substitution studies on \( \text{PrOs}_4\text{Sb}_{12} \) where Os was replaced by Ru have been performed and the resulting physical properties of \( \text{PrRu}_4\text{Sb}_{12} \) are very different than that of \( \text{PrOs}_4\text{Sb}_{12} \). Specific heat and de Haas-van Alpen measurements have identified \( \text{PrOs}_4\text{Sb}_{12} \) as a heavy-fermion material but show \( \text{PrRu}_4\text{Sb}_{12} \) is, at best, a marginal heavy-fermion metal [44].

The onset of superconductivity in \( \text{PrRu}_4\text{Sb}_{12} \) occurs at \( T_c \sim 1.0 \) K and there has been no experimental evidence of a double superconducting transition similar to that seen in \( \text{PrOs}_4\text{Sb}_{12} \) [143]. Sb-NQR [45], penetration depth [46] and thermal conductivity [42] experiments on \( \text{PrRu}_4\text{Sb}_{12} \) have all indicated an isotropic energy gap and the thermal conductivity study also suggested that it is a multiband superconductor.
As the two end compounds PrOs$_4$Sb$_{12}$ and PrRu$_4$Sb$_{12}$ have such different superconducting properties it would naturally be interesting to study how these properties evolve as a function of Ru doping. The superconducting transition temperature of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ as a function of Ru doping $x$ was tracked by electrical resistivity and ac magnetic susceptibility and showed that as the Ru concentration is increased $T_c$ decreases until $x = 0.6$ [3]. Between $x = 0.6$ and $x = 1$, $T_c$ starts to increase. The minimum at $x = 0.6$ suggests that there is a competition between the superconductivity of PrOs$_4$Sb$_{12}$ and PrRu$_4$Sb$_{12}$. Recent specific heat measurements have shown that while the OP for PrOs$_4$Sb$_{12}$ is nodal, in Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ for doping as low as $x = 0.01$ the OP appears to be fully gapped [39]. Point-contact spectroscopy measurements, using Pt-Ir tips, on the c-axis faces of $x = 0.02$ and $x = 0.05$ Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ samples have been performed to spectroscopically observe how the OP evolves upon Ru doping.

![Differential conductance spectrum](image)

Figure 4.10: Differential conductance spectrum as a function of temperature for a Pt-Ir/Pr(Os$_{0.98}$Ru$_{0.02}$)$_4$Sb$_{12}$ point-contact junction at zero magnetic field.

Figure 4.10 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 much smaller than the one seen in
the \( x = 0 \) sample. Additional broad hump-like features, observed at \( \sim \pm 0.6 \) mV and \( \sim \pm 1.4 \) mV, become more pronounced. As the temperature is increased both of these features become less broad and the ZBCP height decreases, eventually disappearing at \( T \sim 1.8 \) K. Our data indicated that introducing Ru has a profound effect on the \( dI/dV \) conductance. For \( x = 0.02 \), the broad hump-like features we observed indicate that the contribution of Andreev bulk states to the \( dI/dV \) spectrum is enhanced compared to \( x = 0 \). These results are consistent with \( C(T) \) measurements that show an exponential low temperature dependence indicating a fully gapped OP for doping as low as \( x = 0.01 \) [39].

Figure 4.11: Temperature dependence of the normalized spectral features seen in the conductance spectrum for a Pt-Ir/Pr(\text{Os}_{0.98}\text{Ru}_{0.02})_{4}\text{Sb}_{12} \) point-contact junction. Shown in the inset are the features corresponding to the symbols. Dashed lines are a guide to the eye.

Figure 4.11 shows the temperature evolution of the excess spectral area, the height of the ZBCP and the features in the \( dI/dV \) occurring at \( \delta_1 \) and \( \delta_2 \) as indicated in Figure 4.10, normalized to their respective values at \( T = 90 \) mK. For the \( x = 0 \) sample the temperature dependence of the ZBCP height followed that of the lower energy spectral feature while the temperature dependence of the excess spectral area followed that of
the higher energy spectral feature. This should be contrasted with the data for the $x = 0.02$ sample where the temperature dependence of both spectral features more closely resembled that of the excess spectral area as opposed to that of the ZBCP height. A change of curvature in the temperature evolution of the ZBCP is observed, as shown by the dashed lines in Figure 4.11, possibly related to a crossover from a peak that results from Andreev surface states to a hump-like feature due to Andreev bulk states. Our results, obtained using a highly local probe, which show that Ru-doping enhances the contribution of Andreev bulk states in the $dI/dV$ spectrum are consistent with $C(T)$ and penetration depth measurements that show an isotropic gap [39, 46].

![Graph](image)

Figure 4.12: Differential conductance spectrum as a function of magnetic field for a Pt-Ir/Pr(Os$_{0.98}$Ru$_{0.02}$)$_4$Sb$_{12}$ point-contact junction at 90 mK. Inset shows the evolution of the excess spectral area (arbitrary units) with field.

Figure 4.12 shows the magnetic field evolution of the $dI/dV$ spectrum for a $x = 0.02$ sample at 90 mK. As the field is increased the hump-like features become less broad and the ZBCP height decreases. However, unlike the $x = 0$ case, above 1.5 T a broad hump-like feature can still be seen up to $\sim 2.2$ T. Shown in the inset is the magnetic field dependence of the excess spectral area. As the field is lowered, the excess spectral
area increases.

Figure 4.13: Differential conductance spectrum as a function of temperature for a Pt-Ir/Pr(Os$_{0.95}$Ru$_{0.05}$)$_4$Sb$_{12}$ point-contact junction at zero magnetic field.

Figure 4.13 shows the temperature evolution of the $dI/dV$ spectrum for a $x = 0.05$ sample. Above $T_c$ the $dI/dV$ conductance spectrum is featureless. Below $T \sim 1.8$ K a small hump-like feature begins to develop and it continues to grow as the temperature is lowered. At 90 mK the hump-like feature is observed between $\sim \pm 0.8$ meV. Neither the multiple spectral features nor the ZBCP seen in the $dI/dV$ spectrum for the $x = 0$ and $x = 0.02$ samples are observed.

On increasing the Ru doping from 2% to 5% it appears that the contribution of Andreev bulk states to the $dI/dV$ spectrum is further enhanced. Our point-contact results, obtained using a highly local probe are once again qualitatively consistent with Frederick et al.’s bulk specific heat data that showed a rapid suppression of the nodal OP component as a function of Ru doping [39]. Furthermore, Frederick et al. showed that while a clear double superconducting transition is present for the $x = 0$ sample, above $x = 0.04$ the double transition is no longer observed. However, due to the broad transition
observed for higher Ru dopings the study could not conclusively determine whether the
double transition no longer existed above $x = 0.04$ or if it was simply indistinguishable.

![Graph](image)

Figure 4.14: Temperature dependence of the normalized spectral features seen in the
conductance spectrum for a Pt-Ir/Pr(Os$_{0.95}$Ru$_{0.05}$)$_4$Sb$_{12}$ point-contact junction. Shown
in the inset are the features corresponding to the symbols.

Figure 4.14 shows the temperature evolution of the excess spectral area, the height
of the ZBCP and the feature in the $dI/dV$ spectrum occurring at $\sim \pm 0.8$ mV in Figure
4.13, normalized to their respective values at $T = 90$ mK. The temperature evolution of
the spectral structure located at $\sim \pm 0.8$ meV closely resembles that of both the excess
spectral area and the peak height. This data, which confirms that the role of Andreev
bulk states is enhanced as $x$ is increased, is consistent with experimental studies which
show that the OP becomes isotropic as the Ru concentration is increased [39, 46].
4.6 Conclusion

Point-contact spectroscopy measurements were performed on single crystal samples of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ to locally probe the superconducting OP. For $x = 0$, at 90 mK, a pronounced zero-bias conductance peak was observed in the $dI/dV$ spectrum indicating the presence of a nodal OP component. Excess spectral was also observed at low temperatures consistent with the presence of a second OP component with different symmetry. While the excess spectral area persisted up to $T \sim 1.8$ K, the temperature evolution of the zero-bias conductance peak height terminated at $T \sim 1.7$ K. The two temperatures correspond with $T_{c1}$ and $T_{c2}$ observed by $\chi_{ac}(T)$ suggesting that the double superconducting transition in PrOs$_4$Sb$_{12}$ is intrinsic in nature (to within 80 nm, the estimated point-contact radius). The magnetic-field evolution of the zero-bias conductance peak at different temperatures was measured to map out the $H-T$ phase diagram. Our results showed that the zero-bias conductance peak vanished at a field $H^*$ lower than the upper critical field $H_{c2}$ as measured by $\rho(T,H)$. Furthermore, we observed that the $H^*(T)$ and $H_{c2}(T)$ curves emerge from distinct low-temperature asymptotes and gradually converge with each other as $T$ approaches $T_c$. The observation of the zero-bias conductance peak vanishing below $H_{c2}$ and the non-parallel behaviour of the two curves is strong evidence for a field-induced change in the symmetry of the OP at $H^*$. For $x = 0.02$, the height of the zero-bias conductance peak compared to $x = 0$ was greatly reduced and additional hump-like features were observed in the $dI/dV$ below $T_c$ and $H_{c2}$. For $x = 0.05$ a single, broad hump-like feature was feature was observed below $T_c$. At both dopings excess spectral area was observed at low temperatures. The spectroscopic evolution of the conductance spectrum upon Ru doping is consistent with $C(T)$ measurements that indicated a rapid change from a nodal OP component at $x = 0$ to a fully gapped OP component for doping as low as $x=0.01$. 
Chapter 5

Spin Polarized Suppression of $d$-wave Andreev States

5.1 Introduction

In a conventional $s$-wave superconductor, Andreev reflection is the process by which an electron incident from a normal metal is converted into a Cooper pair. Since a Cooper pair comprises of two electrons with opposite spin and momentum, the conductance enhancement due to Andreev reflection is maximum when an equal population of spin-up and spin-down carriers exist at the Fermi energy, $E_f$ in the normal metal. Metals that are spin polarized however have a different density of spin-up and spin-down states at the $E_f$ thereby suppressing Andreev reflection [147]. Figure 5.1 illustrates the Andreev reflection process at a metal-superconductor interface. For a normal metal, spin polarization $P = 0\%$, both spin-up and spin-down electrons exist at $E_f$ and a spin-up electron can be retroreflected as a spin-down hole allowing a Cooper pair to enter the superconducting condensate. For a half-metal, $P = 100\%$, only one spin species exists at $E_f$ thus inhibiting the conversion of a normal current to supercurrent via Andreev reflection. Point-contact Andreev reflection is therefore ideally suited to determine the spin
polarization of itinerant ferromagnets as the suppression in the conductance is directly related to the population difference between the spin-up and spin-down bands at $E_f$ [7, 148, 149].

