

Investigating Inhomogeneous FM at SC/FM Interfaces Using Point-Contact Andreev Spectroscopy

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A thesis submitted for the degree of Doctor of Philosophy

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In the Name of God, the most Gracious, the most Merciful

Abstract:

The unconventional long range ($m=1$) spin triplet proximity effect is theorised to be created at a Superconductor/Ferromagnet (SC/FM) interface that is magnetically inhomogeneous and provides the conditions for spin mixing. Many experimental and theoretical works have identified the existence of the $m=1$ spin triplet state using Josephson junctions to show how the critical current does not diminish significantly in a thick FM layer, (thickness being relative to the decay length of a Cooper pair in an FM). In this thesis the challenge was to examine single SC/FM, interfaces via point-contact Andreev Reflection spectroscopy (PCARS), to see if it were possible to find clear signatures of the spin mixing or spin scattering conditions that facilitates formation of the spin triplet state.

PCARS measurements were performed on Ho single crystals and thin films as a function of contact resistance. The results show an anomalous decrease of the polarisation parameter and an increase in interface scattering parameter as the contact resistance decreases. This is interpreted in terms of the tip experiencing a region in which some form of spin mixing or spin scattering dominates.

Measurements of $\text{Ni}_{0.19}\text{Pd}_{0.81}$ spectra were also taken as a function of contact resistance but the change of polarisation and scattering parameter that was observed in the Ho samples was not observed here. PCARS temperature measurements were also taken for $\text{Ni}_{0.03}\text{Pd}_{0.97}$ to investigate if spin fluctuations close to T_C could provide the magnetic inhomogeneity required for spin-mixing. However the trend in the results proved inconclusive. This is likely due to broadening that result in the fitting procedure, and the extremely small polarisation in these samples.

During the course of the thesis I contributed to the development of the spectral fitting routines and examined the challenges associated with three and four parameter fitting, degenerate fits and series resistance.

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1 Introduction

The Andreev reflection process and superconducting proximity effect are phenomena that occur at a superconductor/normal metal interface (SC/NM). Both are expected to be suppressed at a superconductor/ferromagnetic metal (SC/FM) interface because of the shift in the spin-up and spin-down electron density-of-states around the Fermi energy level. However theory suggests that a parallel ($m=1$) spin triplet pairing state can be generated via a spin mixing and spin scattering process, if there is some form of magnetic inhomogeneity at the interface. This $m=1$ spin triplet is robust to magnetic scattering meaning that the distance, over which the amplitude decays, is longer compared to a conventional ($m=0$) Cooper pair in a FM. Therefore, this $m=1$ state that propagates over long distances in the FM (from the SC/FM interface) is known as the long range spin triplet proximity effect (LRSTPE). Early experiments have suggested that the $m=1$ spin triplet state can be induced in the spin spiral ferromagnet, holmium [29], and recently Ho has been used in multi-layered Josephson junctions.[28] Due to its intrinsic magnetic inhomogeneity, Ho would be an ideal material, and is currently viewed as a material that may induce both spin mixing and spin scattering; important in generating the long range triplet state. Therefore in this thesis I use Ho as the FM to create single SC/FM interfaces and explore whether there are any specific signatures of spin mixing/scattering, or even the LRSTPE. Low T_{Curie} systems are also investigated as they may show magnetic inhomogeneity due to spin fluctuations close to T_{Curie} . Near T_{Curie} , this inhomogeneity, may lead to the possibility that they a) might support the triplet pairing or b) could be used to detect the triplet in that temperature range.

In chapter 2 I start with a brief introduction to superconductivity followed by a description of Andreev Reflection at a (SC/NM) interface. The chapter then goes through the Blonder-Tinkham-Klapwijk (BTK) model[11] that describes conductance across the interface with a normal metal. However spin polarised materials suppress the Andreev reflection process at the SC/FM interface. Therefore in order to take account of this spin polarisation, the BTK model was modified by Mazin et al.[30] and chapter 2 examines how we apply this model in

the same depth.[20] The chapter then explains the phenomenon that serves as the motivation for the thesis, which is the superconducting proximity effect at SC/FM interfaces.

The first part of chapter 3 outlines the experimental setup which includes the point-contact Andreev reflection spectroscopy (PCARS) rig and supplementary measurement methods such as magnetometry and Hall imaging. The second part of the chapter describes the fitting routine developed by Dr. Yura Bugoslavsky[20] that was used to analyse experimental spectra in this thesis. The sources of smearing as well as unusual features in the conductance spectra, e.g. conductance dips and background are mentioned but the normalisation procedure is fully explained in chapter 4. I also investigate the reliability of the fitting routine using generated theoretical spectra with specific properties. The effects of fitting with a fixed superconducting gap ($\Delta=1.5\text{meV}$), and fits to spectra generated with suppressed or enhanced Δ (1meV and 2meV respectively) are also modelled to gain some insight in the errors involved for the values extracted from a fixed gap fit.

The long-range spin triplet proximity effect has been investigated in previous experiments by using Ho. In chapter 4 I explore the possible signatures of spin mixing/scattering in the Andreev spectra. I start with a review on the magnetic structure of holmium, which has a magnetic cone spiral structure (i.e. magnetic inhomogeneity) below $\sim 19\text{K}$. The holmium single crystal and thin film samples were initially characterised using magnetometry and Hall imaging. I present Hall images that show surface domain structures in the crystal that are similar to measurements made with circularly polarised X-rays by Lang et al.[22] Results of the PCARS measurements on the holmium single crystal show background features on the spectra which are removed before fitting. The limitations of the 4-parameter fit are discussed together with results from fixed $\Delta=1.5\text{meV}$ fitting procedure. From this, I get results that show anomalous trends in the parameters that describe the polarisation and interface scattering, P and Z respectively, as a function of contact resistance. By considering the effects of a magnetic field on the Andreev spectra, stray field at the SC/FM interface can be ruled out. Sample resistance is also ruled out as the cause of high smearing for low contact resistance in thin film samples. Therefore, I propose that this anomalous trend could be caused by spin mixing or spin scattering.

In addition the proposal was to investigate whether spin fluctuations close to T_{Curie} could provide a form of magnetic inhomogeneity that could also induce in spin mixing. I present PCARS analysis on dilute FM alloys in chapter 5. I examine $Ni_{0.19}Pd_{0.81}$ and discuss if anything meaningful can be obtained from the fixed gap superconducting fits. The behaviour of the parameters P and Z are plotted as a function of contact resistance for $Ni_{0.19}Pd_{0.81}$ and no significant change was observed. I discuss the difficulty in extracting meaningful information in samples with low polarisation and large non-thermal broadening. PCARS measurements were also taken on $Ni_{0.03}Pd_{0.97}$ as a function of temperature. An interesting trend in $Z(T)$ is seen that may be related to spin fluctuations, which was thought to have the property of magnetic (spin) inhomogeneity.

Finally in chapter 6 I present the conclusion and possible future work related to the motivation of the thesis and the results gained from PCARS of Holmium and NiPd.

2 Andreev Reflection and Proximity Effects

Andreev Reflection (AR) is a phenomenon that occurs at a superconductor/metal interface. In this chapter I introduce some key concepts associated with superconductivity followed by description of AR. I then cover the concept of the superconducting proximity effect at a superconductor/normal-metal interface and at a superconductor/ferromagnetic metal interface. I also discuss, phenomenologically, the conditions that would lead to the long range spin triplet proximity effect, which is at the core of the investigations in this thesis.

2.1 Introduction to Andreev reflection

2.1.1 Superconductivity

A detailed description of the superconducting mechanism is beyond the scope of this thesis, but excellent literature exists that cover the subject in detail.[31-33] (Here I only introduce key concepts). A superconductor has two important characteristic lengths; λ_L (penetration depth) and ξ (coherence length). λ_L is the distance over which an applied magnetic field penetrates the superconductor and ξ is a length scale over which there is a significant change in the density of states (DOS) of the superconducting electrons at the superconductor boundary.[31]

A microscopic theory of superconductivity was developed in 1957 by Bardeen, Cooper and Schrieffer, now known as BCS theory. [5, 31] It explains the formation of “Cooper pairs” via electrons interaction with phonons. A Cooper pair is described as being a spin singlet state made of spin-up ($\uparrow$) and spin-down ($\downarrow$) quasiparticles with two electrons having equal and opposite momenta $\underline{k}$, $-\underline{k}$ (zero centre of mass) and opposite spin, ($\uparrow\downarrow - \downarrow\uparrow$). A significant consequence of Cooper pair formation is the energy gap that opens around the Fermi energy, denoted as $\Delta(T)$, such that the energy required to excite a Cooper pair from the

ground state back to the quasiparticle state is $2\Delta(T)$. As Figure 2.1 shows, Δ is temperature dependant and is reduced to zero at the superconducting critical temperature, T_c

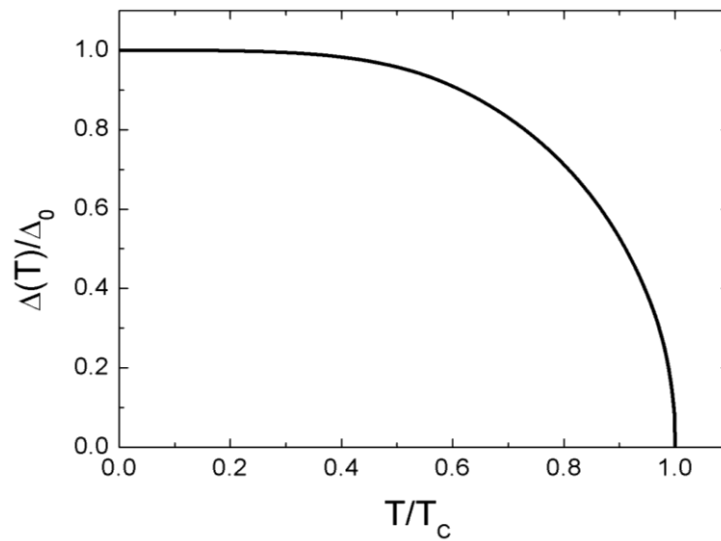


Figure 2.1: Ratio of the Energy gap $\Delta(T)/\Delta_0$ with reduced temperature T/T_c according to the BCS theory [5]. Δ_0 is the energy gap at $T=0K$ and T_c is the critical temperature of the superconductor

2.1.2 Andreev Reflection

At a superconductor (SC)/Normal metal (NM) interface, if an incident electron from the NM side has an energy greater than the superconductor gap energy ($eV > \Delta$) then it is possible for the electron to occupy an excited quasiparticle state in the SC which means transmission across the interface is possible. However, if an incident electron from the NM has $eV < \Delta$ then transmission of the single electron into the superconductor is forbidden as there are no quasiparticle states within the energy gap. However, electrons with $eV < \Delta$ can enter into the superconductor by means of a phenomenon known as Andreev reflection. [34] For the electron to be transmitted across the interface it would need to be paired with another electron which has opposite spin and momentum. This pairing of electrons causes a hole, with opposite spin but equal momentum to the incident electron, to be reflected back into the NM travelling in the opposite direction, i.e. a retro reflection. This is shown in Figure 2.2. As a result of this process the conductance is doubled for $eV \lesssim \Delta$ due to a charge of $2e$ being transmitted across the interface (A classic “Top Hat” signature associated with Andreev reflection)

In order to describe the conductance as a function of applied bias across an interface such as those measured by PCARS, a model of the Andreev reflection across the SC/NM interface needs to be developed. This was the subject of the Blonder-Tinkham-Klapwijk (BTK) model, which will be outlined in section 2.1.4. Since this thesis is concerned with PCARS data, the next section shall introduce point contact concepts that will be used later in this chapter.

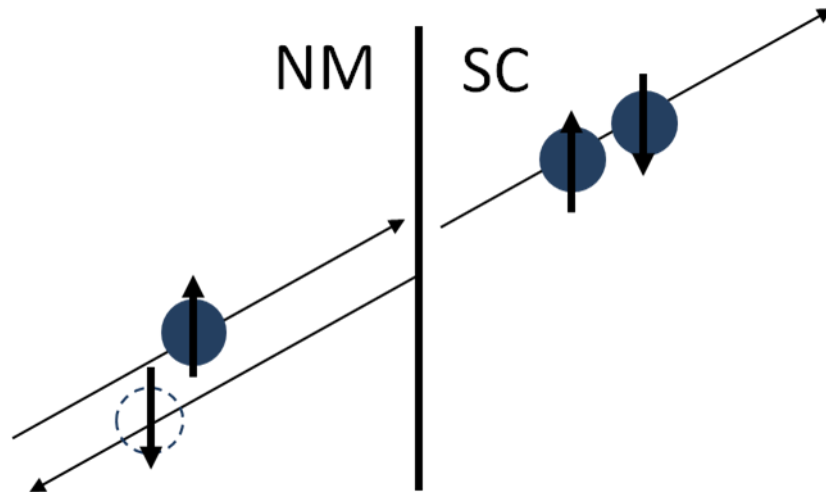


Figure 2.2: An illustration of the Andreev reflection process at a NM/SC Interface. An incident spin-up electron from the NM (filled circle) is retro reflected as a spin-down hole (hollow circle). The incident electron pairs up with an electron with opposite spin from the NM to form a Cooper pair in the SC. Adapted from Dr Yasayuki Miyoshi's thesis [1]

2.1.3 Transport Regimes

A simple point-contact is made by pressing a sharp superconducting tip onto the sample (see Figure 3.1 in section 3.1.1) and, generally, the ideal contact would be under 100Ω as it is stable and gives better spectral resolution. We note that this is from empirical measurements of me and my predecessors working on PCARS.[1, 20] For resistances higher than $\sim 100\Omega$ there is a possibility of an oxide barrier between the SC/Metal interface which will dominate the conductance spectrum.[35] For resistances of $R \ll 100\Omega$ the barrier is penetrated and a large area contact is made at the SC/Metal interface. As the contact resistance decreases the tip either deforms, which would mean that the radius of the SC/Metal contact area, a ,

becomes larger or the tip penetrates further into the sample, or both. The transport regime of the point-contact varies as the tip deforms and is characterised by the mean free path of the electron in the non-superconducting metal, l , and the radius of the contact area, a . These characteristic lengths define three regimes that describe the point contact, 1) the ballistic regime, 2) the diffusive regime and 3) the thermal (Maxwell) regime. The ballistic regime is when the electron propagates ballistically through the contact without collisions. The limit of this regime is characterised as having the mean free path of the electron much greater than the radius of the contact, i.e. $l \gg a$. The contact resistance, in the ballistic regime, R_S , is calculated using the Sharvin equation [36, 37]

$$R_S = \frac{4\rho l}{3\pi a^2} \quad (2.1)$$

where ρ is the resistivity of the material under study.

The opposite limit to the ballistic regime is the thermal Maxwell regime where the contact is characterised as having $l \ll a$, where the resistance, R_M , is given by [36, 37]

$$R_M = \frac{\rho}{2a} \quad (2.2)$$

In this regime the electrons lose energy via inelastic scattering at the interface. This loss in energy occurs over a short distance close to the interface which leads to heating of the contact and could result in the current being non-Ohmic.

The final regime is an intermediate regime called the 'diffusive regime' where the characteristic lengths are between the limits of the ballistic and thermal regime i.e. $l \sim a$. The resistance in this case, as suggested by Wexler[38], is a sum of the Sharvin (equation (2.1)) and Maxwell (equation (2.2)) resistances with some interpolation factor $\Gamma\left(\frac{l}{a}\right)$ which is a slowly varying function of the order of unity [36, 37]

$$R_W = R_S + \Gamma\left(\frac{l}{a}\right) R_M \quad (2.3)$$

There is one further characteristic length scale which needs to be considered and that is the coherence length, ξ . If the contact radius is less than the coherence length, $\xi \gg a$, then it prevents weakening of the superconductivity[39] on the superconductor side of the

interface (which may lead to the proximity effect explained in section 2.3). The de-pairing current density is the current at which the velocity (kinetic energy) of the superconducting current exceeds the velocity that breaks the Cooper pair.[39] If the current density at a constriction exceeds the de-pairing current density, quenching of the superconductivity at the contact occurs (which is the origin of the dip features in the spectra). As mentioned in ref. [39] simple s-wave superconductors, with low T_c , have $\xi \sim 1000\text{\AA}$ and a Sharvin limit would mean $a \sim 100\text{\AA}$ (for a NM with an electron mean free path in the order of $\sim 100\text{nm}$). For Nb and Pb ξ is $380\text{\AA}$ and $830\text{\AA}$ respectively. (This may seem larger than the contact radius, a , however the tip apex is generally $10\text{-}20\mu\text{m}$ [1, 20] but have smaller nanocontacts that have $a \sim 100\text{\AA}$ and so assuming a clean limit of the superconductor coherence length is reasonable.) A contact resistance of $10\Omega - 100\Omega$ would usually satisfy the condition of a ballistic contact. [1, 39] However, for fitting a spectrum the choice of either using the ballistic or diffusive regime could be determined by finding the threshold resistance in which the contact stops being ballistic. This is done using equation (2.1) and assuming $l = a$ as described in section 4.5.1 for holmium.

2.1.4 BTK Model

A model of electron transmission through an NM/SC interface was formulated by G.E. Blonder, M. Tinkham and T.M. Klapwijk and it is conventionally known as the BTK model.[11] The energetically allowed events (reflection and transmission) at the NM/SC interface were first identified and then the Bogoliubov-De Gennes equations were used to find the probabilities of these events.[11]

From their model for an incident electron (at position 0 in Figure 2.3) in the NM side they identified four possible scattering events that can occur at the interface:

- 1) A hole is reflected back into the NM at the interface caused by the pairing of electrons due to Andreev reflection. This is represented as probability $A(E)$
- 2) Ordinary reflection of the electron represented by probability $B(E)$

- 3) An electron-like transmission into the SC quasiparticle state represented by probability $C(E)$
- 4) A hole-like transmission into the SC quasiparticle state represented by probability $D(E)$

It is required that the sum $A(E) + B(E) + C(E) + D(E) = 1$ due to conservation of probabilities. For electrons with energy $eV < \Delta$ this sum is simply reduced to $A(E) + B(E) = 1$. This can be seen in Figure 2.3 in the superconductor side where there are no states below $eV < \Delta$.

To define the current (I) the BTK model [11] assumes ballistic transport (defined in section 2.1.3). across the interface The interface barrier is accounted for in the BTK model by a repulsive potential $V(x) = H\delta(x)$ at the interface between the SC and NM. The delta-function, $\delta(x)$, ensures that the potential barrier H exists only at the interface. This scattering potential can represent an oxide layer at a point contact or the barrier in a high density tunnel junction. [11, 35]

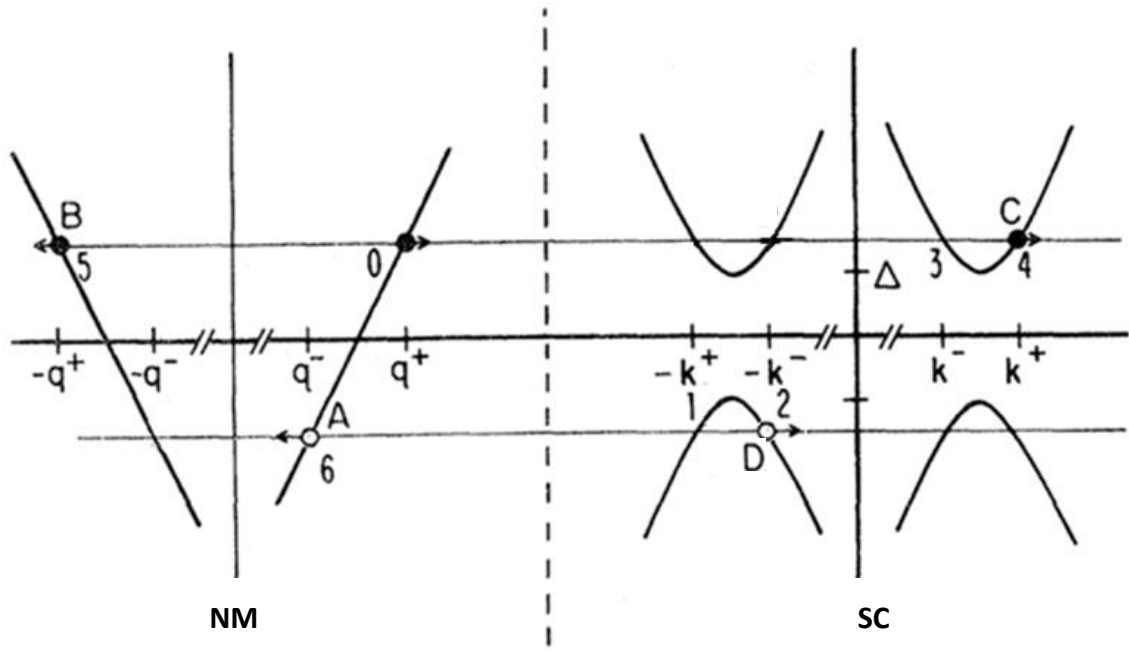


Figure 2.3: The energy vs. momentum of the scattering process at a NM/SC interface (semiconductor representation) as described in the BTK model and adapted from fig 4 in ref [11]. The incident electron is at point 0 which energy above Δ . The open circles denote holes, the closed circles are electrons and the arrows denote the direction in which the particle moves with respect to the interface. This figure illustrates the four possible scattering processes: A) Andreev reflection, B) Normal reflection, C) electron-like quasiparticle transmission and D) hole-like quasiparticle transmission.

In deriving the probability currents (such as the ones shown in Table 2.1, section 2.2.2), a dimensionless parameter $Z = \frac{k_F H}{2E_F} = H/\hbar v_F$ was used to describe the strength of scattering at the SC/NM interface, where k_F , v_F and E_F are the Fermi wavevector, the Fermi velocity and the Fermi energy respectively. This scattering parameter was later shown [35] to incorporate scattering due to the different Fermi velocities of the NM and SC

$$Z_{eff} = [Z^2 + (1 - r)^2/4r]^{1/2} \quad (2.4)$$

The Fermi velocity mismatch is defined as a ratio, $r = v_{F1}/v_{F2}$, between the Fermi velocities of the two metals, this suggests that there is a minimum value for the interface scattering parameter, Z_{min} , even in the case of a clean interface between two dissimilar metals.

The BTK model also assumes that the equilibrium Fermi functions can be used to describe all incoming electrons. This leads to a distribution function for incoming electrons on the superconductor side to be $f_0(E)$, and ones coming from the normal metal to be $f_0(E - eV)$. The current was then evaluated on the normal metal side of the SC/NM interface and the resulting expression for the current was given as [11],

$$I = 2N(0)ev_F\mathcal{A} \int_{-\infty}^{\infty} [f_0(E - eV) - f_0(E)][1 + A(E) - B(E)]dE \quad (2.5)$$

Where $\mathcal{A}$ is the SC/NM cross-sectional area and $N(0)$ is the one-spin density of states at ϵ_F . This equation shows that the Andreev reflection term $A(E)$ increases current while normal reflection $B(E)$ reduces it. The differential conductance $G(V)$ was found by taking the first derivative of equation (2.5) [11] to give $G(V) \propto [1 + A(E) - B(E)]$. The normalised differential conductance curves with various Z (scattering) values are shown in Figure 2.4. This shows the doubling of conductance in the sub-gap region ($eV < \Delta$) if $Z = 0$ and the reduction of sub-gap conductance as a result of increasing Z (increased scattering).

The quasiparticle current has an associated relaxation time of τ_Q^* , and is related to a relaxation length $\Lambda_Q^* = (D\tau_Q^*)^{1/2}$ (where D here is the diffusion coefficient which defines the distance a quasiparticle penetrates into the SC before it relaxes into a supercurrent. [11] However the BTK model explains that even for electrons with $eV < \Delta$ penetrating the NM/SC interface, it travels a distance of $\xi(T)$ (the superconductor coherence length) in the SC before converting into a Cooper pair. In order to study the effects of spin polarisation, the BTK model had to be modified. I briefly consider these modifications to the basic BTK model in the following sections. However this is not the main focus of the thesis.

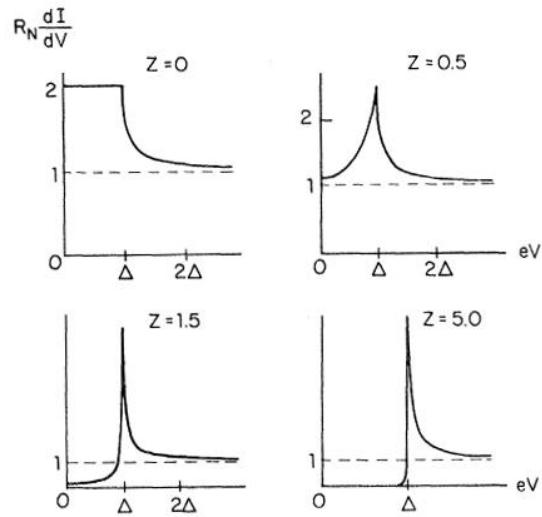


Figure 2.4: The normalised differential conductance vs. voltage at an S/N interface for various barrier strengths Z . From ref. [11]

2.2 Spin Polarisation and the Modified BTK model

2.2.1 Definition of Polarisation

The probability of Andreev reflection depends on the spin density of states of the spin-up and spin-down electrons at the Fermi level. In an NM both spin densities are equal and would allow Andreev reflection at a NM/SC interface which (if $Z=0$ at the interface) gives the doubling of conductance for $eV < \Delta$. However, if the NM was replaced with a Ferromagnetic Metal (FM) (such that there are a majority of spins at the interface which are aligned in a particular direction) then it is expected that the probability of Andreev reflection (and therefore the conductance) would decrease.[40] Since the Andreev reflection process involves electrons at the Fermi level, a shift in the spin density of states of electrons in the FM causes one spin band to be a majority (e.g. spin-up electrons) and the other a minority (e.g. spin-down electrons). The difference in densities of spin up and spin down electrons at E_F is known as *spin polarisation* and would cause the suppression of Andreev reflection, illustrated in Figure 2.5.

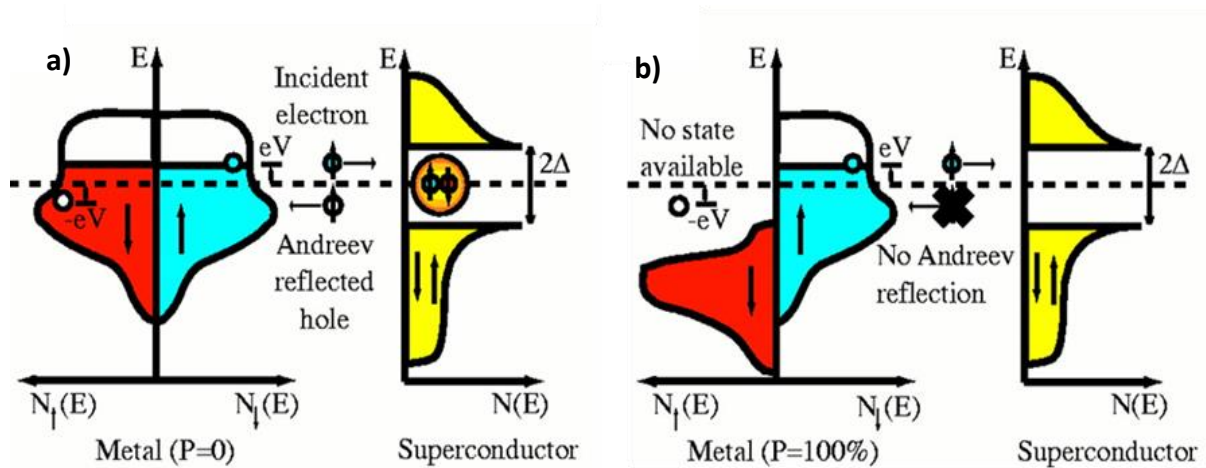


Figure 2.5: Schematic that illustrates the Andreev reflection at a) NM/SC interface and b) the suppression of Andreev reflection at FM/SC interface in which the FM is a half metal (i.e. $P=100\%$). From ref.[23]

The term polarisation, P , can be defined as [23, 41]

$$P_N = \frac{N_{\uparrow}(E_F) - N_{\downarrow}(E_F)}{N_{\uparrow}(E_F) + N_{\downarrow}(E_F)} \quad (2.6)$$

where $N_{\uparrow(\downarrow)}$ are the Fermi energy spin-dependant density of states for the spin-up (spin-down) electrons at the Fermi energy. Equation (2.6) is used for certain experiments such as photoemission spectroscopy. However for transport measurements, Soulen et al. [23] explained that the measured polarisation is not just due to the spin-split DOS but must also include the Fermi velocity, v_F , of the electrons involved in the transport. Mazin et al.[41, 42] also states that the definition of P can be dependent on the contact regime of the SC/FM (either ballistic or diffusive). In the ballistic case and diffusive case respectively,

$$P_{Nv} = \frac{\langle N_{\uparrow}(E_F)v_{F\uparrow} \rangle - \langle N_{\downarrow}(E_F)v_{F\downarrow} \rangle}{\langle N_{\uparrow}(E_F)v_{F\uparrow} \rangle + \langle N_{\downarrow}(E_F)v_{F\downarrow} \rangle}$$

$$P_{Nv^2} = \frac{\langle N_{\uparrow}(E_F)v_{F\uparrow}^2 \rangle - \langle N_{\downarrow}(E_F)v_{F\downarrow}^2 \rangle}{\langle N_{\uparrow}(E_F)v_{F\uparrow}^2 \rangle + \langle N_{\downarrow}(E_F)v_{F\downarrow}^2 \rangle} \quad (2.7)$$

where $v_{F\uparrow(\downarrow)}$ is the spin-dependent Fermi velocity of the spin-up (spin-down) electrons. The value of P will vary significantly between P_N , P_{Nv} or P_{Nv^2} so it is necessary to identify the transport regime for fitting.[41]

2.2.2 Polarised Current in the BTK Model

The effect of spin polarisation on the conductance of a SC/FM interface was first discussed by De Jong and Beeneker.[40] They proposed that the total conductance can be split into conductance channels (CC) with spin-up, $CC_{\uparrow}$ and spin-down, $CC_{\downarrow}$ and for a FM/NM interface with $CC_{\uparrow} \geq CC_{\downarrow}$, the zero bias differential conductance in the absolute zero temperature limit is

$$G_{FN} = \frac{e^2}{h} (CC_{\downarrow} + CC_{\uparrow}) \quad (2.8)$$

However, for an SC/FM interface, all the minority (spin down) electrons in $CC_{\downarrow}$ are Andreev reflected which would contribute to the doubling of the conductance so that $G_{FS\downarrow} = \frac{e^2}{h} 2CC_{\downarrow}$. However only a fraction of the majority (spin up) channels ($CC_{\downarrow}/CC_{\uparrow}$) will be Andreev reflected and so the contribution of this channel to the conductance is $G_{FS\uparrow} = \frac{e^2}{h} \left(\frac{CC_{\downarrow}}{CC_{\uparrow}} \right) 2CC_{\uparrow}$. Therefore this restricts Andreev reflection as it is dependent on the number of minority spin channels ($CC_{\downarrow}$) [40]

$$G_{FS} = G_{FS\downarrow} + G_{FS\uparrow} = \frac{e^2}{h} \left(2CC_{\downarrow} + 2 \frac{CC_{\downarrow}}{CC_{\uparrow}} CC_{\uparrow} \right) = 4 \frac{e^2}{h} CC_{\downarrow} \quad (2.9)$$

In the extreme case of a half-metal (such as CrO_2) in which there is an absence of one of the spins, the Andreev reflection is expected to be fully suppressed.[43]

The effects of polarisation on the Andreev reflection and the conductance spectra were not taken into account in the original BTK model. However in a FM/SC point contact experiment carried out by Soulen et al. a modified BTK model was used which took into account the effects of spin polarisation[23]. The approach was similar to De Jong and Beeneker and decomposed the total current into current contributed by the unpolarised current I_{unpol} and the polarised current I_{pol}

$$I = I_{\uparrow} + I_{\downarrow} = 2I_{\downarrow} + (I_{\uparrow} - I_{\downarrow}) = I_{\text{unpol}} + I_{\text{pol}} \quad (2.10)$$

I_{unpol} is due to Andreev reflection as described in the original BTK model. The polarised current I_{pol} is due to the excess majority spin electrons that are not Andreev reflected and so can be described by the BTK model only by setting the probability of Andreev reflection to zero. As a consequence, the conductance can also be described as a contribution from polarised and unpolarised parts [23] i.e.

$$G(V) = (1 - P)G_{\text{unpol}}(V) + PG_{\text{pol}}(V) \quad (2.11)$$

By assuming low Z , low temperature ($T \approx 0$) and taking the conductance at $eV \rightarrow 0$, the main contribution would be from the unpolarised (Andreev reflected) current and from equation (2.11) the conductance (normalised by the normal state conductance G_N) can be set to

$$\frac{G_{unpol}}{G_N} = 2 \text{ and } \frac{G_{pol}}{G_N} = 0 \text{ to give}$$

$$\frac{G(V \rightarrow 0)}{G_N} = 2(1 - P) \quad (2.12)$$

Soulen et al. [23] obtained their results by imposing some restrictions on the fitting such as minimal elastic scattering, zero temperature and only considering the conductance at zero bias. However, Mazin, Golubov and Nadgourney [42] derived a modified BTK model that includes the effects of polarisation on the conductance. It is also generalised to include conductance for both ballistic and diffusive regimes for $eV < \Delta$ and $eV > \Delta$. The conductance is shown in Table 2.1. In the next chapter I shall discuss the fitting routine which uses this model and fits using the four parameters Δ , Z , P and ω which are the superconductor gap, interface scattering, polarisation and broadening respectively.

Regime	$E < \Delta$	$E > \Delta$
Ballistic	$G_{unpol} = \frac{2(1 + \beta^2)}{\beta^2 + (1 + 2Z^2)^2}$	$G_{unpol} = \frac{2\beta}{1 + \beta + 2Z^2}$
	$G_{pol} = 0$	$G_{pol} = \frac{4\beta}{(1 + \beta)^2 + 4Z^2}$
Diffusive	$G_{unpol} = \frac{1 + \beta^2}{2\beta} \text{Im}[F(-i\beta) - F(i\beta)]$	$G_{unpol} = \beta F(\beta)$
	$G_{pol} = 0$	$G_{pol} = \beta F\left[\frac{(1 + \beta)^2}{2} - 1\right]$

Table 2.1 Analytical form of the normalised conductance in the ballistic and diffusive regime derived by Mazin et al. [42]. The table here are the corrected terms published by

Woods et al. [30]. Where $\beta = \frac{v}{\sqrt{|\Delta^2 - v^2|}}$ and $F(x) = \frac{\cosh^{-1}(2Z^2 + x)}{\sqrt{(2Z^2 + x)^2 - 1}}$

2.3 The Proximity Effect

2.3.1 Proximity Effect at a Superconductor/Normal Metal interface

In this section the phenomenon known as the proximity effect, linked to Andreev reflection at the interface region, shall be explained.

The proximity effect is a phenomenon that occurs at an SC/NM interface and describes the decay or ‘leakage’ of Cooper pair density into the normal metal. The early studies of the proximity effect were done in the 1960s by de Gennes [44] and summarised by Deutscher and De Gennes [45]. At a SC/NM interface the spatial variation of the energy gap $\Delta_N(x)$, where x is the distance from the interface in the NM, is related to the condensate amplitude function $F(x)$. [4, 44, 46-48] $F(x)$ is the probability amplitude of finding two electrons in the condensed state (and related to the Cooper pair density) at a point x from the interface and it follows an exponential decay in the NM (shown in Figure 2.6). However this would be for the ‘dirty’ case (where the electron mean free path in the NM is less than the superconductor coherence length, ξ [49, 50]). In the ‘clean’ case (where the electron mean free path in the NM is more than the superconductor coherence length, ξ), it was pointed out in ref.[46] that for an electron with energy E above the Fermi level d that it’s not easy to define a characteristic decay length.

The length scale of the electron-hole correlation is given by the coherence length in the normal metal (for the ‘dirty’ case)

$$\xi_{NM} = \sqrt{\frac{\hbar \mathcal{D}_{NM}}{k_B T}} \quad (2.13)$$

where $\mathcal{D}_{NM}$ is the NM diffusion coefficient and T is the temperature of the NM. At a distance of ξ from the interface on the SC side the amplitude of $F(x)$ starts to decay from its SC bulk value. A schematic of this is shown in Figure 2.6. There is an abrupt step at the interface in which $F(x)$ drops dramatically but continues to decay in the NM up to a distance of ξ_{NM} from the interface. ξ_{NM} can be thought of as the distance in which the Cooper pair

penetrates into the SC. Experimental studies have been done extensively throughout the 60s, 70s and 80s to test and validate the proximity effect and this is outlined in the next section.