![Schematic illustration showing Andreev reflection for spin polarization](image)

**Figure 5.1:** Schematic illustration showing Andreev reflection for spin polarization (a) $P = 0\%$ and (b) $P = 100\%$. For a normal metal, a spin-up electron (solid circle) is retroreflected as a spin-down hole (empty circle) thus forming a Cooper pair. For a completely spin polarized metal no spin-down holes exist at $E_f$ thereby preventing the formation of a Cooper pair. From Ref. [7]. Reprinted with permission from AAAS.

In an unconventional superconductor with $d$-wave pairing symmetry, the process of Andreev reflection plays a role in the formation of Andreev bound states [83, 84]. Quasi-particles incident from a normal metal, where the node of the $d$-wave order parameter is normal to the interface, undergo Andreev and normal scattering. Due to the sign change in the order parameter at the node, consecutively reflected Andreev and normal quasi-particles constructively interfere with each other leading to a zero-energy bound state at the surface. Andreev-bound states produce a conductance peak at zero-bias and since Andreev reflection is a spin sensitive process, replacing a normal metal with one that is spin-polarized should suppress the zero-bias conductance peak.

The effect of a spin polarized counter-electrode on a $d$-wave superconductor has been previously studied in a planar junction configuration [150, 151] but not using a point-contact junction setup. In this chapter we fabricated a YBCO tip and formed ballistic point-contact junctions on films of both gold (Au) and the near fully spin polarized metal
Chapter 5. Spin Polarized Suppression of $d$-wave Andreev States

CrO$_2$. On YBCO/Au junctions a zero-bias conductance peak was observed while a zero-bias dip was observed on YBCO/CrO$_2$ junctions providing direct spectroscopic evidence for the spin polarized suppression of Andreev bound states in point-contact junctions. The point-contact radius was estimated to range between $\sim 0.7$ - 4.5 nm. Such a small radius can be attributed to the high-impedance nature of the YBCO/CrO$_2$ junctions and demonstrate that YBCO tips could potentially be used to probe spin polarization at the nanoscale. As a control, point-contact junctions between a $s$-wave superconductor/normal metal were formed and a conductance enhancement was observed. $s$-wave superconductor/CrO$_2$ junctions were also formed to confirm the film quality and a conductance suppression consistent with the highly spin polarized nature of CrO$_2$ was observed.

5.2 Normal metal/Conventional superconductor junction

Before using a conventional superconducting tip on thin film samples of the highly spin polarized metal CrO$_2$, normal metal/superconductor point-contact junctions were measured to demonstrate the conductance enhancement associated with Andreev reflection. A sharp, clean superconducting tip was obtained by mechanically cutting Nb wire and rinsing in ethanol. Cu foil, which was sanded down using high-grit sandpaper to obtain a smooth, oxide-free surface and then rinsed in ethanol, was used as the counterelectrode. The tip and sample were mounted on the mechanical driver approach mechanism which was loaded on the $^4$He dipper probe. Junction impedances were typically on the order of 1 $\sim$ 10 $\Omega$. Differential conductance $dI/dV$ measurements were made, with the Lakeshore AC 370 resistance bridge, using the lock-in technique described in Chapter 3.2.1. Data

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1 Diameter 0.02”.
2 Chapter 3.1.1.
3 Chapter 3.3.1.
was collected at different temperatures ranging from 4.2 K to 10 K.

Figure 5.2 shows the temperature dependence of the differential conductance data taken on a Nb tip/Cu foil point-contact junction between 4.2 K and 10.0 K. The spectrum at each temperature was normalized relative to the conductance measured at voltages larger than $\Delta_{Nb}$, the superconducting energy gap of Nb. At 10 K, above the superconducting transition temperature $T_c$ of Nb, the $dI/dV$ spectrum is independent of temperature consistent with the Nb tip no longer superconducting. As the temperature is lowered, a conductance enhancement begins to develop and at 4.2 K the $dI/dV$ spectrum resembles that predicted by BTK theory for a normal metal/conventional superconductor in the high-transparency limit [4], as discussed in Chapter 2.2. Also observed in the conductance spectrum at low temperatures, shown in Figure 5.2, are dips which are not predicted by BTK theory. While these dips can not be explained within the framework of the conventional BTK theory, it has been suggested that they are a result of the proximity
effect whereby Cooper pairs leak into the normal metal from the superconductor creating a weakly superconducting interface [152]. As a consequence, for particular voltage values, both Andreev reflection and quasiparticle transport are suppressed resulting in a dip in the conductance spectrum. Several different experimental studies have also observed similar dips in the $dI/dV$ spectrum of normal metal/conventional $s$-wave superconductor point contact junctions in the high transparency regime [7, 152].

5.3 Spin polarized metal/Conventional superconductor junction

Having observed a sub-gap conductance enhancement due to Andreev reflection on a normal metal/conventional superconductor junction, the conductance characteristics of superconducting point contact junctions formed between a Pb tip and the highly spin polarized metal CrO$_2$ were measured. Epitaxial thin film samples of CrO$_2$ were fabricated on (100) oriented TiO$_2$ substrates using a chemical vapour deposition growth technique\cite[153, 154, 155, 156, 157]. Film thicknesses ranged between 250-500 nm.

Magnetization measurements between 4K and 300 K in an applied magnetic field of $H = 400$ Oe were made to characterize the films using a Quantum Design Physical Properties Measurement System (PPMS). Using a standard 4 point lock-in method the electrical resistivity was also measured in a $^4$He dipper probe. Figure 5.3 shows the typical temperature evolution of the electrical resistivity and magnetization measured on a CrO$_2$ film. The electrical resistance decreases as the temperature is lowered, eventually saturating at low temperatures. CrO$_2$ has a Curie temperature $T_C \sim 395$ K, which is beyond the temperature range of the PPMS, making the magnetization measurements exclusively in the ferromagnetic state. As the temperature is lowered the magnetization increases eventually saturating at low temperatures, consistent with the mean-field

\footnote{Films were grown at Florida State University by I.J. Guilaran and Prof. P. Xiong.}
behaviour expected for ferromagnets. Both the electrical resistivity and magnetization measurements made are consistent with those obtained by other experimental studies on highly epitaxial CrO$_2$ films [153, 154, 158].

Figure 5.3: Electrical resistance and magnetization of a CrO$_2$ film as a function of temperature.

Prior to making point-contact measurements, two gold pads were deposited on opposite ends of the film to ensure intimate contact between the electrical leads and the CrO$_2$ surface. Measurements were made in a $^4$He dipper probe between 4.2 - 9.5 K. Differential conductance data was obtained with the Stanford Research Systems SIM921 AC resistance bridge, using the lock-in technique described in Chapter 3.2.1.

Figure 5.4 shows the temperature evolution of the $dI/dV$ spectrum measured on a Pb/CrO$_2$ point-contact junction. The spectrum at each temperature was normalized relative to the conductance measured at voltages larger than $\Delta_{Pb}$, the superconducting energy gap of Pb. At 7.5 K, above the $T_c$ of Pb, the $dI/dV$ spectrum shows no dependence on the applied voltage. As the temperature is lowered below $T_c$ a reduction in the sub-
Figure 5.4: Normalized differential conductance versus bias voltage data taken on a Pb/CrO$_2$ point-contact junction at different temperatures. The open symbols correspond to the data while the solid lines are fits using the BTK model.

gap conductance is observed indicating that electron transport is suppressed for energies $|V| < \Delta_{Pb}$. While the open symbols represent the data, the solid lines are fits to the modified BTK model to account for spin polarization [152]. The total current $I$, which can be regarded as a sum of the spin polarized current $I_p$ and the unpolarized current $I_u$, is given by:

$$I = (1 - P)I_u + PI_p$$

(5.1)

where $P$ is the spin polarization. The currents $I_u$ and $I_p$ are calculated from the BTK equation:

$$I_\alpha = 2eANvf \int_{-\infty}^{\infty} \left[f(E - V, T) - f(E, T)\right] \left[1 + A_\alpha - B_\alpha\right] dE, \quad \alpha = u, p$$

(5.2)

using the appropriate Andreev reflection $A_u, A_p$ and normal reflection $B_u, B_p$ probabilities.
for the unpolarized and spin polarized current [152]. In calculating \( A_\alpha \) and \( B_\alpha \) the superconducting energy gap \( \Delta \) and dimensionless barrier potential \( Z \) are incorporated\(^5\), making it necessary to involve four parameters, \( P, Z, \Delta \) and \( T \), to fit the data shown in Figure 5.4.

The temperature dependence of the magnetization data shown in Figure 5.3 indicates that the magnetic moment of \( \text{CrO}_2 \) remains unchanged at very low temperatures, making it reasonable to postulate that the spin polarization \( P \) of the film does not appreciably vary within the temperature range (4.2 K - 7.5 K) over which the \( dI/dV \) data was collected. Similarly, since the normal state conductance \( \frac{dI}{dV} (|V| > \Delta_{\text{Pb}}) \) did not change with temperature, the barrier potential \( Z \) can be regarded as constant. With increasing temperature the superconducting energy gap \( \Delta \) decreases and using the generalized BCS gap equation\(^6\) \( \Delta = \Delta_0 \tanh(1.74 \sqrt{(T_c / T) - 1}) \) where \( \Delta_0 \) is the energy gap at \( T = 0 \) K, \( \Delta \) at each temperature was determined [159]. The values of the parameters used to fit the data shown in Figure 5.4 were \( \Delta_0 = 0.95 \) meV, \( Z = 1.2 \) and \( P = 0.85 \). The value of \( \Delta_0 = 0.95 \) meV is consistent with the superconducting energy gap of \( \text{Pb}, \Delta_{\text{Pb}} = 1.08 \) meV. The high spin polarization observed confirms the near half-metallic nature of the \( \text{CrO}_2 \) films studied. It should be noted that several different theoretical approaches have been proposed for determining the spin polarization in a conventional superconductor/ferromagnet junction [152, 160, 161, 162, 163]. The model used to fit the data shown in Figure 5.4 is a simple 1D model that assumes electron transport in one conductance channel is fully spin polarized while transport in another channel is completely unpolarized [152]. More sophisticated theories have accounted for the very small but finite probability of Andreev reflection in a half-metal and extended the simple 1D model to a 3D formulation [160, 161, 162, 163]. A comparison between some of the models showed that they yielded virtually identical values, to within a few percent, for the spin polariza-

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\(^5\)Chapter 2.2.

\(^6\)The equation is valid for weak coupling superconductors and although Pb is strictly speaking a strong coupling superconductor, it was used to simply approximate a value for \( \Delta \).
The fits shown in Figure 5.4 are intended to illustrate that the CrO$_2$ films are highly spin polarized, rather than to extract extremely precise quantitative values for the spin polarization, and as such the approximations incorporated by the simple 1D model suffice.