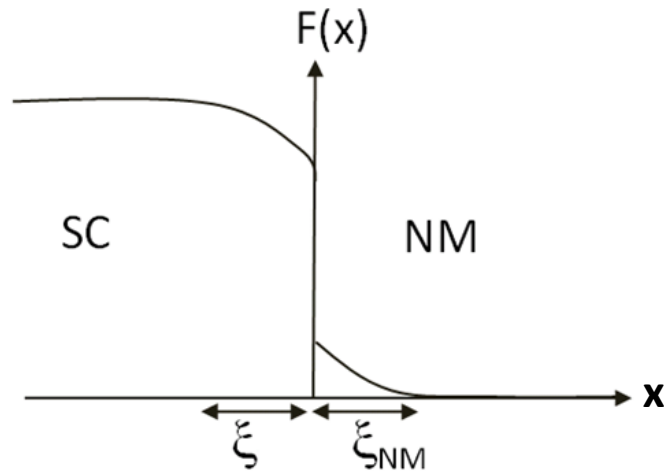


Figure 2.6: The spatial variation of the Cooper density function at a SC/NM interface, adapted from ref [18]

2.3.2 Proximity Effect Experiments

Most of the experiments investigating the proximity effect were based on characterising the transition temperatures [44, 51, 52], tunnelling [4, 53], critical current [48, 54] and thermal conductivity experiments of S/N interfaces.[55, 56] The results have shown what was expected from the de Gennes theory [44], particularly for a thin film with a SC/NM/SC structure. The T_C of the SC is suppressed if the thickness of SC is reduced or if the thickness of the NM is increased [51-53]. However the theory also suggests a spatial variation of the energy gap in the NM, $\Delta_{NM}(x)$. This is clearly seen in tunnelling experiments by Adkins and Kington [4] using planar junctions of Al-collodion (insulator)-Pb-Cu. Measurements were also made for Pb-Ag. Several junctions were created with varying thickness but in both cases the thickness of Pb was kept constant at 5000Å. Measurements for each thickness of Au and Cu were made at temperatures ranging from 1.5 to 4.2K. The energy gap was measured at the surface of the NM for each thickness. The results of the experiment showed that the

energy gap does indeed decrease as the thickness of the NM is increased therefore showing $\Delta_N(x)$ exists under certain circumstances. Their results are shown in Figure 2.7

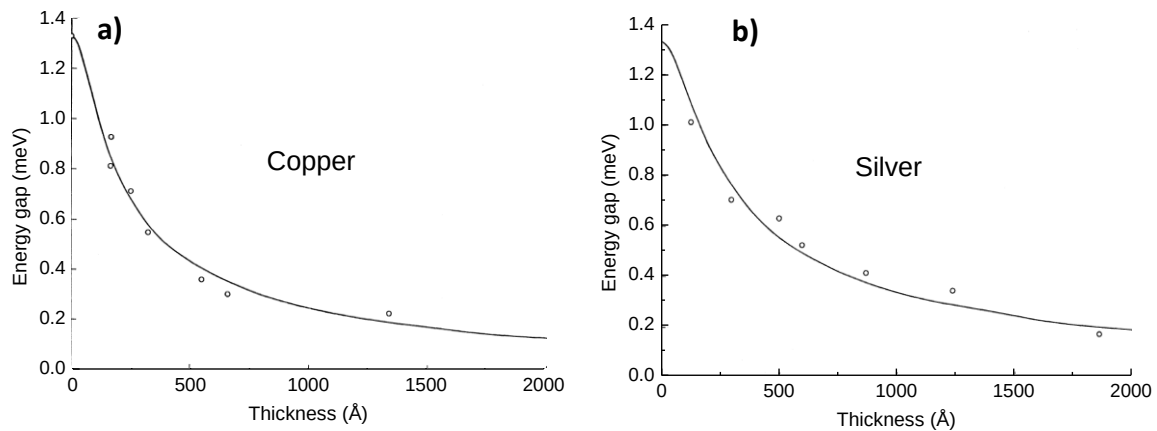


Figure 2.7: a) The energy gap induced at the surface of a) Copper and b) Silver for various thicknesses. The decaying curve verifies the spatial variation of the energy gap. Adapted from ref. [4]

A more recent test of the proximity effect was shown in an experiment by Guéron et al. [14] where superconducting-like properties were observed close to the interface by probing the density of states of the NM, shown in Figure 2.8. The experiment consisted of a SC/NM (Al/Cu) interface and three copper ‘fingers’, F_1 , F_2 and F_3 connected at distances of 200, 300 and 800nm from the interface on the NM side (F_2 was placed on a separate but similar SC/NM junction to that which was used for F_1 and F_3). Tunnelling conductance spectra were taken at F_1 , F_2 and F_3 using the ‘fingers’ as probes for tunnelling spectroscopy. The normalised tunnelling conductance at these three locations, Figure 2.8b (top), was very much in agreement with the theoretical tunnelling conductance Guéron et al. calculated shown in Figure 2.8b (bottom). [14]. They reasonably concluded from their results that Cooper pair correlations are present in the NM hence the indication of the proximity effect.

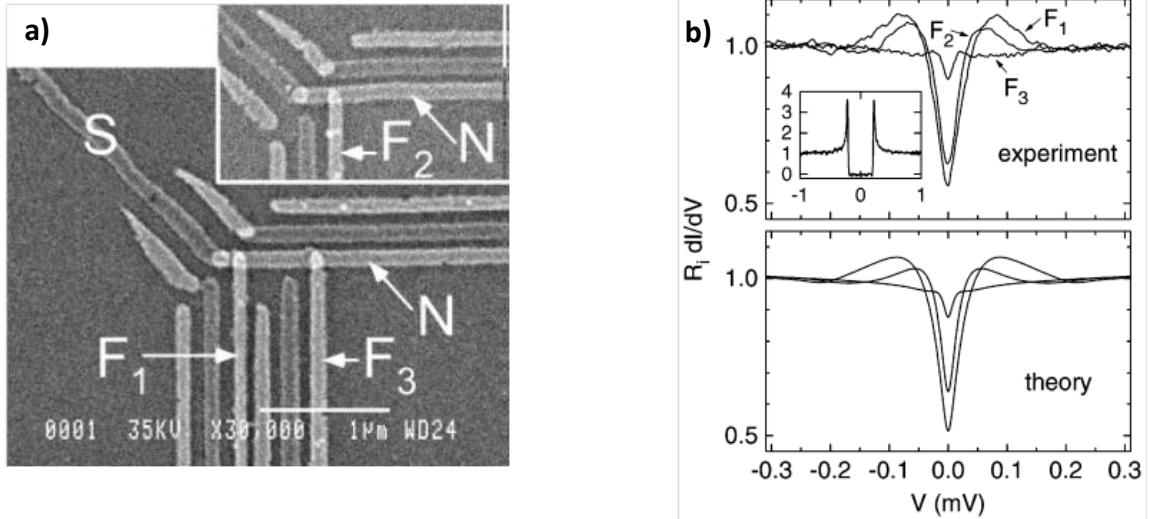


Figure 2.8: a) The SC/NM interfaces located at F₁, F₂ and F₃ (F₂ is an interface in another similar device) taken at T=20mK. SC is Al and NM is Cu. b) the experimental tunnelling conductance (top figure) is remarkably similar to the theory tunnel conductance theory (bottom figure). Both figures taken from [14]

From the early 80s and into the 90s there was interest as to what happens at a SC/FM interface and the proximity effect that is associated with it. [57-59] In the next section the penetration of the Cooper pair in a FM is discussed.

2.3.3 Proximity Effect at a Superconductor/Ferromagnetic Metal Interface

At a SC/FM interface the proximity effect (and Cooper pair decay) is affected by the exchange field (h_{ex}) of the FM that splits the energy levels of the spin-up and spin-down electrons. As a Cooper pair approaches the interface and penetrates into the ferromagnet, h_{ex} splits the paired spin-up and spin-down electrons into different energy levels. This shifts the centre-of-mass momentum of the Cooper pair by $\pm Q \left(= \frac{2h_{ex}}{v_F} \right)$ [15, 59] causing it to become non-zero and changes the momentum of one of the electrons in the Cooper pair to $k_{F\uparrow} = k_F + Q/2$ and the other to $k_{F\downarrow} = k_F - Q/2$. [15, 59] The shift in the momentum caused by h_{ex} , and hence the exchange energy E_{ex} , is illustrated in Figure 2.9a. The penetration length of the Cooper pair, ξ_{FM} , in the FM is then dependent on the strength of E_{ex}

$$\xi_{FM} = \sqrt{\frac{\hbar D_F}{E_{ex}}} \quad (2.14)$$

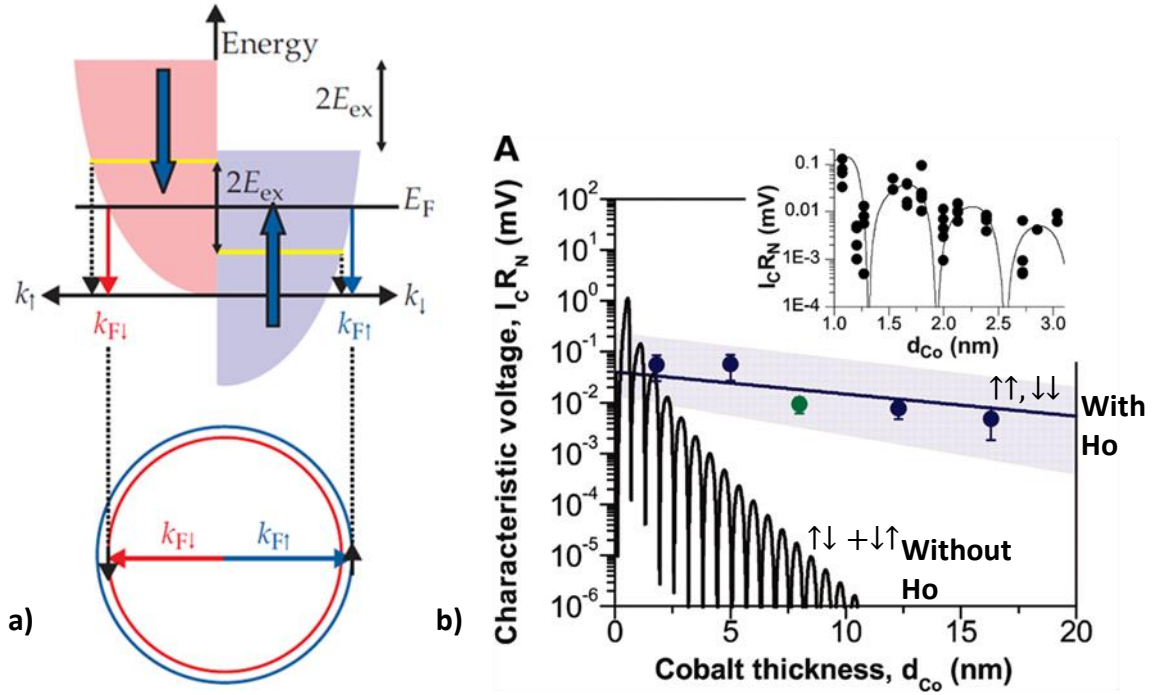


Figure 2.9: a) In the ferromagnet the spin-up band and the spin-down band are shifted with respect to each other by an amount $2E_{ex}$. From Eschrig et al. ref [15] Box 1. b) The oscillating curve is the theoretical model of how the characteristic voltage (or equivalently critical current) decays in a Nb/Co/Nb device, i.e. decay of the $(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ triplet. The solid line indicates that when Ho is used at the interface, the critical current of the Nb/Ho/Co/Ho/Nb junction decays very slowly implying the presence of the long range spin triplet proximity effect discussed in section 2.3.8. The inset shows results from Nb/Rh/Co/Rh/Nb junctions by the same authors.[28] Where the line guides the oscillating behaviour of the current magnetic effect.

The coherence length in the NM (equation (2.13)) is proportional to the inverse of the temperature i.e. proportional to $1/\sqrt{k_B T}$ and so the Cooper pair penetration depth is dependent on thermal energy that causes scattering due to lattice vibrations. However for the FM it is proportional to $1/\sqrt{E_{ex}}$ and therefore the temperature at which thermal energy dominates over the exchange interaction (i.e. when ferromagnetic ordering is destroyed) is the Curie temperature (T_{Curie}). For ferromagnetic metals with strong E_{ex} , T_{Curie} is far above

critical temperature of superconductors such as Nb or Pb (e.g. iron has $T_{Curie}=1043\text{K}$). This would mean that for a ferromagnetic metal at low temperatures (i.e. at 4.2K, where most PCARS is performed using an Nb tip) $E_{ex} \gg k_B T$. This implies that for an SC/FM interface the penetration length of a Cooper pair in an FM interface is expected to be much shorter compared to the SC/NM case (equation (2.13)).[47, 60] It is possible to compare the decay length in a NM (Cu and Ag) with that of an FM (Co) from Figure 2.7 and Figure 2.9b (insert), respectively. In Cu and Ag, ξ_{NM} was measured to be greater than 100nm while in Co the ξ_{FM} is calculated to be 10nm [28, 61].

However there are two possible conditions in which the Cooper pair can survive in the FM, 1) if their spins are paired in parallel which allows the pair to keep a zero centre-of-mass momentum (i.e. converted into an equal spin-triplet pair) which has a long penetration length that is comparable to the SC/NM case [15, 21, 62, 63] or 2) if they continue to be paired with opposite spins but with a non-zero centre-of-mass momentum [15] (i.e. the centre-of-mass of the Cooper pair shifts as it decays in the FM). The characteristic decay length is described by equation (2.14)) [15].

The spin state of the Cooper pair in scenario 1) is the LRSTPE with spins ($\uparrow\uparrow$), ($\downarrow\downarrow$). To obtain this spin-triplet, a mechanism is required to convert the spin singlet Cooper pair into a spin triplet at the interface. This can be achieved via spin splitting at the ferromagnetic interface in a process known as ‘spin-mixing’.[15, 21] An explanation given by Kadigrobov et al. [21] describes the process in the context of Andreev reflection at a SC/FM interface. This is explained in section 2.3.5 with the schematic of the process is shown in Figure 2.10.

One of the outcomes of the non-zero momentum centre-of-mass state, scenario 2) is the observation of the π -junction. The π -junction is a form of Josephson junction in which the sandwich layer is a FM (SC/FM/SC). This junction is explained in the next section.

2.3.4 Josephson 0 and π Junctions

A Josephson junction is a tri-layer of SC/I/SC or SC/NM/SC, where the oscillating supercurrent (I_S) can be described by the Josephson relation $I_S = I_{C0} \sin \Delta\phi$, and $\Delta\phi$ is the phase difference between wavefunctions of the two component superconductors and I_{C0} is the maximum Josephson critical current. A magnetic field can cause $\Delta\phi$ to vary leading to the oscillating behaviour of I_S with field, in the form of a Fraunhofer diffraction pattern. [32, 33]

I_S can also vary spatially, and one way to achieve this is by replacing the NM with FM and inducing a non-zero centre of mass state. This causes a shift in the momentum of the Cooper pair electrons to $k_{F\uparrow} = k_F + Q/2$ for one electron and to $k_{F\downarrow} = k_F - Q/2$ for the other, as it goes through the FM [59, 64]. Consequently, the Cooper pair wavefunction in the FM, and therefore the Cooper pair density, oscillate spatially. [59, 64] The oscillation persists up to a length described by equation (2.14). [65] Since I_{C0} (and therefore I_S) is related to the Cooper pair wavefunction [65] it will also oscillate, switching between positive and negative values. The possibility of negative supercurrent within a Josephson junction containing magnetic impurities in the sandwich layer has been known since the 70s and predicted by Bulaevskii et al. [66]. Therefore if $I_C < 0$ then $I_S = -I_C \sin \Delta\phi = I_C \sin(\Delta\phi + \pi)$; this is effectively having a phase difference of π . [67, 68] The oscillation of I_C also has a dependence on the thickness of the FM [58, 65, 68] and an example of this is shown in Figure 2.9b for a Nb/Co/Nb Josephson junction measured by Robinson et al. [28].

The oscillations in π -junctions were initially understood [59] to be due to the singlet ($|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$) component oscillating in space in the FM and not the triplet ($|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$). This meant that oscillations in the critical current need only be understood in terms of the singlet ($|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$) component. However Eschrig et al.'s [63, 69] recent model would indicate that the triplet ($|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$) component also oscillates in space at a SC/FM interface. However, the subject of this thesis is mainly concerned with the long range spin triplet ($|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle$) proximity effect, which does not oscillate in space. [15, 63, 69]

The proceeding sections will explain the mechanism involved in the conversion of the singlet-state Cooper pair to the ($|\uparrow\uparrow\rangle$), ($|\downarrow\downarrow\rangle$) spin-triplet pair.

2.3.5 Spin-mixing

Here I shall briefly summarise the arguments presented by Kadigrabov et al. [21] on spin mixing at the interface, a schematic is shown in Figure 2.10. If we consider an incident electron, $K^{(e)}$, from the FM side with spin σ . At a point A in the FM it is spin-split into a mixture of spin-up and spin-down electron states as it crosses the magnetic spin-splitter layer. These electrons are then Andreev reflected at the SC/FM interface to produce holes $K^{(h)}$ with the same spin σ and opposite spin, $-\sigma$, as the incident electron. These holes then further undergo a spin-split at points B_1 and B_2 . The result of this three-point scattering process is that the incident electron is reflected into two hole-channels one with spin-up and the other spin-down. This mixture of electrons and holes with both spin-up and spin-down means one of the spin channels of the holes has the same spin as the incident electron. Another way is to view the process in the reverse. As the spin-singlet Cooper pair, $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ from the superconductor penetrates the SC/FM interface it is scattered into a mixture of singlet and triplet states in the magnetic layer.[15, 21, 62]. Such triplet states are of the form $(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ rather than the $(|\uparrow\uparrow\rangle), (|\downarrow\downarrow\rangle)$ state needed for the LRSTPE.[15, 63] Nevertheless spin-mixing is an important (initial) mechanism at the SC/FM interface that is required if the $(|\uparrow\uparrow\rangle), (|\downarrow\downarrow\rangle)$ state is to be generated. The $(|\uparrow\uparrow\rangle), (|\downarrow\downarrow\rangle)$ state can then be achieved by a spin flip mechanism [63] from some form of magnetic inhomogeneity at the interface e.g. a magnetic spin-spiral [21, 47, 70] or by artificially engineering layers of FM with perpendicular and parallel magnetic anisotropy.[17, 71] We see from this that spin mixing is a natural property of any FM/SM interface, but the LRSTPE state can only be produced if, in addition, there is a spin scattering process present.

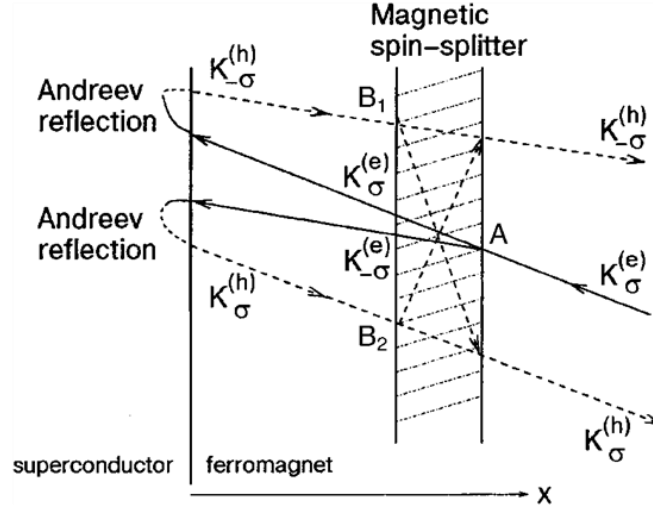


Figure 2.10: A schematic of the Andreev reflection at a SC/FM interface with the incident electron with spin σ being reflected into two hole channels one with spin-up and the other spin down. From ref [21].

2.3.6 Pairing Symmetry at the SC/FM interface

In spin-mixing there are four possible symmetries present at the SC/FM interface and they are classified according to their spin projection with respect to the direction of the magnetisation axis in the FM; triplets have either $m=0$ ($|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$) or $m=\pm 1$ ($|\uparrow\uparrow\rangle$), ($|\downarrow\downarrow\rangle$) spins. (For convenience, from here on, $m=0$ and $m=1$ will be used to describe the ($|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$) and ($|\uparrow\uparrow\rangle$), ($|\downarrow\downarrow\rangle$) triplet pairing, respectively). They are also classified with respect to momentum and frequency (energy). These symmetries of the singlet and triplet pairs at the interface are described by Eschrig et al.[15, 63, 69] and are presented in Table 2.2.

In FM with weak or strong E_{ex} all the four symmetry pairing states are theorised to be present at the interface. [15, 63, 69] The amplitude and penetration length of these pairs in the FM are then dependent on the strength of the exchange field in the FM.[15, 62, 63] In a SC/weak-FM interface, spin mixing of the Cooper pairs generates the $m=0$ triplet pair. This is achieved via the exchange field that causes a shift in the momentum, $k_{F\uparrow(\downarrow)}$, of the Cooper pair electrons (section 2.3.3). The singlet and $m=0$ triplet have centre-of-mass Q that is finite

under an exchange field and this state is similar to what is known as the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state (named after Peter Fulde and Richard Ferrell at the University of Maryland and Anatoly Larkin and Yuri Ovchinnikov at the Moscow Physico-Technical Institute who discovered it in 1964 [72, 73]). The amplitude of the singlet and $m=0$ triplet in the mixed state oscillates in the FM and decays up to a length described by equation (2.14). It is then the magnetic inhomogeneity of the FM, such as a magnetic spiral, that provides a spin-flip mechanism that allows the generation of equal spin triplet $m=1$ with odd frequency and even momentum. The spatial oscillation of the $m=0$ spin-triplet and the spin-singlet follows $\sin(\lambda)$ and $\cos(\lambda)$, respectively, where λ is proportional to the distance from the SC/FM interface.

Spin	Frequency	Momentum	
Singlet (odd)	Even	Even	
$\uparrow\downarrow - \downarrow\uparrow$	Odd	Odd	
$\uparrow\uparrow \downarrow\downarrow$	(1) Even	Odd	
Triplet (even)	(2) Odd	Even	
$\uparrow\downarrow + \downarrow\uparrow$			

Table 2.2 The pairing symmetries that are induced at the SC/FM interface from ref [63]. The labels (1) and (2) are the $m=1$ (LRSTPE) and $m=0$ spin-triplet mentioned in section 2.3.3. The Wavy lines symbolise the odd frequency nature of the pairing symmetry.

A schematic of a Josephson junction with a weak FM (Bloch domain wall) is shown in Figure 2.11a, the singlet (green) and $m=0$ triplet (red) amplitudes oscillate in the FM and the amplitude of the $m=1$ (LRSTPE) triplet (blue) dominates in the polarised region M . For a SC/strong-FM interface the spin mixing already occurs inside the superconductor (within a distance of the superconductor coherence length from the interface) and the $m=1$ triplet is generated via spin flip processes at the interface due to the misalignment of the moments

between the bulk and interface. In the weak FM the $m=1$ spin triplet pair has an amplitude that decays slower over a longer distance (relative to the amplitude decay of the singlet and the $m=0$ spin triplet) and in the strong FM case this is also true, although the singlet and $m=0$ triplet amplitudes are completely suppressed over a very short distance. This is demonstrated in Figure 2.11b where the singlet and $m=0$ triplet amplitudes do not persist into the strongly polarised region M . The direction of moments of the two misaligned interface barriers with respect to the bulk polarisation M can also induce a 0 or π junction.

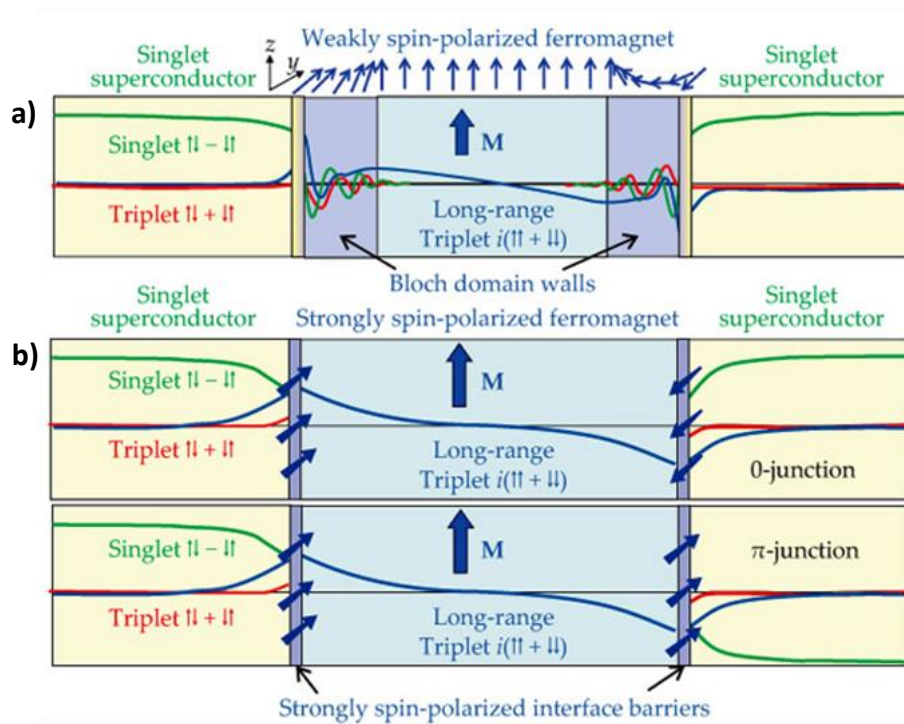


Figure 2.11: a) the singlet (green) and $m=0$ triplet (red) pairs are mixed in the Bloch domain wall FM region and here the $m=1$ triplet is also induced (blue). b) The misaligned interface barrier fully suppresses the singlet and $m=0$ triplet and only the $m=1$ triplet remains. The Josephson junction can be shifted by 0 or π depending on the misaligned interface moment. From ref. [15]

2.3.7 Absence of $m = \pm 1$ Spin-Triplet Proximity Effect in an FM Alloy

The work on observing the LRSTPE took a new turn when Keizer et al., [74] measured NbTiN/CrO₂/NbTiN and reported a supercurrent prevailing over CrO₂ thicknesses of up to $1\mu\text{m}$ at 1.6K . However, before presenting results that give evidence for the $m=1$ spin

triplet pairing at a SC/FM interface, this section will look into some experiments on SC/FM/SC junctions that proceeded Keizer et al., [74] and discuss why they did not show the $m=1$ spin triplet pairing using weak-FM such as $\text{Cu}_{1-x}\text{Ni}_x$ or $\text{Ni}_x\text{Pd}_{1-x}$ unless an additional spin-flip scattering layer is added. This is particularly important as it relates to PCARS measurements on $\text{Ni}_x\text{Pd}_{1-x}$ thin films described later in this thesis.

Khaire et al., [9] measured $\text{Nb}/\text{Pd}_{0.82}\text{Ni}_{0.12}/\text{Nb}$ junctions of varying thickness and observed a decaying oscillating critical current with $\text{Pd}_{0.82}\text{Ni}_{0.12}$, shown in Figure 2.12a, which they attributed to a $0-\pi$ junction crossover. Earlier measurements by Ryazanov et al.[64] and Kontos et.al[75] on SC/FM/SC junctions also show this crossover. It was expected that the $m=1$ spin-triplet would not produce any oscillations in I_C but rather I_C would decrease monotonically. In a later experiment, Khasawneh et al. [26] measured $\text{Nb}/\text{Cu}/\text{Co}/\text{Ru}(0.6\text{nm})/\text{Co}/\text{Cu}/\text{Nb}$ junctions that had magnetic inhomogeneity between the Co layers due to the antiparallel coupling via the Ru layer (i.e. an artificial antiferromagnetic structure, see inset of Figure 2.12b) . Khasawneh et al. results show an exponential decaying critical current with increasing Co thickness with no oscillation was observed, their results are shown Figure 2.12b. The black and red points in the Figure 2.12b are from Khasawneh et al.'s SC/FM/SC junctions with (black) and without (red) a Cu buffer between the Nb and Co. The lack of oscillation is due to the equal thickness, but opposite magnetic spin structure, of the Co layers that results in a zero net phase difference (i.e. one Co layer would induce a phase difference of $\delta\theta$ while $-\delta\theta$ in the other). No spin mixing would be expected in this case. As stated by Khaire et al., [9] a monotonic decrease in I_C , as a function of FM thickness, would be expected for spin triplet pair correlations. However Khasawneh et al. [26] argued that a $m=1$ spin-triplet pair, in particular, would manifest itself as a crossover to a slower decay of the critical current with increasing Co thickness, which was not seen, Figure 2.12b.

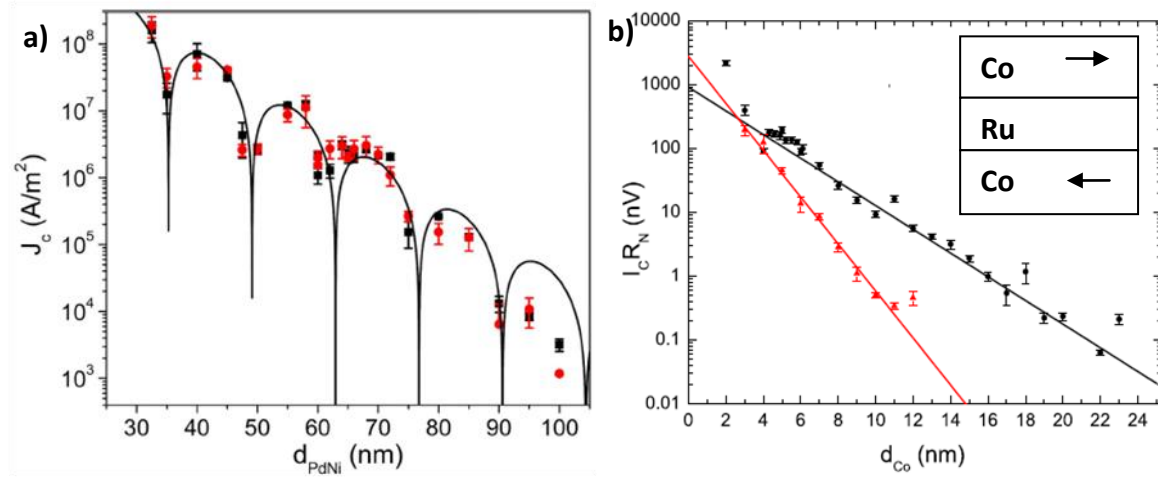


Figure 2.12: a) The behaviour of the critical current for a Nb/Pd_{0.82}Ni_{0.12}/Nb junction with varying Pd_{0.82}Ni_{0.12} thickness. From ref. [9] b) the behaviour of Nb/Cu/Co/Ru/Co/Cu/Nb junctions the critical current with varying Co thickness. From ref. [26]

Arham et al. [76] proposed that the spin memory lengths, i.e. the length in which spin-flip or spin-orbit scattering occurs in the FM [17], of weak ferromagnets may have an effect on the observation of the $m=1$ spin-triplet pair. They measured the spin memory lengths of weak ferromagnetic alloys, Ni_{0.12}Pd_{0.88} and Pd_{0.987}Fe_{0.013}. Arham et al. [76] and found that in Ni_{0.12}Pd_{0.88} the spin memory length is 2.8 ± 0.5 nm. This is shorter than the electron mean free path (determined to be 10.6 ± 1 nm); contrary to what they expected. Implying that Ni_{0.12}Pd_{0.88} would not be suitable in propagating the $m=1$ spin-triplet pair. The short spin memory length was attributed to the out-of-plane moment of Ni_{0.12}Pd_{0.88} caused by spin-orbit coupling of Ni impurities. Attempts to try and suppress the out-of-plane moment by adding a permalloy (Py) layer was a partial success in that the spin memory length increased to 5.4 ± 0.6 nm but not enough to exceed the electron mean free path. In Pd_{0.987}Fe_{0.013} the spin memory length was found to be 9.6 ± 2 nm which is better but the Pd_{0.987}Fe_{0.013} alloy is expected to have a longer electron mean free path than the Ni_{0.12}Pd_{0.88} alloy [76].

It is understood that there are two essential mechanisms (section 2.3.6) in generating the $m=1$ spin-triplet: spin-mixing and spin-flip scattering. These weak ferromagnetic alloys (Cu_{1-x}Ni_x and Ni_xPd_{1-x} alloys) and the Co/Ru/Co interfaces may not contain both of these mechanisms which is why the results of Khaire et al. [9] and Khasawneh et al. [26] did not show signs of the $m=1$ spin-triplet pairing. It is thought that in spin spirals, such as Ho, both

conditions are naturally present and that spin mixing and spin scattering create the necessary conditions for the $m=1$ spin-triplet pairing. The next section presents recent experiments which combine spin mixing and spin scattering at the SC/FM interface to produce the $m=1$ spin-triplet.

2.3.8 Observation of the $m = 1$ Spin-Triplet Proximity Effect

The most notable experiment of Keizer et al., [74] on NbTiN/CrO₂/NbTiN reported a supercurrent prevailing over CrO₂ thicknesses of up to 1 μm at 1.6K, which is longer than what is expected in an FM (of the order of $\sim 1\text{nm}$). Since CrO₂ is a half-metal, the Andreev reflection and the conventional singlet Cooper pair proximity effect is expected to be suppressed. Therefore a supercurrent should not be observed. However it is now known from Eschrig et al.[15, 63] that for strongly spin polarised FM with a spin-active SC/FM interface, there is moment misalignment between the bulk and the interface, it is possible to induce the $m = 1$ spin triplet via spin mixing and spin flip processes (see section 2.3.5). The moment misalignment in Keizer et al.'s [74] case could possibly be an antiferromagnetic CrO₃ layer between the NbTiN/CrO₂ interface if oxidation occurs before depositing NbTiN.

We have mentioned in the previous section that experiments that proceeded Khaizer et al., such as those of Khaire et al.'s [9, 76] Nb/Pd_{0.82}Ni_{0.12}/Nb junction and Khasawneh et al.'s[26] Nb/Cu/Co/Ru(0.6nm)/Co/Cu/Nb junction did not show signs of the spin-triplet pairing. Khasawneh et al.'s[26]critical current measurements are shown as the black data points in Figure 2.13c (this the same black data points from Figure 2.12b).

This would suggest that weak ferromagnetic alloys, such as Cu_{1-x}Ni_x and Ni_xPd_{1-x}, cannot in themselves generate the $m = 1$ triplet proximity effect. However, these FM alloys have been identified as key 'ingredients' for generating spin mixing in these elaborate SC/FM/SC structures as they can be used to create artificially inhomogeneous interfaces (see Figure 2.13a).[9, 17, 71, 77] This is because they can have out-of-plane alignment of the easy-axis of magnetisation due to interface anisotropy.

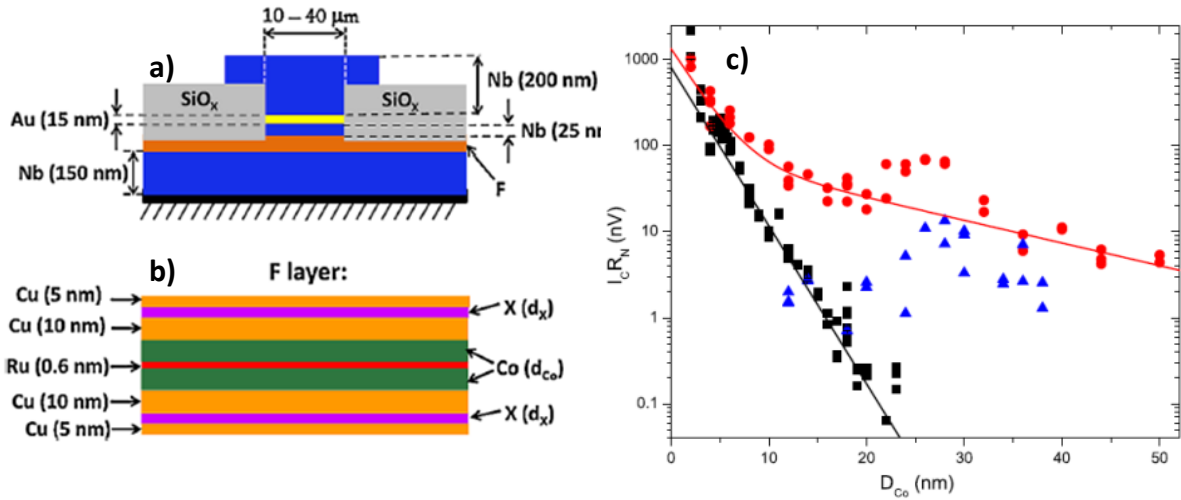


Figure 2.13: a) Cross-section diagram of the SC/FM/SC Josephson junction used ref. [17] in and label F is b) the detailed sequence of the metal layers inside the Josephson junctions. c) The critical current vs. Cobalt thickness for a SC/FM/SC junction without an X layer (black squares), with $X = \text{Cu}_{0.48}\text{Ni}_{0.52}$ (blue triangles) and with $X = \text{Ni}_{0.12}\text{Pd}_{0.88}$ (red circles).

However, more elaborate SC/FM/SC structure was proposed in the experiments of Khaire et al. [17] and Khasawneh et al. [71] in which the FM was a complicated multilayer of $\text{Cu}/X/\text{Cu}/\text{Co}/\text{Ru}/\text{Co}/\text{Cu}/X/\text{Cu}$, shown in Figure 2.13b. The X layer was either a $\text{Cu}_{0.48}\text{Ni}_{0.52}$ or $\text{Ni}_{0.12}\text{Pd}_{0.88}$ layer. The results from this are shown as the red circle data points in Figure 2.13c. The difference in the decaying current of the black and red data points suggests that the $m = 1$ spin triplet pair was present in the more complicated junction structure (red data points). [71] It was proposed that the weak FM alloys can provide a noncolinear magnetisation (i.e. inhomogeneous magnetisation) through either the domains of the weak FM layers or from the carriers experiencing the noncolinear magnetisation between the weak FM and the Co layer. The latter would imply any FM could be used provided that there is some misalignment in magnetisation between the Co. [17]

The experiments on SC/FM/SC junctions using CrO_2 were not quite over as results published by Anwar et al. [78, 79], using $\text{Mo}_{0.70}\text{Ge}_{0.30}/\text{CrO}_2/\text{Mo}_{0.70}\text{Ge}_{0.30}$ junctions, indicated that the substrate used to deposit the CrO_2 can play an important role in generating the $m=1$ spin-triplet pairing. They found that CrO_2 grown onto an Al_2O_3 (sapphire) substrate showed

signatures of the $m=1$ spin-triplet proximity effect while CrO_2 grown onto a TiO_2 substrate lacked the signatures. They attributed this finding to the magnetic disorder of CrO_2 that occurs when a sapphire substrate is used. This does not seem to happen using a TiO_2 substrate. However, when Anwar et al. [79] inserted a Ni/Cu layer to make $\text{Mo}_{0.70}\text{Ge}_{0.30}/\text{Ni}/\text{Cu}/\text{CrO}_2/\text{Cu}/\text{Ni}/\text{Mo}_{0.70}\text{Ge}_{0.30}$ junctions, they found that this structure did show signatures of the $m=1$ spin-triplet pairing proximity effect even on CrO_2 grown onto a TiO_2 substrate.

Other evidence of the long-range $m = 1$ spin triplet proximity effect has been observed in several experiments during the lifetime of this PhD, notably that of Robinson et al. [28] where the critical current across Josephson (SC/FM/SC) junctions was used to determine the observation of the $m=1$ LRSTPE. In terms of the SC/FM/SC structure that generated the $m=1$ spin-triplet proximity effect, Keizer et al. [74] used CrO_2 , a strongly polarised FM, while Robinson et al., [28] used Co sandwiched between two Ho layers (which has a magnetic cone spiral structure below 19K, Figure 4.1b) and the SC (Nb). It was found that the critical current persisted in samples where the Co thickness was greater than ξ_{FM} in Co (10nm). The result for this is shown in Figure 2.9b as the circular data points in the main figure. The SC/FM/SC structures of Robinson et al. [28] and Keizer et al. [74] could be compared to Figure 2.11a and Figure 2.11b, respectively. However, in Anwar et al.'s [79] case, their SC/FM/SC structures may be more attributed to a domain wall (disorder) the SC and strong FM, which is analogous to Figure 2.11a or Bergeret et al.'s [47] model.