Furthermore, for a full quantitative study, the effect of spreading resistance needs to be considered when resistive thin films are used as counterelectrodes. Spreading resistance arises because there is a finite voltage drop across the film as current travels through the film and toward the point-contact. This problem is most significant when the resistance of the film is comparable to the point-contact resistance. Figure 5.3 shows that the resistance of the CrO$_2$ films at 4.2 K was $\sim 0.5 \ \Omega$. As the point-contact junctions were typically on the order of several Ohms, the effect of spreading resistance on the measured conductance spectrum would be negligible. A theoretical model calculating the effect of spreading resistance on conductance curves has shown that the position of the coherence peaks seen at $V \sim \Delta$ are shifted to higher voltages [165]. Figure 5.4 shows that the coherence peaks occur at $V \sim \Delta_{Pb}$, further confirming that spreading resistance is not a major concern in the Pb/CrO$_2$ point-contacts studied.

While the spin polarization can be determined from the full BTK fit, in the special limit where $Z \rightarrow 0$ and $V, k_B T << \Delta$ the normalized conductance $\sigma_s/\sigma_n$ at zero-bias can be expressed as [147]:

$$\left. \frac{\sigma_s}{\sigma_n} \right|_{V,Z,T \rightarrow 0} = 2(1 - P) \quad (5.3)$$

At 4.2 K, the lowest temperature at which $dI/dV$ measurements on the CrO$_2$ films were made, Figure 5.4 shows that the normalized conductance at zero bias $\left. \frac{\sigma_s}{\sigma_n} \right|_{V=0} = 0.26$. Using this value in Equation 5.3 then yields a spin polarization of $P = 0.87$ which corresponds closely with the spin polarization $P = 0.85$ obtained from the full BTK fit. Therefore, even though Equation 5.3 is strictly valid only in the limit $V, Z, T \rightarrow 0$, at 4.2 K for a highly transparent point-contact junction it can still be used to provide a fairly
accurate estimation of the spin polarization.

Several point-contact Andreev reflection studies on CrO$_2$ have reported the spin polarization to be between $P = 90\%-96\%$ [7, 166, 165] and while the spin polarization of our films $P \sim 85\%$ is in close agreement with those experimental studies, it is however slightly lower. A possible explanation is that even though the Pb tip was in intimate contact with the CrO$_2$ film, suggesting a highly transparent junction, the fit to the data showed that $Z \sim 1$, indicating only a moderately transparent junction. Various experimental studies have showed that the measured spin polarization decreases as $Z$ increases [152, 166, 167, 168, 169, 165]. A theoretical proposal has suggested that spin-flip scattering occurring at the interface is dependent on the barrier potential $Z$ thus effectively reducing the value of the spin polarization measured via point-contact Andreev reflection with increasing $Z$ [168]. Given that the junction was not in the extremely high transparency regime, a spin polarization value of $P \sim 85\%$ is consistent with the near complete half-metallic nature of CrO$_2$.

The tip was firmly pressed into the sample yielding junction resistances typically on the order of several Ohms. A possible reason as to why the junction appeared to only be in the moderately high transparency regime is that at ambient conditions CrO$_2$ is metastable and naturally reduces to Cr$_2$O$_3$. It has been shown that a thin native oxide layer of Cr$_2$O$_3$, a few nanometers thick, forms on the surface of CrO$_2$ [170]. Cr$_2$O$_3$ is insulating and anti-ferromagnetic [171] - it has been used a tunnelling barrier to form magnetic tunnel junctions [172] - and when the point-contact is formed, if the tip does not completely puncture through this insulating layer, it will decrease the junction transparency (i.e. increase $Z$) and act as a spin scatterer thereby effectively causing the measured spin polarization of the CrO$_2$ film to be lower than its true value. Surface degradation is obviously undesirable and to minimize its effect point-contact measurements were always made on fresh CrO$_2$ films, but since they were fabricated at Florida State University and because CrO$_2$ naturally reduces to Cr$_2$O$_3$, slight surface contamination is likely
unavoidable. Nonetheless, the measured spin polarization yielding $P = 85\%$ shows that surface contamination is not a major concern and confirms the near half-metallic nature of CrO$_2$.

5.4 Normal metal/Unconventional superconductor junction

YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) is an unconventional superconductor with an anisotropic superconducting energy gap. Having established that our CrO$_2$ films exhibit near complete half-metallicity, the effect of spin polarization on Andreev bound states can be determined by measuring the conductance across YBCO/CrO$_2$ point-contact junctions. The YBCO tips were however first tested on a normal metal (Au) by forming YBCO/Au point-contact junctions to ensure that a zero-bias conductance peak (ZBCP) due to Andreev interference was observed in the $dI/dV$ conductance.

YBCO pieces, typically 2x2x5 mm$^3$, were cut from a large high-density texture melt$^7$. Using progressively higher grit sand paper, the YBCO pieces were mechanically polished to a fine tip. After ultra-sonic cleaning in ethanol, the YBCO tips were re-annealed at 500 °C in flowing oxygen for 36 hours. Figure 5.5 shows a microscope image of a YBCO tip.

To ensure the YBCO tips were superconducting, ac susceptibility $\chi$ measurements were performed. Figure 5.6 shows $\chi(T)$ for a YBCO tip measured at an applied magnetic field of $H = 300$ Oe. The data shows $T_c = 91$ K, consistent with the superconducting transition temperature of optimally doped YBCO.

Thin film samples of gold, approximately 1 $\mu$m thick, were grown by pulsed laser deposition and used as the counter-electrode. The sample and tip were mounted on

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$^7$YBCO high-density texture melt provided by Professor M.K. Wu.
the mechanical driver approach mechanism\textsuperscript{8} which was loaded on the $^4$He dipper probe. Junction impedances when the sample and tip were brought into contact at 4.2 K were typically on the order of 10 - 500 $\Omega$. Differential conductance $dI/dV$ measurements were made with the Stanford Research Systems SIM921 AC resistance bridge using the lock-in technique described in Chapter 3.2.1.

Figure 5.7 shows the normalized $dI/dV$ conductance spectrum measured on a YBCO/Au point-contact junction at 4.2 K. A ZBCP along with dips which begin to form at approximately $\pm$ 20 mV (indicated by the arrows), corresponding to the superconducting energy gap $\Delta_{YBCO}$ of optimally doped YBCO, are observed in the normalized conductance spectrum. At higher biases, the normalized conductance is independent of bias voltage. The dashed line, a guide to the eye, represents a constant normal state conductance background. Such ZBCP structures have commonly been observed

\textsuperscript{8}Chapter 3.1.1.
Figure 5.6: ac susceptibility versus temperature of a YBCO tip indicating a superconducting transition $T_c = 91$ K.

in YBCO and identified as arising due the $d$-wave superconducting order parameter [173, 146, 174, 175, 176, 177, 178]. By subtracting the normal state conductance and numerically integrating between $\pm$ 40 mV it was found that the spectral area was conserved (i.e. the area of the dips was equal to that of the peak) consistent with a ZBCP being formed by Andreev bound states.

Shown in the inset of Figure 5.7 is the unnormalized $dI/dV$ conductance spectrum. For energies larger than the superconducting gap of YBCO $|V| > \Delta_{YBCO} \sim 20mV$, the conductance increases with bias voltage. The $dI/dV$ spectrum was normalized by fitting the conductance background ($|V| > 20$ mV) to a polynomial equation and then dividing the entire spectrum by the fit. A voltage dependent background conductance has been commonly observed in YBCO junctions [179, 180, 181] and although there has been much theoretical work [182, 183, 184], its origin is not entirely understood.

Several different YBCO tips were brought into contact with Au samples and the
junction resistance observed ranged from \( \sim 10 \, \Omega \) to \( \sim 500 \, \Omega \), reflecting that the effective tip area in contact with the sample was different. Andreev bound states predominantly manifest themselves in the low junction transparency regime. However, if the Fermi velocities of the tip and sample are different, the effective barrier potential \( Z_{\text{eff}} \) will be higher [185]:

\[
Z_{\text{eff}} = \sqrt{Z^2 + \frac{(1-r)^2}{4r}}
\]

where \( r \) is the Fermi velocity ratio. Therefore, due to the Fermi wavevector mismatch between YBCO and Au, the effective barrier potential is intrinsically conducive to the formation of \( d \)-wave Andreev states, regardless of junction resistance.

Andreev bound states occur when consecutively reflected quasiparticles experience
a sign change in the order parameter and constructively interfere with each other [83]. Therefore, the ZBCP that results in the conductance spectrum is most pronounced when the node of the $d$-wave order parameter is perpendicular to the junction interface [83, 84]. As the texture melt from which the YBCO tip was cut was polycrystalline there was no way to ensure \textit{a priori} that electron transport across the junction interface was exclusively along the [110] direction. However, the fact that a ZBCP was repeatedly observed with several different tips and the ubiquitous nature of the ZBCP [186] strongly indicate that the conductance characteristics we observed, by forming point-contact junctions using our YBCO tips, were dominated by the contribution of Andreev bound states. Epitaxial YBCO films were grown using pulsed laser deposition and Figure 5.8 compares the normalized conductance spectrum measured at 4.2 K on a YBCO tip/Au film point-contact junction with that taken on a Pt-Ir tip/YBCO film junction. Figure 5.8 confirms that ZBCPs, commonly observed on junctions formed using YBCO films [173, 146, 174, 175, 176, 177, 178], can also be observed on a junction formed using a YBCO tip.
Figure 5.8: Normalized conductance spectrum measured at 4.2 K on (a) YBCO tip/Au film point-contact junction and (b) Pt-Ir tip/YBCO film point-contact junction.
5.5 Spin polarized metal/Unconventional superconductor junction

Having established that the YBCO tips were able to sustain Andreev bound states on Au films, the effect of spin polarization was determined by forming YBCO tip/CrO$_2$ film junctions. Before loading the YBCO tip on the mechanical point-contact driver mechanism it was cleaned in an ultrasonic ethanol bath to ensure that no gold particles remained on the tip surface. A CrO$_2$ film, with two gold pads deposited on opposite ends of the film to ensure intimate contact between the electrical leads and the CrO$_2$ surface, was loaded on the sample stage of the mechanical point-contact driver mechanism which was placed in a $^4$He dipper probe. Junction impedances when the sample and tip were brought into contact at 4.2 K were typically on the order of 100 - 4000 Ω. Differential conductance $dI/dV$ data at 4.2 K was obtained, with the Stanford Research Systems SIM921 AC resistance bridge, using the lock-in technique described in Chapter 3.2.1.