The spin memory length also plays a role in generating the $m=1$ spin-triplet proximity effect. The results from Khaire et al. [17] SC/FM/SC junctions showed the critical current peaking around thicknesses of $2 - 4\text{nm}$ for $\text{Cu}_{0.48}\text{Ni}_{0.52}$ and $3 - 6\text{nm}$ for $\text{Ni}_{0.12}\text{Pd}_{0.88}$ which was explained to be a result of the different spin memory lengths (1.4nm for $\text{Cu}_{0.48}\text{Ni}_{0.52}$ and 2.8nm for $\text{Ni}_{0.12}\text{Pd}_{0.88}$). There is also a difference in the value of the maximum critical current of the SC/FM/SC junctions when different X layers are used. However it is mainly the magnetic inhomogeneity rather than the spin memory length that is important in generating the $m=1$ spin-triplet proximity effect.

The implication of these experiments is that the antiparallel Co/Ru/Cu or the weak FM layers ($\text{Ni}_{0.12}\text{Pd}_{0.88}$ or $\text{Cu}_{0.48}\text{Ni}_{0.52}$) in themselves alone are not enough to convert a short range spin singlet Cooper pair to the long-range spin triplet pair. Rather both layers were

needed (combined) and implies that together they provide the spin-mixing and spin-flip mechanism that would generate the spin-triplet proximity effect. Similarly the results on CrO_2 junctions carried out by Anwar et al. [78, 79] proves that a strongly polarised FM is not enough to generate the $m=1$ spin-triplet proximity effect, but magnetic inhomogeneity is still required, i.e. the Ni/Cu (which can be artificially inserted in-between the SC/FM layers). It is possible to infer from these results that the FM layer may provide the spin-mixing and a disordered layer provides the spin-flip mechanisms. In the case of Robinson et al.[28], a magnetic cone spiral may provide both a spin-mixing and spin-flip mechanism. This is why we anticipate a Ho/SC interface, but not a NiPd/SC interface, might yield possible signatures of the LRSTPE.

2.3.9 Conductance Spectra in the presence of the Spin-Triplet Proximity Effect at a single SC/FM interface

There have been few experimental and theoretical studies on the long range spin-triplet proximity effect that investigate the conductance spectra obtained across a single SC/FM interface. However we shall first look at a theory that may hold the key to understanding the PCARS of Ho in Chapter 4. Löfwander et al. [7] discussed how previous fits using the modified BTK model [42] to Andreev reflection conductance spectra on CrO_2 [23, 30, 80-82] resulted in varying polarisation values. The modified BTK model splits the conductance into channels that are polarised and unpolarised as shown in equation (2.11) in section 2.2.2. Fitting with the model typically produces a Δ value that differs from the bulk. However Löfwander et al. [7] proposed a different model, the “spin mixing” model, in which the Polarisation and Δ are fixed to their expected bulk value (in this case, at $T=0\text{K}$, a fixed $P=100\%$ for CrO_2 ; $\Delta = 1.5\text{meV}$ for Nb and 1.35meV for Pb) and incorporated a spin-mixing parameter, ϑ , in addition to the scattering parameter, Z , and series resistance r_s . Their analysis of CrO_2 spectra from several authors showed that it is possible to have a $P=100\%$ fit to the PCARS spectra using their model although it is indistinguishable from the BTK model since the BTK fitted equally well. However Löfwander et al. [7] gave a suggestion for testing the spin active model by seeing how the normalised zero bias conductance $G(0)/G_n$ evolves with temperature, Figure 2.14.

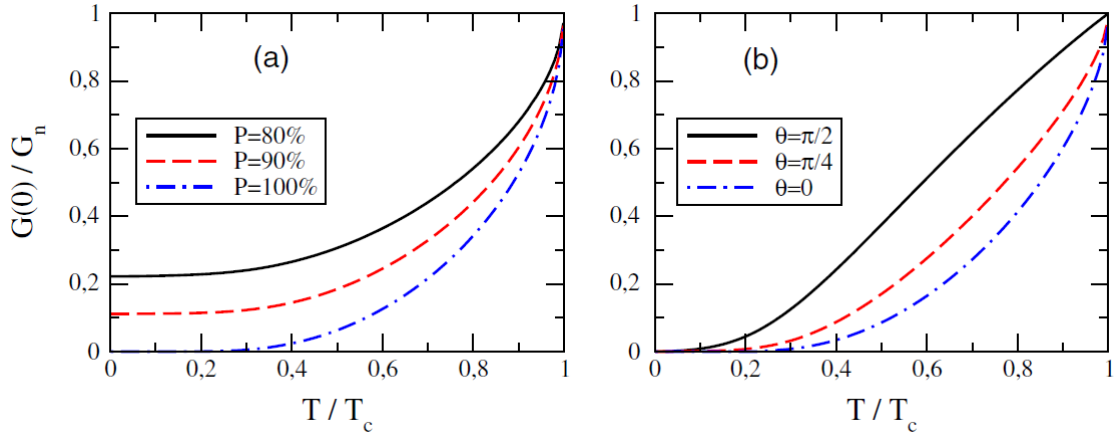


Figure 2.14: a) Normalised zero bias conductance as a function of temperature for the BTK model and b) the spin active model with $P=100\%$. Taken from Ref. [7]

The model given by Löfwander et al. [7] is a specific case for a half-metal. A more generalised model is given by Grein et al. [24] which takes into account the spin mixing angle and spin flip scattering. The spin mixing, ϑ , and spin flip scattering are two processes that are important in generating the equal spin triplet state.[15, 21, 63] The magnitude of both parameters is shown to be sensitive to the impact angle of the incoming electron at the interface, as well as the exchange field and interface thickness. This is shown in Figure 2.15, where it also shows that an increase in SC/FM barrier thickness d would increase spin-mixing but decrease spin-flip. (The barrier is described as a spin-split potential barrier, where one spin has a higher potential barrier than the other [24]). However, high d is a tunnel SC/FM interface while low d is a transparent interface.

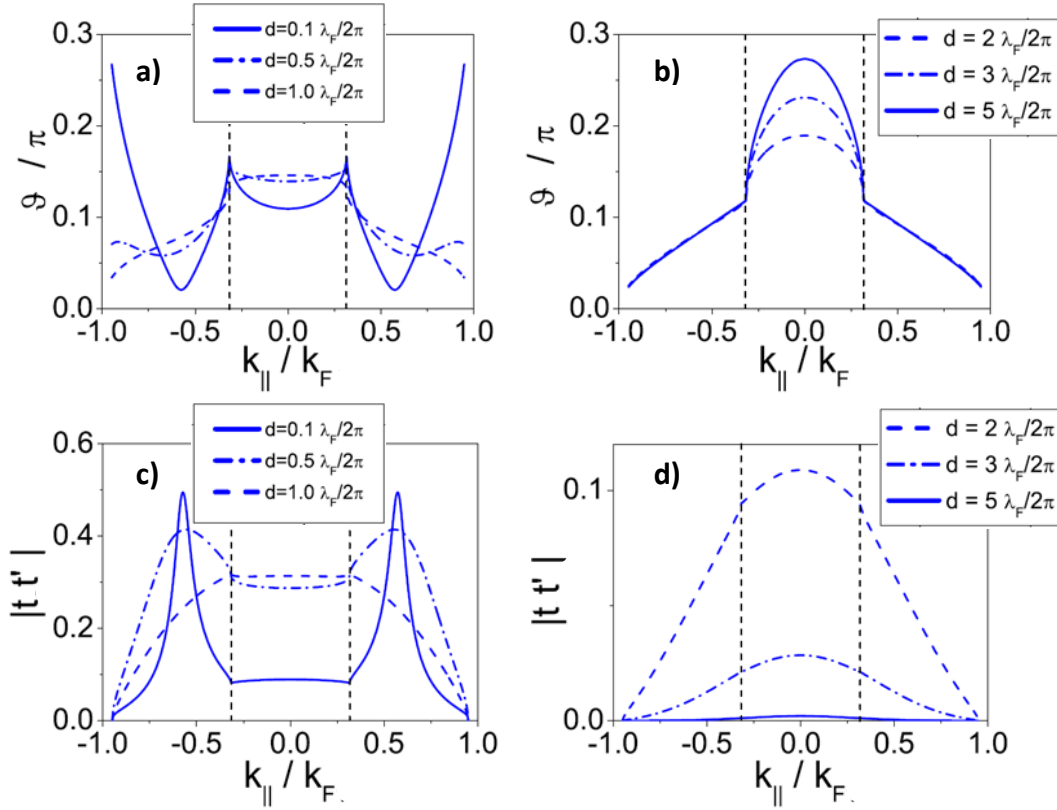


Figure 2.15: a) and b) show the dependence of spin-mixing, ϑ_2/π , as a function of the impact angle, $k_{||}/k_F$. c) and d) show the dependence of the spin-flip $|t_2 t'_2|$ as a function of $k_{||}/k_F$. From ref. [24]. $k_{||}$ is the momentum of the electron in the FM, parallel to the SC/FM interface and k_F is the Fermi momentum in the SC. In the legend, d is the thickness of the SC/FM interface (low d means more transparent interface). λ_F is the Fermi wavelength of the superconductor.

A consequence of their model is the appearance of subgap peaks which are linked to ϑ , so by increasing ϑ the peaks become more prominent. We see that as the barrier thickness, d , is increased (therefore increasing ϑ), it causes a peak to develop around the SC gap energy, Figure 2.16a. This is related mainly to the $m=1$ spin-triplet.[24] A further increase in d , Figure 2.16b, would result in a subgap peak with very low conductance appearing and in the limit of a tunnel SC/FM interface it disappears.

Under increasing exchange energy (field) the sub gap peak moves to lower energies and decreases in magnitude Figure 2.16c. At a finite temperature the peak is too broad and too near the gap edge to be observable, but it would still contribute to the conductance around the SC gap, Figure 2.16d. However at finite temperatures and even for a highly polarised FM

($P=80\%$) the peak is still sensitive to spin mixing and this means an increase in the peak can still be observed with spin mixing, around the gap energy.[24] If this sort of spectra with strong peak features were to be naively fitted using the modified BTK model, it would appear as an increase in the Z parameter. Grein et al. [24] have also compared their model with that of Mazin et al.[42] and commented on how the Mazin model is considered a limiting case of their model, i.e. the formula from Mazin could be derived from the theory of Grein et al. [24] by including setting ϑ to zero.

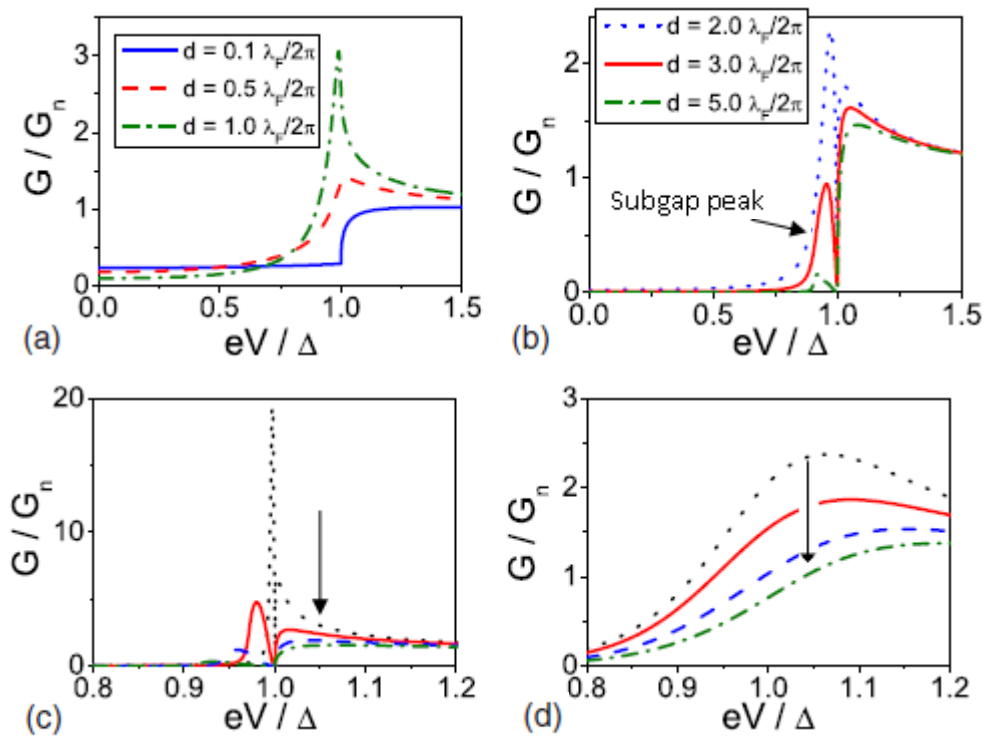


Figure 2.16: a) and b) Normalised conductance as a function of bias for different SC/FM barrier thickness. With $E_{ex} = 0.8E_F$, $T=0K$. c) and d) Normalised conductance as a function of bias for different SC/FM exchange energy at $T=0K$ and $T=0.1T_c$, respectively. Both have $d=0.5\lambda_F/2\pi$ The exchange energy is in units of the superconductor Fermi energy E_F , with values of $0.1E_F$, $0.2E_F$, $0.3E_F$ and $0.4E_F$. The arrow in c) and d) indicate the direction of increasing exchange energy (field). From ref. [24]

Among the few authors that have presented experimental works on conductance spectra across a single interface are Hacohe-Gourgy et al.[13], Almog et al.[83-85] and Krivoruchki and Tarenkov.[6] The first two authors have mainly worked on Co/CoO/In interfaces with

the CoO acting as a spin-active interface that is claimed to produce the spin-triplet pairing. A spectrum taken from an In/Co junction by Almog et al. [83, 84] was compared to conductance spectrum taken from a Sr_2RuO_4 (spin triplet superconductor) point contact measurement. Comparing the central (zero bias) cusp feature of the two spectra lead these authors to claim that this cusp was indicative of the $m=1$ spin-triplet pairing. In the same paper [83] Almog et al. presented Crossed Andreev Reflection (CAR) measurements using a Co/In/Co junction and claimed that by passing current through one junction and measuring a non-local voltage through another, a conductance spectrum can be observed. CAR can only happen if the distance between the two FM is less than the superconductor coherence length [86], $\xi \sim 115\text{nm}$. Since the distance between the two interfaces is 150nm the authors claim this CAR is due to the long range spin triplet proximity. However this would mean that the spin triplet proximity effect would be long range in the SC but from Eschrig et al.'s model, Figure 2.11, there is no obvious reason why ξ_{Triplet} will be longer than ξ .

Krivoruchki et al. measured the conductance spectra of SC/LCMO ($\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$) [87, 88] and Pb/LSMO ($\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) [6] and claimed that it can support spin triplet pairing. Resistance measurements showed that the resistance of the Pb/ $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ contact dropped at the onset of the Pb superconductivity. Conductance measurements showed that the induced gap of the LSMO was 18meV ; much larger than Pb (1.35meV). They observed subharmonic gap structure, Figure 2.17, due to multiple Andreev reflection which they claimed could only happen if the LSMO was in a superconducting state. [6] These observations were argued to be caused by the long range spin triplet and maintained by the intrinsic superconducting fluctuation of LSMO (the authors claimed that LSMO is very thermodynamically close to being a triplet p-wave even frequency superconductor[6]).

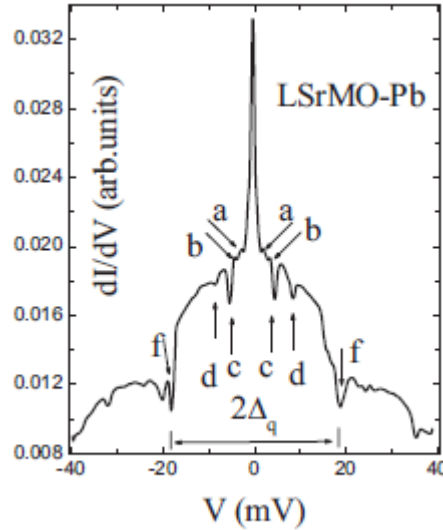


Figure 2.17: a) The conductance as a function of voltage for Pb/LSMO point contact at 4.2 K. The letters represent to the subharmonic gap structure, where $a=\Delta_{pb}$, $b=(\Delta_{pb}+\Delta_{LSMO})/5$, $c=(\Delta_{LSMO})/3$ and $d=(\Delta_{LSMO})/2$. From ref. [6]

Hacohen-Gourgy et al.[13] however presented conductance measurements on In/CoO/Co interfaces with the CoO believed to act as a spin active barrier. They attempted to fit their conductance spectra with an s-wave SC/FM conductance model (i.e. the modified BTK model of Mazin [42] and Strijkers [19]) but it did not fit the shape of their conductance spectra at low bias (red curve on Figure 2.18). They obtained energy gaps that were 14% to 90% higher than indium (0.525meV) and polarisation values of 10% to 30%, less than the previously measured values for Co ($\sim 42\%$).[23, 89] Their solution was to combine contributions from an s-wave conductance model [89] with a p-wave SC/FM conductance model[90] and include a ratio $R = \text{s-wave/p-wave}$; they showed a better fit to their spectra using this model (black curve on Figure 2.18). The discussion in this chapter shows that various theoretical predictions exist, but the experimental picture is limited and inconclusive. It is clearly desirable to set an experiment where parameters are changed systematically by changing the interface parameters, or by altering the temperature. This attempt is described in chapter 4.

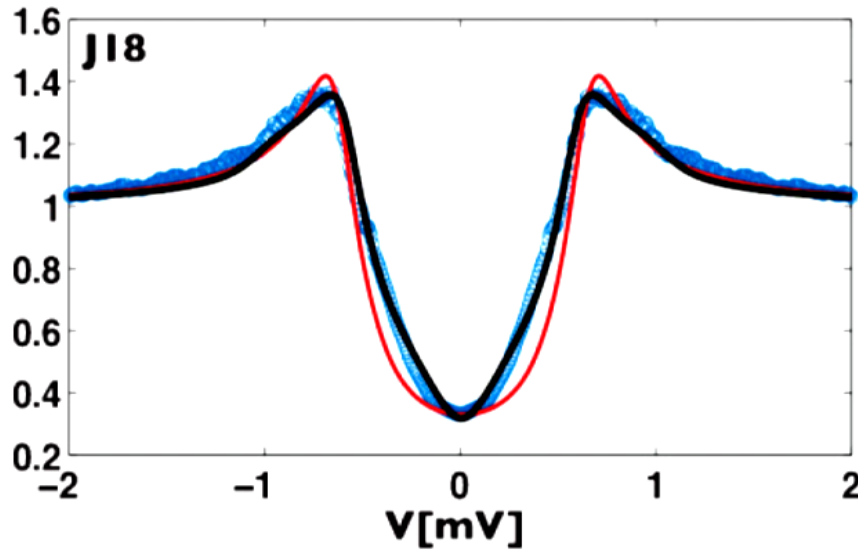


Figure 2.18: the normalised conductance as a function of bias for a Co/CoO/In junction at 0.5 K. The red curve is the modified BTK fit and the black curve is the author's fit that takes into account the s-wave SC/FM conductance model and a p-wave SC/FM conductance model that takes into account contribution from triplet p-wave superconductivity. From ref. [13]

2.3.10 P-Z relation

Before we conclude this chapter we shall briefly discuss what can be observed in terms of P (Polarisation of the current) and Z (interface scattering parameter). The modified BTK model described in section 2.2.2 has the potential of finding the polarisation, P of the transport electrons across an SC/FM interface. The parameter P has the effect of suppressing conductance due to Andreev reflection (i.e. reducing the sub-gap conductance). However the dimensionless parameter Z also has a similar effect (i.e. reducing sub gap conductance) but produces more pronounced peaks in the Andreev conductance spectrum near $V \approx \Delta$.