Figure 5.9 shows the typical normalized $dI/dV$ conductance spectrum observed on a YBCO tip/CrO$_2$ film junction at 4.2 K. For voltages above the superconducting energy gap of YBCO, $\Delta_{YBCO} > 20$ meV, the normalized conductance is independent of voltage. For $|V| < \Delta_{YBCO}$, a zero-bias dip (ZBD) in the normalized conductance was observed. Shown in the inset is the unnormalized spectrum. The normalized conductance was determined by fitting the normal-state conductance ($|V| \gtrsim 20$ mv) to a polynomial and dividing the entire spectrum by the fit. Two kinks (change in curvature) are observed in the the conductance spectrum and their positions are indicated by the arrows in the inset. The position of these kinks, which corresponds with the superconducting energy gap of YBCO, indicate a crossover from the normal-state to sub-gap regime where a suppression in the conductance was observed.

To confirm that the ZBD observed in the conductance spectrum at 4.2 K was attributable to the spin-polarization of CrO$_2$ and not the normal-state background of
Figure 5.9: Normalized conductance spectrum measured on a CrO$_2$ film using a YBCO tip at 4.2 K. Inset shows a plot of the unnormalized conductance spectrum showing the voltage dependent normal state background characteristic of YBCO. Kinks in the conductance spectrum, indicated by the arrows, are observed at the position of the superconducting energy gap for YBCO.

YBCO, the conductance spectrum for a YBCO/CrO$_2$ junction was also measured at $T = 100 \text{ K} > T_c$. Figure 5.10 compares the conductance spectrum obtained at 100 K and 4.2 K. Above $T_c$, YBCO is not superconducting and the conductance data, which does not show the kinks that were observed in the spectrum at 4.2 K, can be fit over the entire voltage bias range using a simple polynomial. Below $T_c$, a similar polynomial can only fit the normal-state conductance data i.e. in the region where $|V| > \Delta_{YBCO}$. For $|V| < \Delta_{YBCO}$, YBCO is in the superconducting state and the measured conductance deviates from the fit to the normal-state background, indicating that the sub-gap suppression is directly related to the inherent spin polarization of CrO$_2$ and not the conductance background characteristic of YBCO.
Figure 5.10: Unnormalized differential conductance spectrum taken on a YBCO tip/CrO$_2$ junction at (a) $T < T_c$ (4.2 K) and (b) $T > T_c$ (100 K). Open symbols represent the experimental data while the solid lines are a polynomial fit to the background. The arrows shown in (b) correspond with the position of the superconducting energy gap for YBCO.
Due to the complex oxide nature of both the tip and sample, the YBCO/CrO$_2$ junction resistance at 4.2 K ranged from 100 - 4000 Ω. A high junction resistance $R$ indicates a small contact area, implying that the electron transport across the interface is highly local. The effective point-contact radius, $a$ can be calculated using the Wexler formula [127]:

$$R \approx \frac{4\rho l}{3\pi a^2} + \frac{\rho}{4a}$$

(5.5)

where $\rho$ is the residual resistivity and $l$ is the mean free path. Using $\rho = 50 \mu\Omega\text{cm}$ and $l = 10$ nm as estimates for YBCO [146] and $R = 0.1 - 4$ kΩ, the junction radius was found to range from $a \sim 0.7 - 4.5$ nm attesting to their ballistic and microscopic nature. When forming point-contact junctions between CrO$_2$ and a conventional $s$-wave superconductor, where the electronic mean path is larger than that of YBCO, the typical interface resistance varied between $\sim 1-10$ Ω. As a consequence, when using a conventional superconducting tip the effective point-contact size was much larger, $a \sim 10 - 100$ nm, than that compared to using a YBCO tip. Fabricating a high-impedance point-contact interface using a YBCO tip is therefore highly desirable since the resulting junction size is extremely small. The microscopic nature of the junctions demonstrates the feasibility of using YBCO tips as a nanoscale spin-sensitive probe of itinerant ferromagnets.

Figure 5.11 compares the normalized conductance spectrum obtained on junctions formed using a YBCO tip with both Au and CrO$_2$ films at 4.2 K. For $|V| > \Delta_{YBCO}$ the normalized conductance measured on both films was identical and independent of voltage. At $|V| \approx \Delta_{YBCO}$ (indicated by the arrows), it is clear that the normalized conductance measured on the Au and CrO$_2$ films begins to deviate with very different sub-gap conductance behaviour. For the voltage range $|V| < \Delta_{YBCO}$ a pronounced ZBCP, a signature of Andreev bound states, was observed in the normalized conductance spectrum measured on Au films while data taken on CrO$_2$ films showed a ZBD in the normalized conductance. These results confirm that Andreev interference, the process
Figure 5.11: Normalized conductance spectrum measured on a YBCO tip/Au film (red symbols) and YBCO tip/CrO$_2$ film (blue symbols) junction at 4.2 K. The arrows indicate the position of the superconducting energy gap for YBCO.

by which Andreev bound states are formed, is indeed suppressed by spin polarization.

5.6 Conclusion

Thin films of CrO$_2$, a near half-metal, were used to determine the effect of spin polarization on Andreev bound states in unconventional superconductors. YBCO tips were fabricated by mechanically polishing slivers cut from a high-density YBCO texture melt. A pronounced ZBCP was seen in the normalized conductance spectrum taken on YBCO/Au junctions consistent with the occurrence of Andreev bound states. However, a sub-gap conductance suppression was observed on YBCO/CrO$_2$ point-contact junctions. Our results are the first providing spectroscopic evidence that spin polarized transport across a $d$-wave superconductor/ferromagnet point-contact interface prevent the formation of An-
dreev bound states. Using YBCO tips, high-impedance junctions were formed resulting in point-contact areas that ranged between $\sim 0.7$ - $4.5$ nm. Such microscopic junction sizes demonstrate the potential of using YBCO tips as a spin-sensitive nanoprobe of itinerant ferromagnets. The conductance across a $s$-wave superconductor/CrO$_2$ junction was also measured and confirmed that the CrO$_2$ films exhibit near complete spin polarization.
Chapter 6

Temperature and Field Dependence of the Conductance Spectra in CeCoIn$_5$

6.1 Introduction

The discovery of superconductivity in CeCoIn$_5$ has attracted much interest, particularly because it has the highest superconducting transition temperature $T_c = 2.3$ K among the Ce-based heavy-fermion metals [55]. Several experimental studies have revealed evidence for a unconventional superconducting state, including the observation of low-energy quasiparticle excitations, indicative of nodes in the superconducting gap function [56, 58, 57, 59], consistent with $d$-wave pairing symmetry [187, 13]. Multiple sheets cross the Fermi surface of CeCoIn$_5$ [60, 61, 62, 63, 64], giving rise to the possibility that multiple bands are involved in superconductivity [65, 66, 42].

In this chapter, point-contact Andreev spectroscopy data taken on high quality single crystal samples of CeCoIn$_5$ is presented. The temperature evolution of the $dI/dV$ conductance between 150 mK - 2.5 K and the magnetic field dependence at base tem-
temperature up to 6 T was measured. Multiple structures, whose dependence on junction impedance indicate two co-existing order parameter (OP) components with nodal characteristics, were observed. The magnitude of the OP components was large relative to $T_c$ (compared to BCS theory) and both evolved differently with temperature, suggesting a highly unconventional pairing mechanism, possibly involving multiple bands.

6.2 Experimental Details

Single crystal samples of CeCoIn$_5$ were grown using a self-flux method [55] and characterized by both x-ray diffraction and magnetic susceptibility, which showed a sharp superconducting transition at $T_c = 2.3$ K$^1$. Prior to making measurements, the crystals were etched in HCl and rinsed in an ultrasonic ethanol bath to ensure that any residual In flux was removed. High purity Pt-Ir tips were used as the normal-metal counterelectrode and the crystal platelets, which were approximately 1x1x0.2 mm$^3$ in size, were mounted such that $c$-axis point-contact junctions were formed. Both a spring-cushioned differential micrometer$^2$ and piezo driven$^3$ approach mechanism were used to bring the sample and tip into contact at low temperatures. The point-contact driver was attached to the mixing chamber of a $^3$He-$^4$He dilution refrigerator which enabled the junction impedance to be varied in situ at low temperatures. The temperature evolution of the $dI/dV$ conductance was measured in the superconducting state down to 150 mK and at base temperature the magnetic field dependence, with the applied field oriented perpendicular to the $c$-axis face, was also measured. To minimize Joule heating a pulsed technique$^4$ was used to acquire the data. 2 ms current pulses were applied through the contact in the 20% duty cycles and the junction voltage was measured 80 times within each pulse and averaged. The current vs voltage $I-V$ curves were obtained by varying the current

$^1$CeCoIn$_5$ single crystals grown and characterized by C. Petrovic at Brookhaven National Laboratory.
$^2$Chapter 3.1.1.
$^3$Chapter 3.1.2.
$^4$Chapter 3.2.2.
and then numerically differentiated to obtain the $dI/dV$ conductance spectrum.

### 6.3 Low-temperature Conductance Spectra

The sample and tip were brought into contact at low temperatures with the point-contact resistance typically varying between $\sim 0.2 - 1 \, \Omega$. Two different types of conductance spectra were observed, depending on the junction impedance. The measurements were repeated on multiple spots and on different samples and the typical spectra is presented. Figure 6.1 shows the normalized $dI/dV$ spectrum taken at 0.43 K, well below $T_c$, on a (a) 0.4 $\Omega$ and (b) 0.2 $\Omega$ junction. The data was normalized relative to the respective $dI/dV$ spectrum measured above $T_c$. In Figure 6.1(a) a pronounced zero-bias conductance peak (ZBCP) with characteristic dips occurring at $\sim \pm 1 \, \text{mV}$ and a broad spectral hump $\sim \pm 2.5 \, \text{mV}$ in width are seen. For junctions with a higher transparency, as shown in Figure 6.1(b), the ZBCP becomes an asymmetric hump like structure with width $\sim \pm 1 \, \text{mV}$ and the dips get filled in while the outer hump like structure remains largely unchanged. The hump-like structures are the classic signature of Andreev reflection, which introduces excess spectral states inside the superconducting energy gap [4]. The excess spectral area expectedly diminishes with temperature, as shown by the dashed line in Figure 6.1(b) taken at 1.5 K. The ZBCP on the other hand is key spectral evidence for nodes in superconducting OP [83].

The point-contact junction resistance $R$ typically ranged between $\sim 0.2 - 1 \, \Omega$. Using the Wexler formula:

$$R \simeq \frac{4 \rho l}{3 \pi a^2} + \frac{\rho}{4a}$$

with values for the resistivity $\rho \sim 1.0 \, \mu\Omega\text{cm}$ [188] and mean free path $l \sim 1600 \, \text{nm}$ [189], an estimate for the point-contact radius $a \sim 133 \, \text{nm}$ is obtained. This shows that spectra was measured on junctions that were well in ballistic regime ($a \ll l$).
Figure 6.1: Normalized $dI/dV$ conductance measured on a Pt-Ir/CeCoIn$_5$ point-contact at 0.43 K for (a) $R = 0.4$ Ω and (b) $R = 0.2$ junction. Data taken at 1.5 K (dashed line) is shown in (b) to clearly illustrate the double hump-like feature.

Peak and hump structures of similar shapes and energy scales to those shown in Figure 6.1 have been reported in an earlier point-contact study of CeCoIn$_5$, although appearing separately in different spectra [190]. The spectra shown in Figure 6.1 are clearly hybrid in character, each containing multiple structures. A recent point-contact study on CeCoIn$_5$ also reported spectra containing multiple features [191] which resembled that shown in Figure 6.1. Point-contact spectroscopy measurements on CeCoIn$_5$ where a single spectral feature with an energy scale of $\sim 1$ mV have been reported [192, 193]. However, the measurements in Ref.[192, 193] were obtained using a DC bias technique.
while our data was collected using a pulsed technique. At low temperatures, for small point-contact resistances ($R \sim 1 \ \Omega$), Joule heating becomes a concern and employing a DC measurement technique could result in a thermal smearing of the $dI/dV$ conductance.

Figure 6.2: $dI/dV$ conductance measured on a $R = 0.4 \ \Omega$ point-contact junction. Data taken at 0.4 K using a pulsed and DC measurement technique is compared with that taken at 1.3 K (pulsed) to illustrate the effect of Joule heating.

Figure 6.2 illustrates the difference between using a pulsed and DC bias measurement technique. The $dI/dV$ spectrum at $T = 0.4 \ K$ was measured on a $R = 0.4 \ \Omega$ junction using both a pulsed (red) and DC (blue) bias. The peak and dip height were suppressed and the position of the hump-like feature had moved inward when the spectrum obtained using a DC bias was compared with that obtained using a pulsed bias, highlighting the effect of thermal smearing. In fact the $dI/dV$ spectrum measured at $T = 1.3 \ K$ using a pulsed bias (green) corresponded with that obtained at $T = 0.4 \ K$ using a DC bias, illustrating the severity of Joule heating and the necessity of using a pulsed bias technique for low temperature point-contact measurements.
6.4 Analysis Using the Generalized BTK Model

The conductance spectrum observed in both the high and low impedance junctions was analyzed using the extended BTK model [83, 84]. A key spectral signature of $d$-wave gap nodes is the ZBCP which arises from surface states bound by phase interference between consecutively Andreev-reflected quasiparticles. This peak structure should be contrasted with the hump-like structure associated with conventional Andreev bulk states. The relative manifestation of Andreev surface or bulk states in the conductance spectrum is dependent upon the junction orientation and $Z$, the junction transparency. Figure 6.3(a) and (b) shows the theoretical conductance spectra of a $d$-wave OP for a high-impedance ($Z=1$) and low impedance ($Z=0.5$) junction respectively. The voltage $eV$ has been normalized relative to $\Delta$, the $d$-wave gap maximum. Both the nodal (blue line) and anti-nodal (red line) junction orientations are depicted in each plot. It should be noted that the conductance spectrum of an ideal $c$-axis junction would resemble that of the anti-nodal case since, for both orientations, there is no sign change in the OP about the junction normal which would result in the formation of Andreev bound states. The peak and hump-like structures in the conductance spectrum are a direct manifestation of the competition between Andreev surface and bulk states respectively.

The $dI/dV$ spectrum observed on Pt-Ir/CeCoIn$_{5}$ junctions, as shown in Figure 6.1, can be interpreted as a superposition of theoretical simulations shown in Figure 6.3. The sharp peak structure can be identified as originating from Andreev surface states due to a high-$Z$ nodal junction while the hump-like structure can be attributed to Andreev bulk states due to a low-$Z$ anti-nodal junction. The appearance of two effective $Z$’s, with different dependences on junction impedance, is indicative of different Andreev coupling to two distinct OPs. To demonstrate this two-OP scenario, a superposition model was developed, based on the ‘serial’ precedence of surface over bulk states in

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5Theoretical model used to generate simulated curves is described in Chapter 2.2.
junction transmission. When bulk spectra from two OPs co-exist, the bulk states can be accessed in ‘parallel’ thus making the superposition of the conductance essentially additive [194]. However, when surface and bulk spectra are involved, the states are accessed in a ‘serial’ manner thus making the superposition of the conductance essentially multiplicative.

Figure 6.4 shows the theoretical conductance resulting from the superposition outlined above. Figure 6.4(a) superposes a peak structure (shown in the left inset) with a hump-like structure (shown in the right inset). The voltage was normalized relative to $\Delta_1$, the OP amplitude of the peak structure, and the OP amplitude of the hump-like structure was chosen such that $\Delta_2 = 3\Delta_1$. For $|eV| < \Delta_1$ both surface and bulk states contribute serially to the overall conductance thus in this voltage range each component spectra were
multiplied. For $|eV| > \Delta_1$ surface states no longer exist and so each component spectra were added together. Figure 6.4(b) superposes two hump-like structures with one having an OP amplitude triple of the other ($\Delta_2 = 3\Delta_1$) as shown in the insets. Since bulk states can be accessed in parallel, the overall conductance was produced by adding together each component spectra. The peak and hump-like structure seen in the data shown in Figure 6.1(a) are remarkably well reproduced here in Figure 6.4(a). Similarly, the double hump-like structure seen in the data shown in Figure 6.1(b) is generically reproduced in Figure 6.4(b). The strong resemblance between the data and the simulations provides robust evidence for the coexistence of two OPs.

![Figure 6.4: Spectral simulations of the normalized $dI/dV$ for the (a) serial and (b) parallel model. Shown in the respective insets are two spectra, with the orientation and junction transparency indicated, that were superposed (in serial or parallel) to obtain the main spectrum.](image)

Although the model is able to reproduce the experimental data, some general remarks about the two-OP spectral analysis should be made. The model was formulated to show
generically how two coexisting OPs with gap nodes could produce the multiple spectral structures. The distinctively serial relationship between the peak and hump structures clearly establishes the surface-state nature of the former, as arising from Andreev interference for a nodal OP. However, although our data can be explained within a \( d \)-wave framework, the presence of other OP line or point nodes, along either the pole or the equator, such as in the case of UPt\(_3\) [22], can not be ruled out. The choice of using a \( d \)-wave order parameter in the model was motivated by both thermodynamic and transport data [58, 59]. Precise determination of the pairing symmetry in CeCoIn\(_5\) would require a systematic study of the spectral anisotropy [146], along with an extension of the generalized BTK theory beyond its two-dimensional formulation. Also, the non-trivial spectral evolution observed by changing junction impedance indicates a complex \( k \)-space dependence of \( Z \), with the nodal junction states dominating at high \( Z \) and anti-nodal junction states dominating at low \( Z \). While surface roughness could allow for nodal-junction surfaces to exist on a \( c \)-axis crystal, a detailed explanation of the peak-to-hump evolution would require a full understanding of how \( Z \) depends on the complex band structure of CeCoIn\(_5\) [195]. Furthermore, the spectral heights tend to be smaller in the data than in the model, a difference which could be attributed to non-superconducting spectral contributions from either uncondensed quasiparticles [196, 197] or Kondo scattering [16].

6.5 Temperature Evolution

Figure 6.5 shows the temperature evolution, between 0.15 - 2.5 K, of the \( dI/dV \) spectrum measured on both the \( R = 0.2 \) and 0.4 \( \Omega \) junctions. The spectra have been staggered for clarity and the arrows in Figure 6.5(a) indicate the position of the two spectral features. The solid line in Figure 6.5(b) was added to illustrate the excess spectral area observed in the \( dI/dV \) spectrum. Figure 6.5(c) shows the temperature dependence of the two OP amplitudes \( \Delta_1(T) \) and \( \Delta_2(T) \), indicated by the arrows in Figure 6.5(a), along with
theoretical curves (dotted lines) calculated from the BCS gap equation. Figure 6.5(d) shows the temperature evolution of the excess spectral area observed in the conductance spectrum shown in 6.5(b). The excess spectral area \( S \) was normalized relative to its base temperature value \( S_0 \) [125]. Figure 6.5(c) shows that the two OP amplitudes emerge from two distinct zero-temperature values, \( \Delta_1 = 0.95 \pm 0.15 \text{ mV} \) and \( \Delta_2 = 2.4 \pm 0.3 \text{ mV} \), gradually converge with each other and eventually vanish near \( T_c = 2.3 \text{ K} \), consistent with both components being of the same superconducting order [65]. This common \( T_c \) also argues against the presence of a proximity induced superconducting layer in the junctions, which should cause the smaller OP component to vanish below the bulk \( T_c \) [194]. However, while \( \Delta_1(T) \) is well described by the BCS gap equation (dotted line), \( \Delta_2(T) \) deviates markedly from mean-field behaviour. Figure 6.5(d) shows that the temperature evolution of the excess spectral area also departs from the theoretical predication. Similar deviations have been observed in other heavy-fermion superconductors and attributed to the nodality of highly complex pairing symmetries [125, 198, 126].

Assigning \( \Delta_1 \) and \( \Delta_2 \) to a superconducting OP, from the low temperature asymptote in Figure 6.5(d), they would correspond to gap-to-\( T_c \) ratios of \( 2\Delta_1/k_B T_c = 9.5 \pm 1.5 \) and \( 2\Delta_2/k_B T_c = 24 \pm 3 \). These ratios are both much larger than the conventional weak-coupling BCS value of 3.5 for phonon-mediated electron pairing and in fact also beyond the strong-coupling limit even after \( d \)-wave corrections [199]. One conceivable way to enhance the gap-to-\( T_c \) ratio is through interband coupling whereby carriers from different bands interact with each other, resulting in multiple pairing potentials sharing a common \( T_c \) [65]. Such a multiband scenario is physically plausible considering the complex Fermi topology of CeCoIn\(_5\) [61, 62, 63]. In fact Andreev scattering for a heavy-mass sheet would be inherently weaker than that for a light-mass sheet, due to a greater Fermi velocity mismatch across the junction [185, 195], thus providing a natural explanation for the different \( Z \) scales observed in the spectra.
Figure 6.5: Temperature dependence of the normalized $dI/dV$ spectrum measured on a Pt-Ir/CeCoIn$_5$ point-contact for (a) $R = 0.4\;\Omega$ and (b) $R = 0.2\;\Omega$ junction. Curves have been offset for clarity. The temperature dependence of the OP amplitudes $\Delta_1(T)$ and $\Delta_2(T)$, as indicated by the orange and green arrows in (a), have been plotted in (c). The reduced spectral area $S/S_0$ (see text for description) calculated from the spectra in (b) has been plotted in (d). Theoretical BCS curves are depicted in (c) and (d) by solid lines.
6.6 Magnetic Field Evolution

The magnetic field dependence of the $dI/dV$ spectrum at 100 mK was also measured on Pt-Ir/CeCoIn$_5$ point-contacts by applying a field parallel to the $c$-axis. Figure 6.6(a) shows the field evolution for a $R = 0.3$ Ω junction at $T = 100$ mK while (b) shows the field dependence of the OP amplitudes $\Delta_1$ and $\Delta_2$. At zero field, both the peak-dip and hump-like structures are visible. As the field is increased the peak height becomes smaller and the position of the dips and hump-like structure move inward eventually vanishing at $H \sim 5.0$ T, corresponding with $H_{c2,||c}$, the upper critical field of CeCoIn$_5$ along the $c$-axis. As shown in Figure 6.6(b), both the peak-dip and hump-like feature associated with $\Delta_1(H)$ and $\Delta_2(H)$ persist up to $H_{c2,||c}$, providing further evidence for a highly unconventional multiband pairing scenario in CeCoIn$_5$ [144].