A P(Z) trend that is commonly seen at SC/FM interfaces are ones, such as one seen by Kant et al. [91], Figure 2.19, and discussed by Woods et al. [92] and Strijkers et al.[19] (i.e. P decreasing with increasing Z). In some literature that analyse PCARS it is claimed that the “intrinsic” value of P can be found by extrapolating a P(Z) fit to $Z = 0$. Kant et.al.[91] have

measured various magnetic materials using PCAR and showed that an exponential fit can describe the trend in their $P(Z)$, while Strijkers et al.[19] were able to use a parabolic fit in their $P(Z)$ plots. However Woods et al.[92] investigated the meaning of the $P(Z)$ relation and whether it is possible at all to extract the “intrinsic” value of the polarization by extrapolating to $Z = 0$. It was pointed out that neither the parabolic or exponential fit was better at defining a trend in $P(Z)$ that would give the value of P at $Z = 0$. However if there exists a minimum Z due to the Fermi velocity mismatch, $Z_{\min}$ (equation 2.3), then it could be considered that the P value at $Z = Z_{\min}$ would represent a real scattering effect that causes a reduction in P . However if it is considered that $Z_{\min}$ is real and defines a P value then it is reasonable to assume that other values of Z in a $P(Z)$ trend would also correspond to a particular P . Making the extrapolation to $Z = 0$ unnecessary.

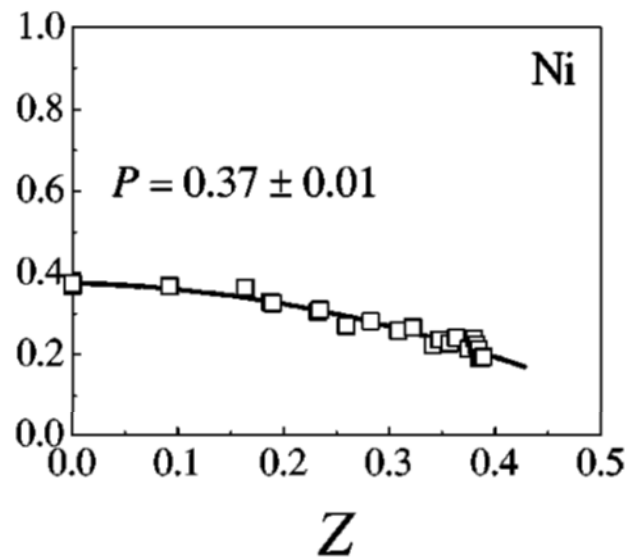


Figure 2.19: The $P(Z)$ trend for Ni PCARS. The value of $P = 0.37 \pm 0.01$ is the value at $Z=0$.

Adapted from ref. [19]

However, Kant et al. [91], Woods et al. [92] and Strijkers et al.[19] pointed out that the trends in $P(Z)$ are not necessarily artefacts as they can occur due to surface scattering from impurities at the interface. In their analysis of SC/FM interfaces, Kant et al. [91] calculated the Fermi velocity mismatch for different combinations of SC(Nb or Pb)/FM (Co, Fe, Gd or CrO_2) interfaces and found that the Fermi velocity mismatch could not solely be the source of the large Z values and was instead attributed to impurities that can cause spin-flip scattering. It was interpreted that in the presence of strong spin flip scattering, Z increases

and as a consequence P tend towards zero.[92] It was mentioned earlier in section 2.3.8 that spin flip scattering is an essential part of the spin triplet pairing generation. Therefore it is possible that, for Nb/Ho contacts, the $P(Z)$ trend (e.g. in section 4.6.1) may indicate the presence of spin-flip scattering at the interface. However in section 2.3.9 it was suggested that spin mixing, indicated by the formation of peaks in the conductance spectra, could also lead to an apparent increase in the value of Z using Mazin [42] et al.'s rather than Grein et al.'s [24] model. Although quantifying the spin mixing and spin flip scattering contributions towards Z is interesting, it is not within the scope of this thesis and would require a controlled interface which is not likely in PCARS. Therefore it is only possible to state that there is some form of spin mixing/scattering mechanism if similar $P(Z)$ trends and conductance peaks are observed.

Another explanation of the observed $P(Z)$ behavior would be stray fields at the interace as modeled by Miyoshi et al. [93]. The model showed the $P(Z)$ effect/trend can be caused by stray field. However, a comparison of how other parameters change with Z , such as ω (broadening), showed that it is far from similar to the stray field model and therefore rules it out as the cause of the $P(Z)$ trend. The two-channel model is the tool that is used to analyse whether stray field is having an effect on the results and is discussed in section 3.2.8.

2.4 Chapter 2 Conclusion

In conclusion, Andreev reflection is the process at the interface of a SC/NM (FM) metal in which electrons are able to propagate from the metal to the superconductor at energies below the superconductor gap. This happens by pairing spin-up and spin-down electrons from the metal into a Cooper pair in the superconductor at the interface. The proximity effect can be described as the 'leakage' of the Cooper pair density in the NM over a distance ξ_{NM} in the NM, and it is over this distance that the Andreev reflection can take place. In a FM the spin bands are shifted by an exchange energy, causing one spin band around the Fermi energy level (i.e. spin-up) to be a majority spin band and the other (i.e. spin-down) to be the minority. This split in the DOS will suppress the Andreev reflection process at an SC/FM interface. The exchange interaction causes an oscillatory decaying order parameter that is short lived in the FM, resulting in the proximity effect in the FM being shorter than the NM, $\xi_{\text{FM}} < \xi_{\text{NM}}$. However if there is some magnetic inhomogeneity at the SC/FM interface, whether it is intrinsic such as a magnetic cone spiral in Ho or from artificial moment misalignment from multi-layered FM structures, then it is possible to create a long-range spin triplet proximity effect (LRSTPE). This $m = 1$ (LRSTPE) happens via spin mixing and spin-flip scattering of (singlet) Cooper pairs. The majority of evidence for the long range proximity effect is from the observation of the long range critical current across a Josephson junction as a function of the FM thickness in SC/FM/SC junctions. Very limited work currently exists that examines single SC/FM interfaces theoretically and experimentally (certainly none existed at the start of this thesis work). The theory presented by Grein et al. [24], has proved promising in the interpretation of features that are obtained from the PCARS of Ho presented in chapter 4.

Rather than make artificial planar junctions, this thesis presents results from single SC/FM interfaces, interrogated by point-contact Andreev spectroscopy. What we see in Ho, but not in $\text{Ni}_x\text{Pd}_{1-x}$ alloys, is an unusual behaviour in P and Z as a function of tip pressure, which I interpreted as something that may be related to spin mixing. This will be discussed further in chapter 4.

3 Experiment and Analysis

The first part of this chapter shall go through the experimental methods used in this thesis, including PCARS and other supplementary experimental methods. Point-contact Andreev reflection spectroscopy (PCARS) is used to obtain differential conductance spectrum across a superconductor/metal interface. Another possible choice would be creating planar SC/FM interfaces similar to those employed by Magnus et al.[3] This would create a stable contact between the SC and Metal; however it would also require creating many junctions over a number of samples to explore interface effects. To probe such a variety of interfaces PCARS would be a more efficient method.

The second part of this chapter explains how the conductance spectra, from PCARS, are analysed (fitted) using software developed by Dr. Yura Bugoslavsky [20] using the Blonder-Tinkham-Klapwijk (BTK) model modified by Mazin et al.[42]. This model takes into account the contribution of spin polarised conductance and is used to obtain the SC gap, broadening, polarisation and interface scattering parameter of a spectrum. However, there are limitations in fitting heavily broadened spectra, which would result in a number of equally likely polarisation values. This effect is investigated via simulating broadened spectra. The effect of fitting a fixed gap to spectra that has a suppressed and enhanced Δ is also modelled.

In addition there are issues that need to be considered that may affect the result of fitting such as spectral background and sample resistance and indeed these may need to be removed/accounted for before fitting.

3.1 Experimental Methods

3.1.1 The Point-Contact Rig

The PCARS method utilises a needle-anvil setup in which a sharp superconducting tip is used as the 'needle'. The tip is mechanically cut using a scalpel blade which makes the size of the apex generally 10-20 μm . [1, 20] The tip is then placed on a tip holder with two copper strips, one for current the other for voltage, and is held firmly in place by clamping the tip with two screws, Figure 3.1a. The tip holder is attached onto a pin that is connected to a long shaft. This will allow a vertical movement of the tip holder using a differential screw mechanism operated by a stepper motor at the top of the rig. The stepper motor is controlled via the parallel port of a computer and has a tip-motion precision of approximately 0.5 μm . [1] The sample is mounted onto a sample stage that is connected to a lever. This lever is attached to another shaft that allows manual control of the sample stage and this controls the position of a point-contact on the sample. This has a precision, for a spacing of 1cm between contacts, of $\sim 0.1\text{mm}$. The differential conductance (and hence resistance) measured between the sample and tip is done via four contact set up, with the tip and sample each having a current and voltage lead, Figure 3.1a. It is possible to obtain conductance spectra of varying resistance for a single point-contact position by applying pressure on to the tip/sample contact (controlled via the differential screw).

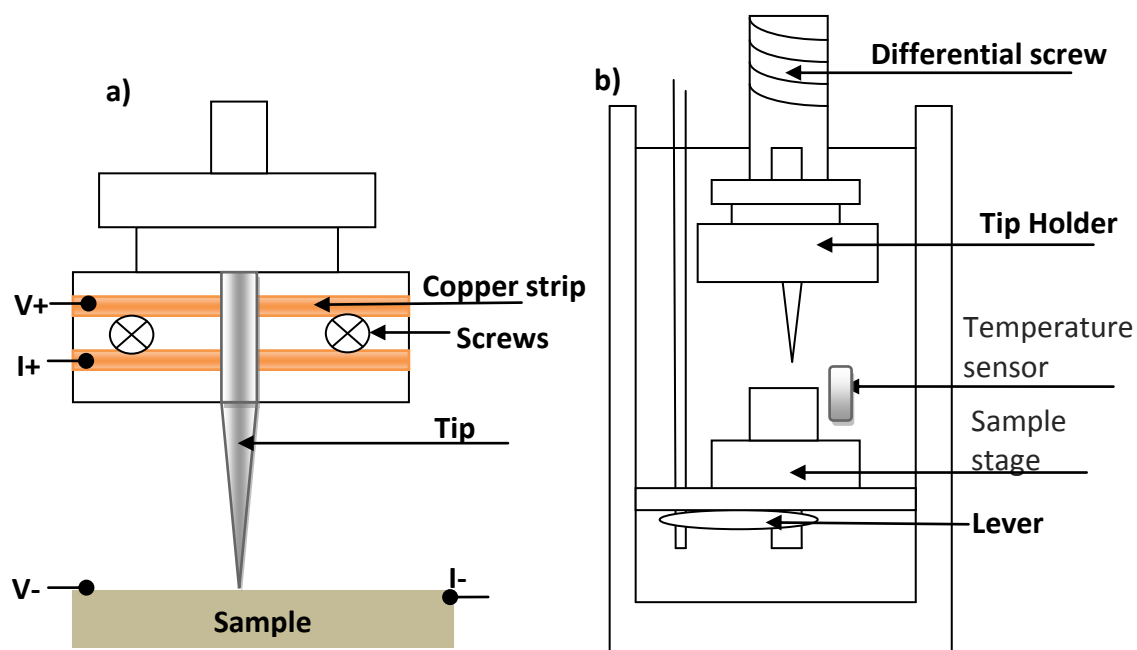


Figure 3.1: a) the tip holder and sample with voltage (V) and current (I) lead, b) the brass compartment which encloses the sample stage, temperature sensor and tip holder. Adapted from Ref. [1]

The tip holder and sample stage are installed inside a brass compartment at one end of the rig (See Figure 3.1b), mounted inside this compartment is a silicon diode temperature sensor that is connected to an Oxford Instrument Intelligent Temperature Controller (ITC4). Enclosing the brass compartment is a copper cylinder with heater wire (0.5m of $60\Omega\text{m}^{-1}$ constantan wire); this heater is also controlled by the ITC4. Cooling is done by inserting the brass compartment end of the rig into a liquid He Dewar and immersing the brass end into liquid He. This method enables a stable operating temperature of 4.2K . Application of the heater whilst it is immersed in He would result in the boil off of He and lead to tip instability. Therefore any PCARS measurements as a function of temperature would usually start from a base temperature of at least 4.6K (when the probe is above the liquid level in the dewar).

3.1.2 Electrical Construction

The conductance spectrum of a point contact can be measured by applying an AC signal with frequency $\omega_{a.c.}$ ($I_{a.c.} = I_0 \cos(\omega t)$) on top of DC current $I_{d.c.}$ that sweeps over a bias voltage range. The voltage of the contact can be represented as a Taylor Series[37]

$$\begin{aligned}
 V(I = I_{d.c.} + I_0 \cos(\omega_{a.c.} t)) \\
 &= V(I_{d.c.}) + \frac{dV}{dI} I_0 \cos(\omega_{a.c.} t) + \frac{1}{2I} \frac{d^2V}{dI^2} I_0^2 \cos^2(\omega_{a.c.} t) + \dots \\
 &= V(I_{d.c.}) + \frac{dV}{dI} I_0 \cos(\omega_{a.c.} t) + \frac{1}{4} \frac{d^2V}{dI^2} I_0^2 (1 + \cos(2\omega_{a.c.} t)) + \dots \quad (3.1)
 \end{aligned}$$

If the AC current ($I_0 \cos(\omega_{a.c.} t)$) is sufficiently small then the higher order terms in the series can be neglected and the AC voltage (and therefore current) can be measured, using a standard lock-in, across the contact at a frequency of $\omega_{a.c.}$ (the first harmonic), which is proportional to the differential resistance. The circuit diagram for the conductance/resistance measurement is shown on Figure 3.2.

The DC component, Figure 3.2, is supplied via a function generator (Thurlby Thandar Instruments TG1010) that drops a voltage, $V_{d.c.}$ across the contact of resistance R_C . It is a quasi-DC triangular wave with frequency 0.05Hz, however this is an upper limit used to obtain a quick scan to establish the quality of the contact. A lower frequency for $V_{d.c.}$ is usually used (e.g. 0.005Hz) during data acquisition and, depending on the time constant setting on the lock-in, will reduce the effect of noise during data acquisition. This gives a better spectral resolution. The DC voltage can be adjusted by changing $R_{d.c.}$ (called the attenuator/shunt resistor in the experiment) which is set to be greater than the contact resistance (i.e. 2k Ω). The AC signal, $V_{a.c.}$ is driven by a lock-in amplifier (Stanford Research Systems SR830 DSP Lock-in Amplifier) which generates a sinusoidal oscillation with a frequency of 10.321 kHz and is coupled to a resistor, $R_{a.c.}$, which is also greater than the contact resistance (fixed at 100k Ω). A 10.321 kHz frequency is used in point-contact spectroscopy because it avoids multiples of 50Hz and sufficiently reduces 1/f noise. [1, 37]

The DC voltage across the contact, $V_{d.c.contact}$, is measured using the auxiliary lock-in amplifier via a preamplifier (Laplace Instruments, Versatile Instrumentation Preamplifier (VIP-20)), with a gain x100 (this can be varied between 50 and 200). The first harmonic AC signal is measured using the lock-in amplifier and the differential conductance is obtained by treating the AC-side of the circuit in Figure 3.2 as a potential divider

$$V_{a.c.contact} = \frac{R_c V_{a.c.}}{R_{a.c.} + R_c} \quad (3.2)$$

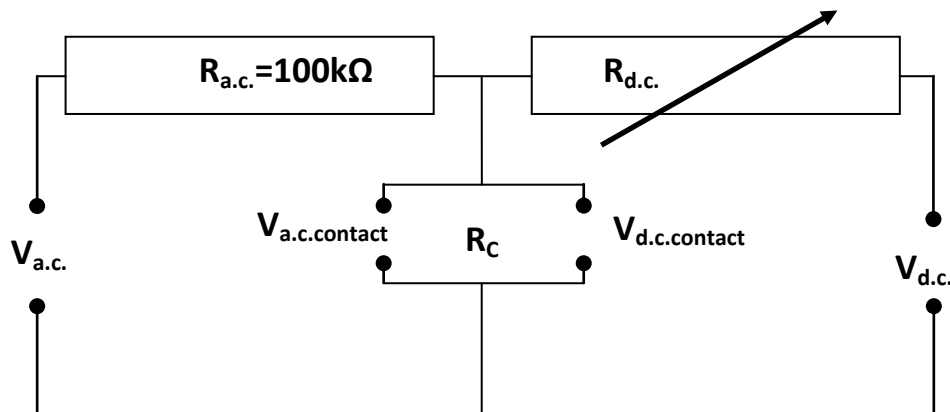


Figure 3.2: The Circuit diagram showing the D.C. and the A.C. applied current across the interface. Adapted from ref. [1]

Provided that $R_{a.c.} \gg R_c$, equation (3.2) can be rearranged to give the differential conductance, G_c , across the contact

$$\frac{dI}{dV} = \frac{I_{a.c.}}{I_{a.c.}(dV/dI)} = G_c \frac{1}{R_c} = \frac{V_{a.c.}}{(R_{a.c.})V_{a.c.contact}} \quad (3.3)$$

The measurement is controlled using a computer with data acquisition software written in Labview by Dr. Yura Bugoslavsky. The Lock-in and function generator are controlled using this software via a GPIB interface connected to the computer. The stepper motor is also controlled by the same software. Temperature readings are read directly from the ITC4 and the temperature can be manually controlled using ITC4 interface.

3.1.3 Supplementary Measurement Techniques

Magnetometry measurements were also used in this thesis to obtain M-H and M-T magnetisation data of Ho single crystals and thin film samples as well as $\text{Ni}_{0.19}\text{Pd}_{0.81}$ and $\text{Ni}_{0.03}\text{Pd}_{0.97}$ thin film samples. Magnetometry measurements were taken using an Oxford Instruments Transverse Vibrating Sample Magnetometer (TVSM). The TVSM works by vibrating a sample in a static magnetic field (Figure 3.3a) and using a Mallinson coil set (pick-up coils) to measure the induced current caused by the magnetic moment. The magnetisation measurements were performed between room and liquid helium temperatures. The TVSM has a magnetic field range of $\pm 4\text{T}$.

Hall images showing the surface magnetic structure of Ho were taken using a Hall probe sensor that is typically $20 \times 20 \mu\text{m}^2$. The sensor was patterned (by Dr James D. Moore) on InSb on GaAs and featured large area contacts for voltage and current leads, as shown in Figure 3.3b. The sensor is attached to a lever at one end of the Hall probe that is designed to move in the x, y and z directions, in Figure 3.3c. The height, z, in which the sensor is above the sample is calibrated before a measurement is taken to ensure that the sensor is at a constant height from the sample and will not touch the surface during measurement.[2, 94] The height calibration of the Hall sensor is done using two capacitor plates placed below the sample; as the sensor is pushed together capacitance increases. This change is measured as the change in voltage across the two plates. Height calibration is done at 10 equally spaced positions in the x and y directions across the area of the sample. This calibration identifies the parabolic dependence of the sensor height as a function of x and y and used during scanning to ensure constant probe height. Magnetic field measurements are done by inserting the Hall Probe into the TVSM cryostat with the sensor positioned perpendicular to the field.