In the high-$T_c$ cuprates, experimental evidence has shown that ZBCPs which form as a result of $d$-wave pairing symmetry undergo a field splitting [181, 200, 201, 202]. However the Doppler splitting of Andreev peaks [203, 204], is not generally observed when $H_{c2}$ and $T_c$ are low [205], and recent tunnelling studies have raised questions about its robustness [175, 206]. Also, although Zeeman splitting of Andreev peaks is theoretically possible [207], this has not been experimentally observed in any superconductor. Furthermore, a recent experimental point-contact study of CeCoIn$_5$ also observed that the ZBCP did not split in an applied field, consistent with our measurements [193].

In this study the evolution of the $dI/dV$ spectrum of CeCoIn$_5$ for a magnetic field applied parallel to $c$-axis was investigated. The upper critical field in CeCoIn$_5$, which is Pauli limited, is anisotropic and while $H_{c2,||c} \sim 5$ T, when the field is oriented perpendicular to the $c$-axis $H_{c2,\perp c} \sim 12$ T [67, 68]. CeCoIn$_5$ is therefore a prime candidate for the possible realization of the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) superconducting state [72, 73]. Several experimental studies have shown evidence for the existence of an FFLO state for fields applied both parallel and perpendicular to the $c$-axis [74, 75, 76, 77, 78, 79]. Point-contact spectroscopy could be used probe the magnetic field-vs-temperature $H - T$
phase diagram of CeCoIn$_5$ particularly since recent theoretical work has calculated the conductance spectrum in the FFLO state [208, 209]. Measuring the low-temperature field evolution of the $dI/dV$ spectrum could therefore provide spectroscopic evidence for the FFLO superconducting state. Although evidence for the FFLO state has been observed for $H||$ to the $c$-axis, the $dI/dV$ measurements in this study did not show any indication of a transition to this state. A possible explanation for this is that even at the lowest temperatures, when a field is applied parallel to the $c$-axis, the FFLO phase only exists in a very narrow field range ($H \sim 4.8 - 5.0$ T) [75, 79] and therefore might be difficult to resolve spectroscopically. For $H \perp$ to the $c$-axis the FFLO phase, at low temperatures, has been predicted to exist within the field range $H \sim 9 - 12$ T, making it interesting to study the spectroscopic evolution of the conductance for this field orientation. However, the point-contact driver mechanisms used in this study travel in the same direction as the applied magnetic field. Therefore applying a field perpendicular to the $c$-axis would require that either the CeCoIn$_5$ crystal mounted on the sample stage be oriented such that [100] or [010] point-contact junctions are formed or for the driver mechanism to traverse perpendicular to the field. Both pose minor technical difficulties - rotating the driver mechanism is complicated by space restrictions inside the dilution refrigerator and forming $a$- or $b$-axis point-contact junctions is difficult because the platelet-like crystals are extremely thin - but can be overcome and would allow point-contact measurements with a field oriented perpendicular to the $c$-axis thus potentially revealing a spectroscopic probe of the FFLO state.
Figure 6.6: Magnetic field dependence of (a) the differential conductance spectrum measured on a $R = 0.3 \ \Omega$ junction at 100 mK and (b) the OP amplitudes $\Delta_1$ and $\Delta_2$. Curves in (a) are offset for clarity. The magnetic field was applied parallel to the $c$-axis.
6.7 Conclusion

Point-contact spectroscopy measurements were performed on the heavy-fermion superconductor CeCoIn$_5$. Andreev reflection characteristics with multiple structures that depended on junction impedance were observed in the spectra. For higher junction impedances a peak-dip and hump-like structures were observed while for lower junction impedances two hump-like structures were observed. Spectral analysis using the extended BTK model revealed two coexisting order parameter components with nodal symmetry. The low-temperature order parameter amplitudes corresponded with large gap-to-$T_c$ ratios suggesting a highly unconventional pairing mechanism in a multiband scenario. The magnetic field dependence of the $dI/dV$ spectrum, for a field applied parallel to the $c$-axis, was measured and the upper critical field observed was consistent with other experimental studies.
Chapter 7

Point-contact Spectroscopy on ZrZn$_2$

7.1 Introduction

Superconductivity and ferromagnetism tend to be competing types of order. The intermetallic, ferromagnetic compound ZrZn$_2$ has shown evidence for superconductivity under certain circumstances$^1$ in the ferromagnetic state [93, 97], suggesting their possible coexistence and complex interplay [51, 90, 92, 210]. A plausible scenario for this coexistence involves spin-mediated electron pairing, which could produce a spin-triplet, odd-parity superconducting order parameter (OP) with nodes in $k$-space [211]. To probe the pairing symmetry, point-contact spectroscopy measurements on spark-cut single crystals of ZrZn$_2$, using normal-metal tips, were performed in a dilution refrigerator down to 100 mK and up to 2 T. Low-energy peak structures which evolve systematically with temperature and field were observed in the $dI/dV$ conductance spectrum. These state-conserving peak spectra can be interpreted as a signature of Andreev surface states consistent with the presence of nodes in the superconducting order parameter.

$^1$The spark-erosion procedure used to fabricate the single crystals alters the chemical composition at the surface inducing a superconducting surface layer.
7.2 Experimental Setup

Single crystal samples of ZrZn$_2$ were grown using a directional-cooling technique and cut to expose (111)-faces by spark-erosion$^2$ [97]. These crystals show bulk ferromagnetic susceptibility below $\sim 30$ K, and a resistive downturn below $\sim 0.3$ K [93]. Prior to making measurements, the crystals were etched in aqueous HCl solution and rinsed in an ultrasonic ethanol bath. Point-contact spectroscopy measurements on the (111) face of the ZrZn$_2$ crystals were made in a dilution refrigerator using both Pt-Ir and gold tips as a counterelectrode. Both a spring-cushioned differential micrometer$^3$ and piezo driven$^4$ approach mechanism was used to bring the sample and tip into contact at low temperatures. Figure 7.1 shows an image of a Pt-Ir tip making making contact with a ZrZn$_2$ sample mounted on a mechanical point-contact driver. To minimize Joule heating a pulsed technique$^5$ was used to acquire the data. 2 ms current pulses were applied through the contact in 20% duty cycles and the junction voltage was measured 80 times within each pulse and averaged. The current versus voltage $I-V$ curves were obtained by varying the current and then numerically differentiated to obtain the $dI/dV$ conductance spectrum.

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$^2$Crystals provided by Professor Stephen Hayden from the University of Bristol.
$^3$Chapter 3.1.1.
$^4$Chapter 3.1.2.
$^5$Chapter 3.2.2.
7.3 Temperature and Field Dependence of the Conductance Spectrum

Typical $dI/dV$ conductance spectra measured are plotted in Figures 7.2 and 7.3. Figure 7.2 plots the data taken with a Pt-Ir tip, showing the spectral evolution with temperature up to $\sim 1.0$ K, above which the conductance was independent of bias voltage. Figure 7.3 plots the data for a Au tip, showing a similar evolution up to $\sim 1.1$ K. The spectra shown in each plot were normalized relative to the highest temperature data. The generic similarities between the two plots attest to the reproducibility of the measured spectra, as well as to their independence on tip material. At base temperature in each plot, a pronounced low-energy peak structure was observed, flanked by symmetric dip structures. The spectral details and their evolutions varied slightly between junctions.
and samples. In some cases, discernible peak-and-dip structures persisted to as high as \( \sim 1.5 \) K. With increasing temperature these spectral features evolve such that the total integrated \( dI/dV \) spectral area is conserved, as shown in the inset of each figure. The spectral area was calculated by numerically integrating each curve between \( \pm 0.5 \) mV and normalizing relative to the area at base temperature. Figure 7.4(a)Pt-Ir tip and (b)Au tip shows explicitly that at each temperature the area of the peak and dip structures are equal. Figure 7.5 shows the typical magnetic field evolution of the \( dI/dV \) spectra taken on a Pt-Ir/ZrZn\(_2\) point-contact at 150 mK. The ZBCP and symmetric dip structures evolve systematically with magnetic field and above \( H \sim 1.0 \) T the \( dI/dV \) spectrum is independent of voltage. The integrated \( dI/dV \) spectral area is conserved as a function of field.

![Graph](image)

**Figure 7.2:** Tunnelling conductance vs voltage as a function of temperature for a 0.4 \( \Omega \) Pt-Ir/ZrZn\(_2\) junction. Shown in the inset is the total integrated \( dI/dV \) spectral, between \( \pm 0.5 \) mV, as a function of temperature.

The presence of OP nodes can be detected by Andreev spectroscopy, in the form of ZBCPs, which are a manifestation of surface states due to Andreev interference that oc-
cur as a result of a sign change in the order parameter at a node [83, 84]. This Andreev phenomenology has been used to reveal OP nodes in several unconventional superconductors, ranging from YBa$_2$Cu$_3$O$_{7-\delta}$ [173, 146] to Sr$_2$RuO$_4$ [118, 119] and CeCoIn$_5$ [100].