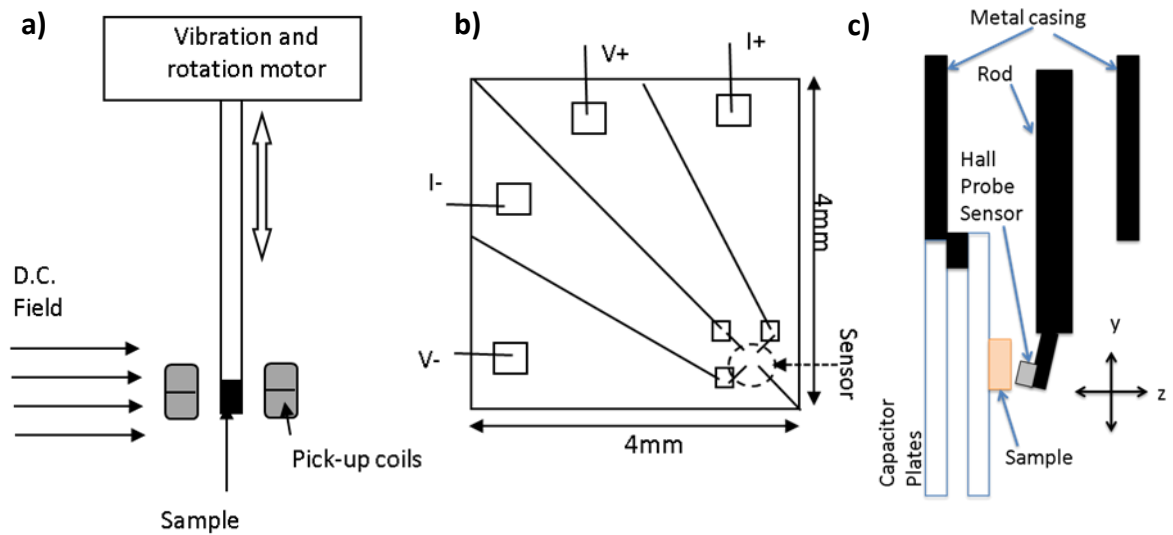


Figure 3.3: a) the vibrating sample holder of the TVSM magnetometer b) the schematic of the Hall sensor that is used to perform the hall probe imaging, the sensor is the dashed circle. c) the Hall sensor and sample set up on the rig. Adapted from ref. [2]

3.2 Analysis

3.2.1 Andreev Spectrum Fitting Procedure

Fitting of the Andreev spectra was done using software written by Dr. Yura Bugoslavsky[20] and it is based on the BTK model modified by Mazin et al.[42] (see section 2.2.2). The fitting procedure uses four parameters to fit an experimental conductance spectrum and allows it to be fitted in either the ballistic or diffusive regime. These parameters are the superconductor energy gap Δ , a dimensionless interface barrier parameter Z , the spin polarisation, P and the spectral broadening parameter, ω . The fitting procedure uses an optimisation algorithm which finds the minimum of the normalised sum of the squared deviations, χ^2 , between the experimental conductance spectrum and the theoretical spectrum

$$\chi^2(\Delta, Z, P, \omega) = \frac{1}{N} \sum_i \left[[g(V_i) - G(V_i; \Delta, Z, P, \omega)] \right]^2 \quad (3.4)$$

Where $g(V_i)$ is the experimental spectrum which is comprised of N points and $G(V_i)$ is the theoretical spectrum generated either in the ballistic or diffusive regime of the modified BTK model. Allowing all four parameters to freely change during the fitting procedure may produce a set of values but not the ones with the lowest χ^2 (i.e. the best fit). A method to resolve this would be to perform a three-parameter fit with a fixed P value (P_{trial}) and from the minimum of the $\chi^2(P_{\text{trial}})$ we would find the corresponding Δ , Z and ω value. Doing this within the range $P_{\text{trial}}=0\%$ to $P_{\text{trial}}=100\%$, with a step size $\Delta P_{\text{trial}}=0.5\%$, produces a one-dimensional function $\chi^2(P_{\text{trial}})$ and would ideally produce a minimum in $\chi^2(P_{\text{trial}})$. [20] An example of a full four-parameter $\chi^2(P_{\text{trial}})$ fit (from this point I will define it as just $\chi^2(P)$) is given in Figure 3.4a for a theoretical spectrum with $\Delta=1.5$, $Z=0.3$, $P=30\%$ and $\omega=0.36\text{meV}$. This spectrum is also presented in section 3.2.3 where I will identify the broadening conditions in which the four-parameter does not give a distinct minimum.

When fitting a spectrum there are certain things to be aware of such as background conductance, dip features and the fitting procedure's normalisation point on the Andreev conductance spectrum. The issue of the normalisation point and its effect has been studied by Bugoslavsky et al.[20]. It was shown that, for a theoretical spectrum, if the conductance

value used for normalisation point was displaced $\pm 0.5\%$ off from its theoretical value, it would produce an artificial minimum in the $\chi^2(P)$. For spectra showing flat backgrounds, it can be normalised by dividing the spectra to a conductance value at a voltage $V_{\text{norm}} \gg \Delta$. For any set of spectra V_{norm} is held at a constant in the programme. However some materials show background spectra at ($T > T_C$) that are not flat in which case they need to be normalised either by dividing the spectra with a spectrum taken just above T_C (or H_{C2}) or by using a normal (non-superconducting) tip. Heating at the contact causes a decrease in the conductance at high bias[95] and it may be seen as a parabolic background (similar to the $\text{Ni}_{0.03}\text{Pd}_{0.97}$ sample in section 5.4). However, other mechanisms may also induce background features such as phonon scattering[96] or tunnelling at the interface. In these cases, the normalisation point becomes more than a simple matter of choosing a point in the region $V \gg \Delta$ of the spectrum, see Figure 3.4b. The particular method for subtracting the background will be discussed in chapter 4.

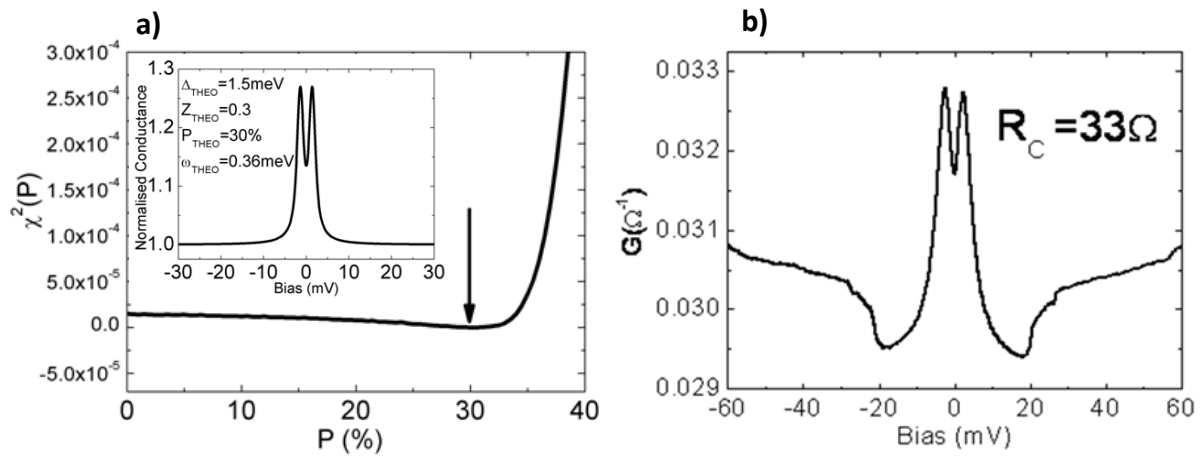


Figure 3.4: a) $\chi^2(P)$ showing a minimum for a four-parameter fit to a known theoretical spectrum generated with values indicated in the inset. The arrow indicate the minimum point (i.e. at $P=30\%$) b) Data from the PCAR measurements on Ho single crystal in chapter 4 at contact resistance of 33Ω . Here we see it has dips (see section 3.2.7) on each side and a non-flat background at high conductance. This shows the difficulty of systematically identifying a normalisation point.

3.2.2 Spectral Broadening

The BTK model was derived in the zero temperature limit and so the Fermi distribution function is a step function at the Fermi Energy level. However at finite temperatures the Fermi distribution is broadened (thermal broadening) so there is a finite probability of transport electrons being above as well as below the Fermi energy. The usual way to fit a spectrum at a finite temperature would be to convolute it with the derivative of the Fermi-Dirac function ($-df/dx$) which would give broadening in terms of the half-width of $-df/dx$, i.e. $\omega_{Fd}=k_B T$. [20]

Another possible contribution to spectral broadening would be from non-thermal effects. These include quasiparticle lifetime broadening and other inelastic scattering at the SC/Metal interface. Lifetime broadening is due to electrons with energies near the gap, Δ , relaxing into a Cooper pair over a period known as the recombination time τ_R and this would broaden the density of states (DOS). This broadening can be represented with the parameter $\Gamma = \hbar/\tau_R$ [97-99] [100] . However, broadening can also be from inelastic scattering mechanisms such as electron-phonon scattering, spin fluctuations and spin-flip scattering at the interface.

In the limit of thermal broadening only, it is sufficient to use $-df/dx$ to model the broadening. However it does not take into account other forms of broadening. Additional broadening can be accounted for by using Gaussian curve as it takes the form of a $-df/dx$ curve and would account for any excess broadening as an effective temperature. The Gaussian function for a spread of energy E from its mean value μ is of the form $e^{-\left[\frac{(E-\mu)^2}{2\omega^2}\right]}$ [1, 20], shown in Figure 3.5.

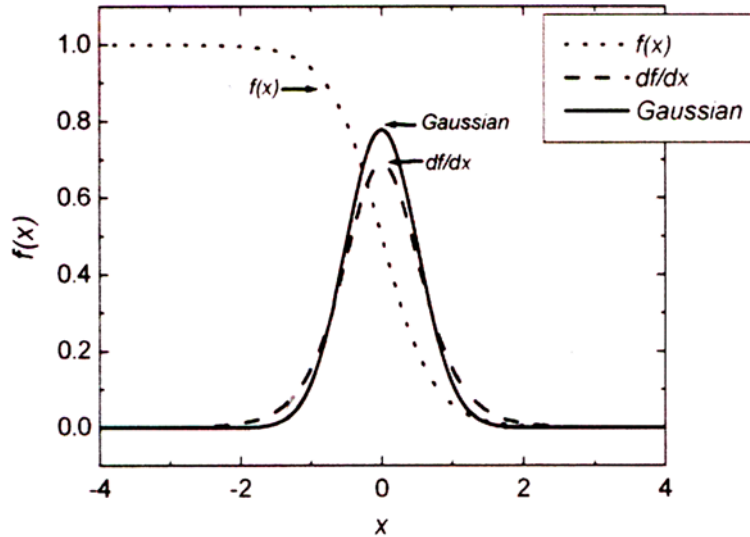


Figure 3.5: Comparison of the derivative of the Fermi-Dirac function with Gaussian of equivalent width. Where $x = E$ for $\mu=0$. From ref. [1]

These two curves, $-df/dx$ and the Gaussian, are compared in Figure 3.5. Although they are similar there is a slight discrepancy between the width (Full width at half max) of Gaussian and the $-df/dx$ curve which (after comparison between the equations of the two curves, as shown by Dr Yasayuki Miyoshi [1]) is a factor of $\sqrt{2}$. The fitting procedure calculates this broadening as a percentage of Δ in units of meV. The value of this broadening is $\omega_{Fd}\sqrt{2}$ and the contribution to the thermal broadening can then be extracted by simple division with $\sqrt{2}$ to give, $\omega_{Fd} = k_B T$, at a temperature T . However, the value of T is only true if thermal broadening is present, other mechanisms of broadening would contribute to the value of ω_{Fd} and a simple division with $\sqrt{2}$ would result in an “effective temperature” that is higher than expected. These additional contributions to the broadening are generally termed as “non-thermal broadening”.

The effects of fitting spectra with (excessive) non-thermal broadening will be shown in the next section, where theoretical Andreev spectra are generated and then fitted using the four-parameter fitting procedure. We shall see that there are limits in which the fitting procedure can find a minimum in $\chi^2(P)$.

3.2.3 Effects of Broadening on the fitting procedure

The purpose of this section is to simulate the effect that ω (and also Z) have on the fitting procedure and demonstrate the conditions in which it becomes difficult to obtain accurate parameter values using the $\chi^2(P)$ fit procedure. To explore this further, theoretical spectra were generated with superconducting gap values of $\Delta=1.5\text{meV}$, various, P and ω values and grouped into three Z regimes: low, intermediate and high ($Z = 0.3, 0.6$ and 1.2 respectively).

Low Z Spectra

Low broadening: Here, theoretical spectra are generated with a value of Z that is representative of a typical Fermi velocity mismatch, $Z = 0.3$, with low broadening $\omega = 0.36\text{meV}$ (thermal contribution at 4.2K), Figure 3.6a. There is a clear minimum in $\chi^2(P)$ for P up to $P = 50\%$ but not for $P > 50\%$; The $\chi^2(P)$ fit of the $P = 60\%$ spectrum, yellow curve in Figure 3.6b, shows a broad minimum in $\chi^2(P)$, close to the theoretical value of $P = 60\%$ (with a difference of -0.02 from the theoretical value). Looking at Table 3.1 (left set) we see that the Δ , Z , P^* and ω are all reasonable when compared to their theoretical values. However, for $P = 60\%$ Δ is suppressed while Z and ω are much higher than the theoretical values.

High broadening: When spectra broadening is increased to 1.06meV , shown in Figure 3.6c, the conductance peak features are smeared and are barely identifiable. The results of the $\chi^2(P)$ fit to the spectra then become ambiguous and it is only possible to discern upper bounds in $\chi^2(P)$, Figure 3.6d. The values presented in Table 3.1 (right set) are mainly values extracted from these upper bounds and we see that most of the values are grossly overestimated for Δ and underestimated for Z . ω is high but also under the theoretical value. The only exception is $P = 60\%$, where there is quite a broad minimum in $\chi^2(P)$. In this case P is reasonably close to the theoretical value but not so for other parameters as Δ is highly suppressed while Z and ω are overestimated. The Δ , Z and ω values seem to be either suppressed or enhanced in a similar way to the $P=60\%$ for the $Z=0.3$ low broadening case.

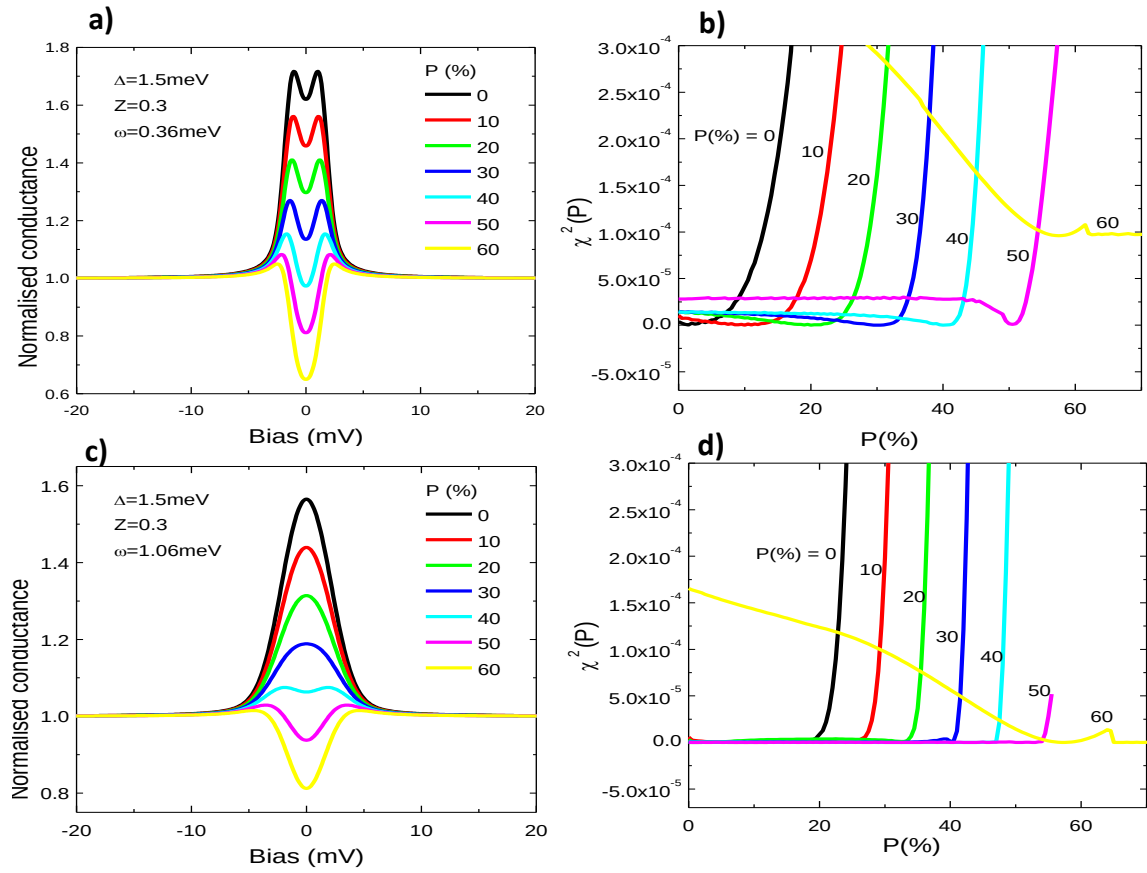


Figure 3.6: Theoretical spectra with $\Delta = 1.5\text{meV}$, $Z = 0.3$ and a) $\omega = 0.36\text{meV}$ and c) $\omega = 1.06\text{meV}$. b) and d) are the $\chi^2(P)$ fits to a) and c), respectively.

P (%)	<u>Δ (meV)</u>	<u>Z</u>	P* (%)	<u>ω (meV)</u>		<u>Δ (meV)</u>	<u>Z</u>	P* (%)	<u>ω (meV)</u>
	<u>1.50meV</u>	<u>0.3</u>		<u>0.36meV</u>		<u>1.50meV</u>	<u>0.6</u>		<u>1.06meV</u>
0	1.53	0.29	1.5	0.35		1.82	0	18	0.97
10	1.49	0.30	10	0.36		1.74	0.03	24	1.03
20	1.50	0.30	20	0.36		1.83	0	32.5	0.98
30	1.48	0.31	29.5	0.37		1.83	0.03	39.5	1.01
40	1.50	0.30	40	0.36		1.83	0.11	46	0.84
50	1.53	0.29	50.5	0.36		1.82	0.01	54	0.83
60	0.92	1.45	57.5	0.74		0.93	1.05	57.5	1.20

Table 3.1: Δ , Z , P^* and ω values extracted from $\chi^2(P)$ in Figure 3.6b (left set) and in Figure 3.6d (right set). 'P' is the original (theoretical value) and P^* is the extracted value. The theoretical values for the remaining parameters are underlined at the top of each set. Bold values are extracted from upper bound of $\chi^2(P)$.

Z = 0.6 Spectra

Low broadening: In the $Z = 0.6$ case with low broadening, Figure 3.7a, the peaks are now more pronounced in comparison to the spectra in Figure 3.6a. The fitting of the spectra in Figure 3.7a, shown in Figure 3.7b, have minima in $\chi^2(P)$ for the correct value of P up to $P=40\%$. We also see that, in Table 3.2 (left set), other parameters are also close to their theoretical value. For $P=50\%$ the $\chi^2(P)$ fit curve is very broad and shows a minimum, although incorrect, at $P=28\%$. Other parameters are also deviated from their theoretical values, Table 3.2 (left set). However the minimum in $\chi^2(P)$ for $P = 60\%$ is located close to the correct value, with a difference of $+2.5\%$. The values in Table 3.2(left set), however, indicate some irregularities between the theoretical and fitted values for the $P = 60\%$ fit. We see that Δ is suppressed while Z and ω are highly overestimated. Similar to the $Z = 0.3$ case.