The conductance spectra observed provide further support for the existence of a superconducting surface layer in spark-cut ZrZn$_2$, although the composition of this layer is still unknown [97]. The observed spectral peaks can be interpreted as a distinct signature of Andreev surface states arising from a nodal OP. First, the spectral peaks were generally taller than twice the normalized spectral background, as is expected from the generalized Blonder-Tinkham-Klapwijk formalism [83, 84, 178]. Second, the conservation in the $dI/dV$ spectral area is entirely consistent with the conservation of quasiparticle states which mediate the Andreev interference process [83]. Third, the point-contact radius $a$ estimated using the Wexler formula [127]:

Figure 7.3: Tunnelling conductance vs voltage as a function of temperature for a 0.4 $\Omega$ Au/ZrZn$_2$ junction. Shown in the inset is the total integrated $dI/dV$ spectral, between $\pm$ 0.5 mV, as a function of temperature.
Figure 7.4: Temperature dependence of the peak and dip area for ZrZn$_2$ point-contact junctions formed with (a) Pt-Ir and (b) Au tips.

\[ R \simeq \frac{4\rho l}{3\pi a^2} + \frac{\rho}{4a} \]  

with residual resistivity $\rho \sim 0.6 \, \mu\Omega\text{cm}$ and mean free path $l \sim 55 \, \text{nm}$ for ZrZn$_2$ [97] for a 0.4 $\Omega$ junction yields $a \sim 20 \, \text{nm}$, confirming the ballistic ($a < l$) nature of the junction. The microscopic scale of the probe largely rules out spurious scenarios based on material inhomogeneity, especially those involving conventional superconductivity with a non-nodal OP symmetry [210].
7.4 Conclusion

In conclusion, the apparent robust formation of Andreev surface states could be regarded as strong evidence for local pairing correlations on the surface of ZrZn$_2$. It is remarkable that these Andreev surface states seem to persist above the apparent resistive transition [93]. This observation may suggest that in ZrZn$_2$ it is easier for the electrons to pair microscopically than for them to phase condense macroscopically. This picture would be consistent with the fragile nature of the resistive transitions reported thus far [97]. More detailed studies correlating the spectral and transport data with surface preparation, in particular the effect chemical etching has on the surface [97], are currently under way to elucidate this picture. It is curious however to note that although a surface layer may be responsible for superconductivity in ZrZn$_2$, measurements under pressure showed that both superconductivity and ferromagnetic order vanish at the same pressure [93]. This
behaviour, which is reminiscent of that observed in UGe$_2$ [90], would suggest that perhaps superconductivity in the surface layer is influenced by the ferromagnetic nature of ZrZn$_2$. 
Chapter 8

Conclusion

The number of superconductors that are classified as unconventional is ever increasing and in order to be able to formulate a possible mechanism for superconductivity in these materials it is necessary to determine their pairing symmetry. Point-contact Andreev spectroscopy is a microscopic technique sensitive to the phase of the superconducting order parameter, making it a very powerful tool to study unconventional superconductors.

Andreev spectroscopy measurements on single crystal samples of the heavy-fermion skutterudite superconductor PrOs$_4$Sb$_{12}$ were performed. Low-temperature differential conductance measurements revealed multiple features, including a robust zero-bias conductance peak. The temperature and magnetic field dependence of the conductance indicated multiple superconducting order parameters, including one containing nodes and another consistent with being fully gapped. A magnetic-field driven change in the order parameter symmetry was observed, consistent with multiple superconducting phases, and highlights the unconventional nature of the superconducting state in PrOs$_4$Sb$_{12}$. The evolution of the conductance spectrum with Ru doping in Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ indicates a suppression of the nodal OP for $x$ as small as 0.02. These results, which are consistent with that obtained by specific heat studies, confirm that the superconducting states of the two end compounds, PrOs$_4$Sb$_{12}$ and PrRu$_4$Sb$_{12}$, are different and compete with each
Multiple structures, whose characteristics depend on the junction impedance, were observed in the differential conductance spectrum of the heavy-fermion superconductor CeCoIn$_5$. Spectral analysis revealed two coexisting order parameter components with nodal symmetry. These results indicate a highly unconventional pairing mechanism in CeCoIn$_5$ where multiple bands may be involved in superconductivity. The dependence of the conductance spectrum on an applied magnetic field oriented parallel to the $c$-axis was measured. While the upper critical field determined from point-contact measurements was consistent with other experimental results, spectroscopic evidence for the FFLO state was not observed. Future studies to investigate whether this novel pairing state can be observed spectroscopically for an applied magnetic field oriented perpendicular to the $c$-axis would be prudent.

The intermetallic ferromagnet ZrZn$_2$ is not a bulk superconductor at ambient pressure. However, the spark-erosion process used to cut the crystals induces a Zn depleted surface superconducting layer. Andreev spectroscopy measurements on ZrZn$_2$ samples revealed low-energy peak structures, which for different contacts and samples vanished at different temperatures and magnetic fields. These results are consistent with a inhomogeneous surface superconducting layer.

Andreev reflection has been extensively used to determine the spin polarization of various ferromagnetic materials, with conventional $s$-wave superconductors as a counter-electrode. In this work, tips fabricated from the high-$T_c$ superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) were used to investigate how the $d$-wave Andreev interference characteristics are affected by spin polarization. A zero-bias conductance peak, characteristic of Andreev bound states, was observed in YBCO/normal metals junctions while a sub-gap conductance suppression was observed in YBCO/CrO$_2$ point-contact junctions. These results confirm that the formation of Andreev bound states are suppressed by spin-polarized transport across a $d$-wave superconductor/ferromagnet point-contact interface.
Estimates of the YBCO/CrO$_2$ point-contact radius were typically on the order of several nanometers and illustrate the possibility of using superconducting YBCO tips to probe spin polarization at the nanoscale.
Appendix A

The manifestation of Andreev Bound States as a zero bias conductance peak (ZBCP) in the $dI/dV$ conductance spectrum has been extensively used to identify the existence of nodes in the superconducting order parameter (OP) for several materials. However, alternative mechanisms which can also produce zero bias anomalies in the $dI/dV$ must be ruled out before attributing a nodal OP as being responsible for the ZBCP.

In 1962, Josephson predicted that pair tunnelling occurs between two superconductors separated by a thin insulating barrier [212]. In the absence of an applied electric field a dc current would result, while if a voltage difference were maintained across the junction an ac current would be observed. The observation of a dc supercurrent at zero voltage in the $I−V$ characteristics of a Josephson junction leads to a ZBCP in the $dI/dV$. An immense number of experiments, involving junctions fabricated using conventional and unconventional superconductors, have confirmed the Josephson effect.

Further studies have extended Josephson’s initial prediction and shown that the Josephson effect can be sustained across two superconductors separated by any physical weak-link. In point-contact spectroscopy such a weak-link can be formed in a ‘dirty-tip’ scenario, illustrated in Fig A.1, where the tip is not in direct contact with the sample but rather in contact with a small grain which is in contact with the sample. Gener-
ally, the ‘dirty-tip’ scenario is only realized in polycrystalline superconductors since such samples are granular by nature. When using high quality single crystal samples, such as the PrOs₄Sb₁₂ ones investigated in this study, the ‘dirty-tip’ scenario is unlikely to be a concern. Nonetheless, the possibility that the PrOs₄Sb₁₂ point-contact junctions were not ‘clean’ was investigated.

![Diagram of a ‘clean’ and ‘dirty’ point-contact junction](image)

Figure A.1: Illustration of a ‘clean’ and ‘dirty’ point-contact junction formed between a normal metal tip and superconducting sample.

To eliminate the ‘dirty-tip’ scenario, point-contact junctions on single crystal PrOs₄Sb₁₂ samples were formed using a superconducting Sn tip instead of a normal metal Pt-Ir tip. Figure A.2 shows a schematic $H - T$ phase diagram for Sn (red line) and PrOs₄Sb₁₂ (blue line). Compared to PrOs₄Sb₁₂, Sn has a higher superconducting transition temperature ($T_c \sim 3.72$ K) but lower upper critical field ($H_{c2} \sim 0.03$ T). Therefore there are three distinct regions where (i) the Sn tip is superconducting while the PrOs₄Sb₁₂ sample is normal, (ii) both the Sn tip and PrOs₄Sb₁₂ sample are superconducting and (iii) the Sn tip is normal while the PrOs₄Sb₁₂ sample is superconducting.

Before forming point-contact junctions on PrOs₄Sb₁₂, the conductance spectrum of a Sn tip/normal metal junction was measured in a $^3$He refrigerator. Sn shots that had been drawn to a sharp point were used as the tip and Au foil was used as counter-electrode. A pulsed $I - V$ measurement technique¹ was used to collect the data and the junction

¹Chapter 3.2.2.
was formed using a piezoelectric driver\textsuperscript{2}. However, to bring the tip and sample into contact, rather than applying a continuous waveform across the piezo, a gentler pulsed approach technique was employed. Commonly used in scanning tunnelling microscopy, the approach is made by applying single waveform across the piezo and observing if any current is measured between the voltage biased tip and sample. Individual waveform pulses are sent until a current is detected. Currents on the order of nanoamps can be measured and as the junction is typically biased at a voltage on the order of one volt, a high resistance junction that is in the tunnelling, as opposed to point-contact, regime is obtained [213]. Once a high-impedance junction is formed, a DC voltage can gradually be applied to the piezo to bring the sample and tip gently into contact.

Figure A.3 shows the normalized $dI/dV$ conductance spectrum taken on Sn/Au junction at 0.4 K. At zero-field, the observed conductance resembles that predicted by BTK

\textsuperscript{2}Chapter 3.1.2.
theory (shown in the inset) for a normal metal/s-wave superconductor junction in the moderately high transparency range. On applying a magnetic field, the superconductivity in Sn was suppressed and the conductance spectrum went normal at $H \sim 0.2$ T. The upper critical field in bulk Sn is $H_{c2} \sim 0.03$ T. However, it is well known that in thin film form, type I superconductors exhibit critical fields much higher than the bulk $H_{c2}$ [214]. When the thickness of a film $d$ is smaller than the London penetration depth $\lambda$ ($d < \lambda$) the effective London penetration depth $\lambda_{eff}$ along the surface goes as $\lambda_{eff} \sim \lambda^2/d$ [19]. The enhanced $\lambda_{eff}$ allows the sample to remain superconducting while being penetrated by a magnetic field thus increasing the upper critical field value. An analogous argument can be used to explain why junctions formed using superconducting tips, which are extremely small in diameter, have critical fields much higher than the bulk value [215, 216].

![Figure A.3](image)

Figure A.3: Normalized conductance vs bias voltage at different fields for a Sn/Au point-contact at 0.4 K. Inset shows the conductance spectrum predicted by BTK theory in the moderately high transparency regime.

Point-contact spectroscopy measurements on Sn/PrOs$_4$Sb$_{12}$ junctions were also performed in a $^3$He refrigerator. Sn shots that had been drawn to a sharp point were used
as the tip. Prior to each measurement the PrOs$_4$Sb$_{12}$ samples were etched in a dilute aqueous HCl solution as described in Chapter 4.2. The same pulsed $I - V$ technique, piezoelectric driver and approach mechanism used to collect data for the Sn/Au junction was employed.

Figure A.4 shows the normalized $dI/dV$ conductance taken on a Sn/PrOs$_4$Sb$_{12}$ junction at 2 K. At 2 K the Sn tip is in the superconducting state while the PrOs$_4$Sb$_{12}$ sample remains normal, corresponding to region (i) in Figure A.2. The field dependence of the $dI/dV$ shows that the Sn tip becomes normal at $\sim 0.4$ T. The experimentally observed enhancement in the sub-gap conductance of $\sim 25\%$ (at $H = 0$ T) is lower than that predicted by standard BTK theory for an $s$-wave superconductor. Quasiparticle lifetime broadening is a possible explanation for the reduced sub-gap enhancement and its effect can be incorporated into BTK theory by replacing $E = Re(E - i\Gamma)$ [217]. Shown in the inset of Figure A.4 is the conductance spectrum predicted by BTK theory in the high transparency regime using a large $\Gamma$ value. As there is no a priori way of determining $\Gamma$, it is difficult to ascertain how large a value would be reasonable. Another
possible explanation, however, for the reduced sub-gap conductance is a breakdown in the Andreev approximation [218]. When an electron is retroreflected as a hole at a superconductor/normal metal (S/N) interface the Andreev approximation assumes that the magnitude of the electron and hole momentums are identical. However, in actuality, a momentum difference between the incoming electron and retroreflected hole exists, proportional to the ratio of the superconducting energy gap to the Fermi energy ($\Delta/E_F$). If $\Delta << E_F$, a criterion satisfied by conventional BCS $s$-wave superconductors, the Andreev approximation is valid and retroreflection occurs. For heavy-fermion superconductors however, $E_F$ is relatively small thus suppressing retroreflection which could result in a reduced enhancement in the sub-gap conductance.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Normalized conductance vs bias voltage at (a) low fields and (b) high fields for a Sn/PrOs$_4$Sb$_{12}$ point-contact at 0.4 K. Inset to (a) shows the conductance spectrum predicted using the modified RSJ model.}
\end{figure}

Having measured the $dI/dV$ conductance at 2 K, the junction was cooled to 0.4 K. At this temperature both the Sn tip and PrOs$_4$Sb$_{12}$ sample are superconducting, corresponding to region (ii) in Figure A.3. Figure A.5 (a) shows the normalized $dI/dV$ conductance taken at low fields. For small capacitances, $C$ the Josephson junction $I - V$ characteristics can be simulated by the modified resistively shunted junction (RSJ) model
given by Lee [219]:

\[ V = \frac{2}{\gamma} I_c R_N \frac{\exp(\pi \gamma \alpha) - 1}{\exp(\pi \gamma \alpha)} T_1^{-1} (1 + \Omega^2 \frac{T_2}{T_1}) \]  

(A.1)

where

\[ T_1 = \int_0^{2\pi} d\theta I_0 \left( \gamma \sin \frac{\theta}{2} \right) \exp \left[ - \left( \frac{\gamma \alpha}{2} \right) \theta \right] \]  

(A.2)

\[ T_2 = \int_0^{2\pi} d\theta \sin \frac{\theta}{2} I_1 \left( \gamma \sin \frac{\theta}{2} \right) \exp \left[ - \left( \frac{\gamma \alpha}{2} \right) \theta \right] \]  

(A.3)

and \( I_c \) is the Josephson current, \( R_N \) is the normal state resistance, \( \alpha = I/I_C \) the normalized current, \( \gamma = \hbar I_c / e k_b T \), \( \Omega = (2 e I_c C / \hbar)^{1/2} R_N \) and \( I_0(x) \) and \( I_1(x) \) are the modified Bessel functions.

Shown in the inset of Figure A.5 (a) is a numerical simulation for the Josephson conductance resembling the \( dI/dV \) conductance taken at \( H = 0 \) T. From Figure A.3 it was observed that the Sn tip went normal at \( H \sim 0.4 \) T and for magnetic fields higher than this value the Sn tip is normal but the PrOs\(_4\)Sb\(_{12}\) sample remains superconducting. Figure A.5 (b) shows the \( dI/dV \) conductance at high fields. At \( H = 0.7 \) T a ZBCP was observed and persisted up to \( \sim 1.5 \) T consistent with the \( dI/dV \) data observed using a Pt-Ir tip.

The \( H - T \) phase diagram in Figure A.2 showed three distinct regions and in region (i) where the Sn tip is superconducting but the PrOs\(_4\)Sb\(_{12}\) sample is normal, an enhanced sub-gap conductance in the \( dI/dV \) was observed. In region (ii) where the both the tip and sample are superconducting the measured \( dI/dV \) spectrum resembled that predicted by the modified RSJ model for Josephson junctions while in region (iii) where the tip is normal but sample superconducting, the \( dI/dV \) conductance was consistent with previous measurements made on PrOs\(_4\)Sb\(_{12}\) using a Pt-Ir tip. While the \( dI/dV \) spectrum observed in all three regions was consistent with a ‘clean’ Sn/PrOs\(_4\)Sb\(_{12}\) junction, the presence of
a superconducting grain between the tip and sample can not be completely ruled out
as distinct change in the conductance spectrum on going from region (ii) to region (iii)
was not observed. If a superconducting grain existed between the sample and tip, in
region (ii)where the Sn, PrOs₄Sb₁₂ sample and PrOs₄Sb₁₂ grain are all superconducting
a ZBCP in the $dI/dV$ spectrum due to a Josephson junction would be observed. In
region (iii), however where Sn goes normal but the PrOs₄Sb₁₂ sample and PrOs₄Sb₁₂
grain are still superconducting and the weak-link formed between the two could produce
a ZBCP in the $dI/dV$ spectrum. At zero field, the ZBCP predicted by the modified
RSJ model for Josephson junctions and that predicted by the generalized-BTK model
for nodal superconductors are qualitatively similar and therefore at high fields, where the
spectral features are heavily smeared, it becomes very difficult to distinguish between the
two.

Point-contact measurements on another Sn/PrOs₄Sb₁₂ junction were made. The sam-
ple preparation and measurement technique used was identical to that outlined earlier. At
2 K the tip and sample were brought into contact using a gentle STM-feedback approach
mechanism to guard against rough tip crashes [213]. Figure A.6 shows the measured
conductance spectrum. At zero magnetic field two peaks centered at $\pm 0.6$ mV are
observed, corresponding with the superconducting energy gap value of Sn. On increasing
the field the Sn tip goes normal at $0.4$ T. For a $s$-wave superconductor/normal
metal junction BTK theory predicts the conductance spectrum in the continuum from
the high transparency limit to the low transparency limit\(^3\). Shown in the inset of Figure
A.6 is a simulation using BTK theory for an intermediate junction transparency and the
predicted conductance resembles the measured $dI/dV$.

After measuring the $dI/dV$ conductance at 2 K, the junction was cooled to 0.4 K.
At this temperature both the Sn tip and PrOs₄Sb₁₂ sample are superconducting. Figure
A.7 shows the normalized $dI/dV$ conductance at (a) low fields and (b) high fields. At

\(^3\)Chapter 2.2.
zero field, while a ZBCP is seen in the $dI/dV$, and broad hump-like feature is also observed. At low temperature and low field both Sn and PrOs$_4$Sb$_{12}$ are superconducting and the conductance spectrum should resemble that predicted by modified RSJ model for Josephson junctions. However, the hump-like features can not be accounted for by said model. The inset of Figure A.7 (a) compares the conductance taken at 0.4 K to that at 2.0 K. Noting that at 0.4 K spectral features will appear sharper than at 2.0 K due to less thermal smearing, it appears that the position of the hump-like feature seen at 0.4 K corresponds with that observed in the conductance spectrum at 2.0 K where Sn is superconducting but PrOs$_4$Sb$_{12}$ is not. Figure A.7 (b) shows that at 0.4 K, for high fields where PrOs$_4$Sb$_{12}$ is superconducting but Sn is not, a ZBCP is seen in the $dI/dV$ but the hump-like feature is absent. This observation further supports the notion that the presence of the hump-like feature is due to the superconductivity of the Sn tip. Therefore at low fields and low temperatures it appears that the observed conductance is a combination of superconducting Sn tip/normal state PrOs$_4$Sb$_{12}$ and

Figure A.6: Normalized conductance vs bias voltage on a Sn/PrOs$_4$Sb$_{12}$ point-contact at 2 K. Inset shows conductance obtained from BTK simulation.
normal Sn tip/superconducting PrOs₄Sb₁₂.

Figure A.7: Normalized conductance vs bias voltage at (a) low fields and (b) high fields for a Sn/PrOs₄Sb₁₂ point-contact at 0.4 K. Shown in the inset of (a) is the zero-field $dI/dV$ conductance taken at 0.4 K and 2.0 K. The conductance curves in (b) have been shifted vertically for clarity.

As mentioned earlier, the modified RSJ model for Josephson junctions cannot account for the observed low temperature, low field conductance. The observed conductance suggests that the tip was in contact with a small surface (dead) layer on the PrOs₄Sb₁₂ sample that was not superconducting. Such a scenario is proposed in Figure A.8 (a). If a dead surface layer exists between the tip and sample (indicated by $N'$) the conductance in region (ii) will resemble a combination of a $S/N'$ and $N'/S''$ junction where $S$ is the tin tip and $S''$ is the bulk PrOs₄Sb₁₂. As $N'$ can be treated as a normal layer, the $I−V$ characteristics for each junction can be found and by adding the respective voltages and differentiating the result, the conductance can be obtained. The conductance $\sigma(V)$ is given by:

$$\sigma(V) = \left[\frac{d}{dI}(V_{SN'} + V_{N'S''})\right]^{-1} \tag{A.4}$$

From the observed $dI/dV$ at 2.0 K, where the bulk PrOs₄Sb₁₂ sample is normal, the conductance $d(V_{SN'}(I))/dI$ due the $Sn/N'$ junction is known. At 0.4 K a ZBCP is
expected in the conductance \(d(V_{N'S'}(I))/dI\) resulting from the \(N'/PrOs_4Sb_{12}\) junction. Using the BTK model to simulate the conductance for the \(Sn/N'\) junction and the generalized-BTK model \[84\] to simulate a ZBCP for the \(N'/PrOs_4Sb_{12}\) junction, the total conductance was calculated and is shown in Figure A.8. Shown in the left and right insets are the conductance for the \(Sn/N'\) and \(N'/PrOs_4Sb_{12}\) junctions respectively. They were added in a 1:4 ratio as indicated in the Figure. The calculated conductance resembles the \(dI/dV\) spectrum obtained at 0.4 K and zero field indicating that the Sn tip was in contact with a small surface layer on PrOs\(_4\)Sb\(_{12}\) that did not go superconducting. As the \(N'\) layer resides between the Sn tip and bulk PrOs\(_4\)Sb\(_{12}\) it largely rules out the possibility that a superconducting grain is present between the tip and sample. It should be noted that when using a normal metal tip, a small surface layer \(N'\) would simply act as an extension of the tip and the bulk superconductivity in the sample would still be probed.

Figure A.8: (a) Schematic \(H - T\) phase diagram for Sn (red) and PrOs\(_4\)Sb\(_{12}\) (blue). Regions (i), (ii) and (iii) correspond to distinct combinations of Sn (red) and bulk PrOs\(_4\)Sb\(_{12}\) (blue) being either normal or superconducting, separated by a surface layer \(N'\) which is normal in all 3 regions. (b) Simulation combining the conductance of a serial Sn\(/N'\) (left inset) and \(N'/PrOs_4Sb_{12}\) (right inset) junction. \(\alpha/\beta\) is the combination ratio.
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