High broadening: In the highly broadened spectra, Figure 3.7c, peaks are present in the spectra but are broadened and the $\chi^2(P)$ fits are degenerate up to $P=40\%$. In Table 3.2 (right set), the parameters are beyond their theoretical values. The $P=50\%$ fit has a minimum in $\chi^2(P)$ but it appears not to be reliable as it is at a lower value. The $\chi^2(P)$ for the $P=60\%$ fit has a minimum at the same value as its theoretical value. However, other parameters are suppressed (i.e. Δ) and enhanced (i.e. Z and ω), Table 3.2 (right set), in a similar manner to the $Z=0.6$ low broadening case.

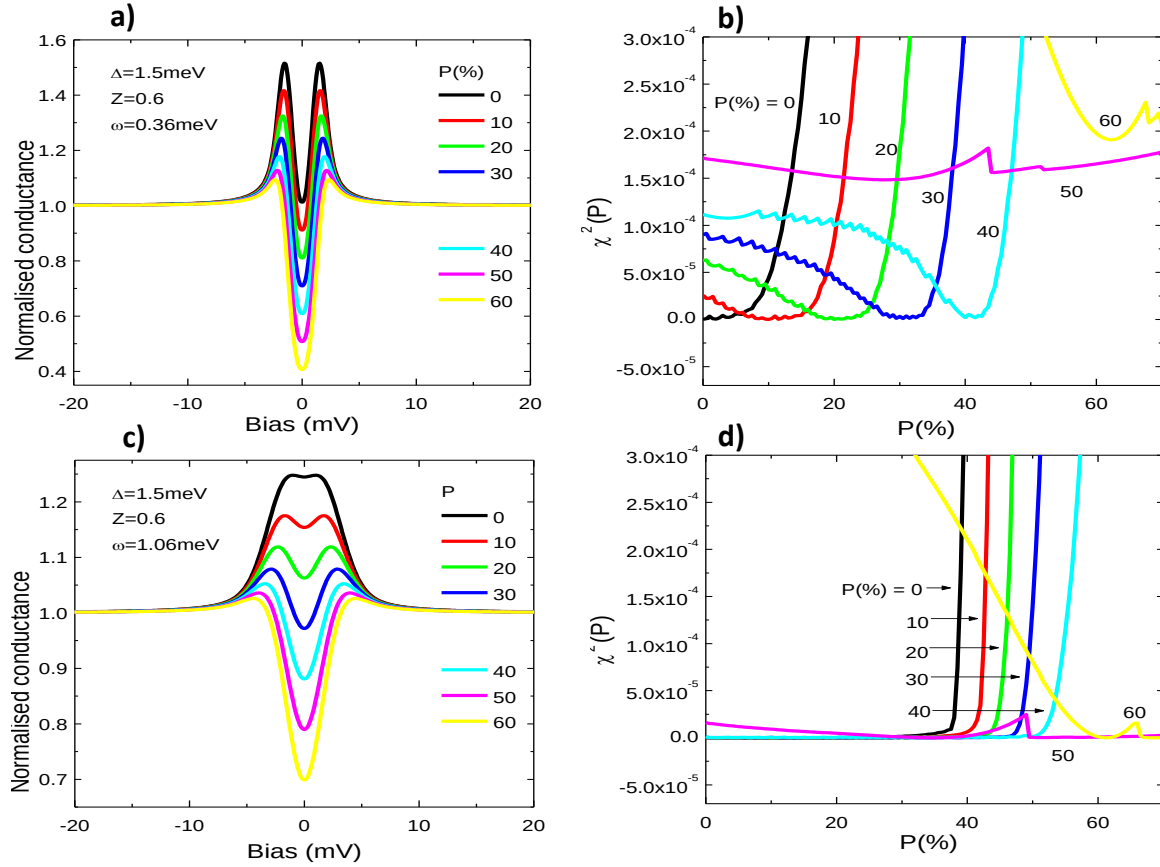


Figure 3.7: Theoretical spectra with $\Delta=1.5\text{meV}$, $Z=0.6$ and a) $\omega=0.36\text{meV}$ and c) $\omega=1.06\text{meV}$. b) and d) are the $\chi^2(P)$ fits to a) and c) respectively.

P	Δ (meV)	Z	P* (%)	ω (meV)	Δ (meV)	Z	P* (%)	ω (meV)
	<u>1.50meV</u>	<u>0.6</u>		<u>0.36meV</u>	<u>1.50meV</u>	<u>0.6</u>		<u>1.06meV</u>
0	1.55	0.58	2.5	0.35	1.99	0.27	28	0.92
10	1.50	0.60	10	0.36	2.27	0.16	34	0.80
20	1.50	0.6	20	0.36	2.09	0.25	40	0.83
30	1.51	0.60	30.5	0.36	2.18	0.23	46	0.77
40	1.55	0.58	41.5	0.35	2.01	0.29	50	0.86
50	1.02	3.17	28	0.62	1.00	2.69	34.5	1.17
60	1.18	1.36	62.5	0.60	1.22	1.01	61	1.13

Table 3.2: Δ , Z , P^* and ω values extracted from $\chi^2(P)$ in Figure 3.7b (left set) and in Figure 3.7d (right set). 'P' is the original (theoretical value) and P^* is the extracted value. The theoretical values for the remaining parameters are underlined at the top of each set. Bold values are extracted from upper bound of $\chi^2(P)$.

Z = 1.2 Spectra

Low broadening: The $\chi^2(P)$ fit, Figure 3.8b, to the spectra in Figure 3.8a show the correct minimum for each P value. We see that for P up to P = 60% all the parameters are reasonable compared to their theoretical values, Table 3.3 (left set). For P=50% and 60% Δ is suppressed and Z and ω are enhanced.

High broadening: The increase in broadening, Figure 3.8c, causes ambiguous fits in $\chi^2(P)$, Figure 3.8d for spectra up to P=20%, this clearly gives the wrong values for all parameters, Table 3.3 (right set). The $\chi^2(P)$ fits for P = 30% and P = 40% have minima, but are very broad and have a much lower value of P, in Table 3.3 (right set) we see how Δ and Z also deviate from their theoretical values but ω seems to take reasonable values. The $\chi^2(P)$ fits for P = 50% and P = 60% show minima that are at the correct values. The P = 50% fit show Δ is suppressed and Z is enhanced but ω seems to be reasonable. Furthermore, the P = 50% fit seems to show Δ , Z and ω that are only slightly deviated from the theoretical values.

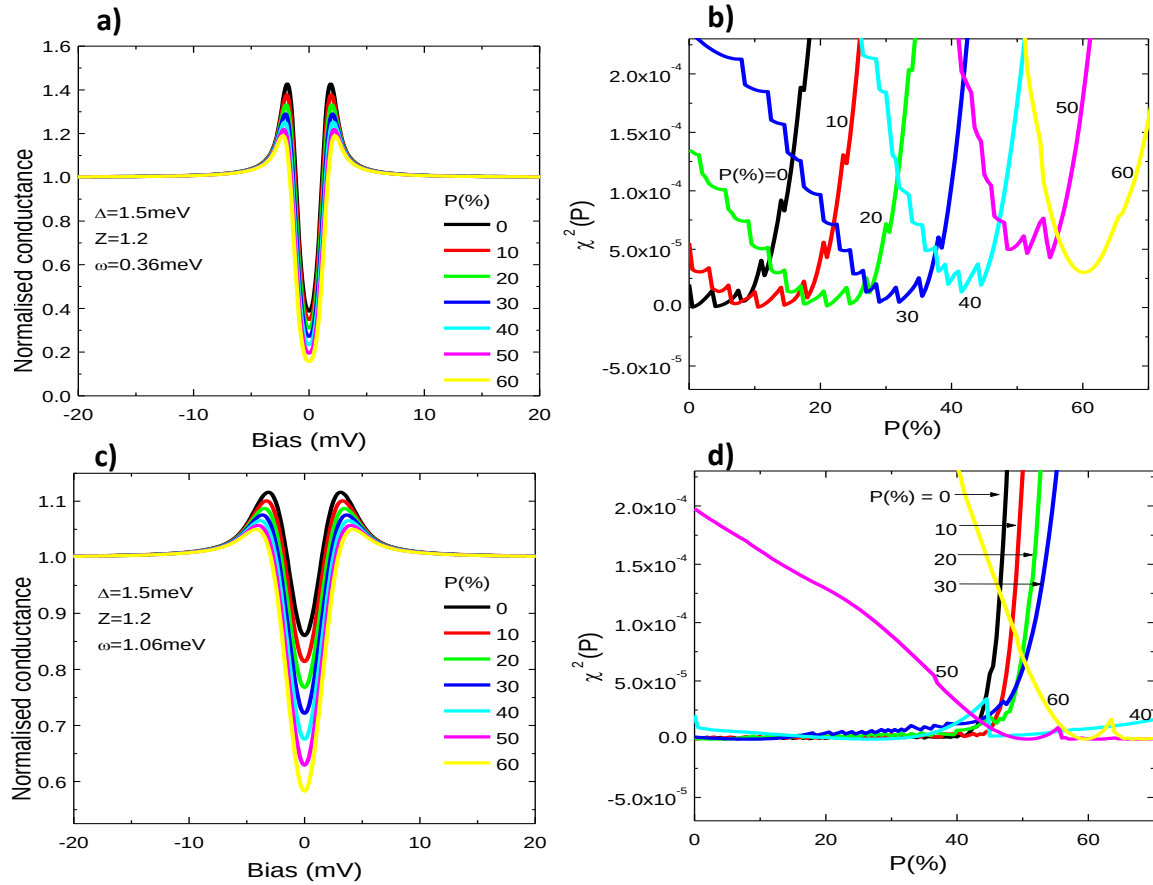


Figure 3.8: Theoretical spectra with $\Delta=1.5\text{meV}$, $Z=1.2$ and a) $\omega=0.36\text{meV}$ and c) $\omega=1.06\text{meV}$. b) and d) are the $\chi^2(P)$ fits to a) and c) respectively.

P	<u>Δ (meV)</u>	<u>Z</u>	<u>P* (%)</u>	<u>ω (meV)</u>		<u>Δ (meV)</u>	<u>Z</u>	<u>P* (%)</u>	<u>ω (meV)</u>
	<u>1.50meV</u>	<u>1.2</u>		<u>0.36meV</u>		<u>1.50meV</u>	<u>1.2</u>		<u>1.06meV</u>
0	1.50	1.20	0.5	0.36		1.72	0.83	21.5	1.03165
0.1	1.51	1.20	10.5	0.36		1.63	0.96	22.5	1.0535
0.2	1.51	1.20	21	0.36		1.38	1.71	3	1.08857
0.3	1.52	1.20	32	0.36		1.33	2.16	8.5	1.09835
0.4	1.50	1.23	41.5	0.37		1.29	3.14	27	1.10598
0.5	1.44	1.33	51.5	0.39		1.35	1.92	50	1.09015
0.6	1.46	1.35	60	0.39		1.46	1.32	59.5	1.06824

Table 3.3: Δ , Z , P^* and ω values extracted from $\chi^2(P)$ in Figure 3.8b (left set) and in Figure 3.8d (right set). 'P' is the original (theoretical value) and P^* is the extracted value. The theoretical values for the remaining parameters are underlined at the top of each set. Bold values are extracted from upper bound of $\chi^2(P)$.

In all the cases presented above excessive broadening of a spectrum does have the effect of obscuring the correct minimum in $\chi^2(P)$. Also, in the presence of excessive broadening, the increase in Z , can have any effect in finding the correct P , however in the $Z=0.6$ case, although a reasonable P was found the other parameters were grossly deviated. However in the high $Z=1.2$ case, and for $P=60\%$ only, all the parameters appear to be much closer to the theoretical values than other highly broadened $P=60\%$ fits.

However the results obtained from my PCARS experiment involved spectra that had degenerate $\chi^2(P)$ when fitting using the four-parameter procedure. However I believe it may be possible to resolve the issue of degenerate and the method that is implemented, in this thesis, is to fit the spectra series with a fixed superconducting gap value (i.e. 1.5meV for Nb) thereby only allowing the Z , P and ω parameters to vary. The parameters obtained from this fixed gap fitting cannot be correct, unless the superconducting gap is (coincidentally) that of the expected SC, however this approach would ensure that the error introduced is systematic across a of spectra series. Therefore, it is imperative that fixed gap fitting is performed with a set of spectra in which external parameters such as temperature or contact resistance are varied. This allows trends in P , Z and ω to be explored but any conclusion drawn would be qualitative rather than quantitative. Later, in section 3.2.6, we consider the reliability of fixed gap fits and what information, if any, they give to individual spectra or series of spectra. However in the next section we introduce another form of broadening that can affect the fit of a spectra.

3.2.4 Effect of Sample Resistance

We have discussed how excessive broadening can result in the degenerate $\chi^2(P)$ fits of the spectra or may give a minimum in $\chi^2(P)$ but have incorrect Δ , Z , P , ω . Another way in which the $\chi^2(P)$ fit of the spectra can be affected is from the sample resistance, R_S , associated with the sample's inherent resistance. The sample resistance, Figure 3.9a, may have a substantial effect on the fitted parameters of a spectra if it is not taken into account when it becomes significant compared to the contact resistance R_C . If R_S is large then the contact resistance R_C is not the dominant resistance and would result in a significant decrease of the effective

conductance in addition to broadening of the spectra. This would make the peaks of the spectra (which are usually associated with Δ), Figure 3.9b, appear at voltages much larger than the expected Δ of the SC. Therefore the fitted spectra would result in an anomalously large gap, Δ , value [95, 101].

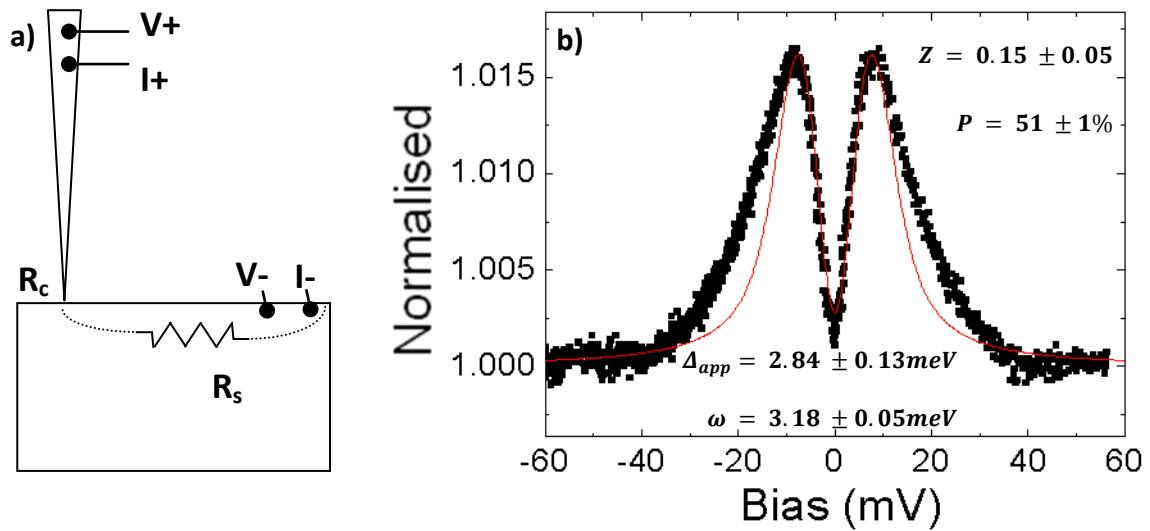


Figure 3.9: Figure 3.6 a) Schematic of the tip in contact with the sample. The sample resistance R_s is in series with the interface resistance R_c . b) A spectrum taken from 50nm thick Ho thin film that has high apparent Δ value at $R_c = 49\Omega$. The tip used was Nb which has a bulk $\Delta=1.5\text{meV}$

An example is shown in Figure 3.9b. The spectrum is from a 50nm thick thin Ho film using a Nb tip, at 4.2K. The spectrum is heavily broadened as a consequence of the sample's high resistance and consequently the fitting procedure overestimates the Δ as well as returning high values of ω (the thermal value for ω at 4.2K is 0.36meV). Four-point resistance measurements of Ho thin films with varying thicknesses have been measured by Dudas et al. [102-105] and results of 36nm Ho thin film at low temperature (up to 2K) are shown to have resistance of $\sim 104\Omega$ at 4.2K [102] while samples of 98nm[103], 147nm[104] and 196nm[105] have resistances of 7 Ω , 13 Ω and 1.7 Ω respectively at 2K. For holmium thin film (5mmx5mm, 300nm thick) at 10K the sheet resistance, measured using four-point Van der Pauw, was 0.29 Ω . A simple way to resolve series resistance would be to use a bulk sample in which the resistance from the sample is negligible leaving the contact resistance the dominant resistance.[92, 101] However for thin films the sample resistance is no longer

necessarily negligible and can even be comparable to the contact resistance. [101] To account for the sample resistance in the fitting procedure, an additional fitting parameter [92, 101, 106] to the current four parameters would be needed. Chiang et al. [106] found different values of polarisation for GaMnAs; 74% from applying the series resistance and 90% from applying a broadening parameter. Auth et al. [107] fitted their PCARS results on $\text{Sr}_2\text{FeMoO}_6$ with a sample (series) resistance parameter and obtained the best theoretical fit with $P=98\%$, $Z=0$. When Auth et al. [107] then introduced a broadening parameter in the form of an effective temperature T_{eff} they obtained ambiguous fits that was not able to distinguish between a spectrum with parameters $P=100\%$; $Z=0$ and $P=0$; $Z=1$. The broadening that was characterised by T_{eff} , for $\text{Sr}_2\text{FeMoO}_6$, was 3.2mV (far higher than the thermal contribution at 4.2K, 0.36mV). We learn from Chiang et al. [106] and Auth et al. [107] that if the sample resistance is significant it needs to be accounted for properly before attempting to fit the spectra.

To summarise, the effect of this sample resistance has been shown to increase the value of Δ to values greater than the Δ of the SC tip. This has also been reported by Woods et al.[92], Baltz et al.[95] and Chen et al. [101]. The solutions to fit a spectrum affected by sample resistance are either to include an additional parameter in the fitting process that would take into account the sample resistance [101, 106, 107] or to rescale the spectrum before fitting[95]. In the next section I shall look at the latter technique in treating a spectrum that is affected by significant sample resistance.

3.2.5 Rescaling the Spectrum and the Mn-Al doped ZnO example

A way to examine the effect of excessive sample resistance on the fitted parameters is by having the conductance spectra rescaled. Both the bias and conductance need to be considered in the rescaling of the spectrum (which has also been demonstrated by Baltz et al.[95]). An example of rescaling the spectrum in Figure 3.9b is shown in Figure 3.10.

A simple approach to rescaling a spectrum is to assume the measured total resistance, R_T , is the sum of R_S and R_C in series and rescaled bias axis V_C of the spectrum can be calculated by

$$V_C = \frac{V_{Bias}\Delta_{SC}}{\Delta_{eff}} \quad (3.5)$$

where V_{Bias} is the voltage axis (total voltage drop across R_T), Δ_{SC} is the superconductor energy gap of the tip and Δ_{eff} is the effective energy gap as a result from the fitting procedure. Another assumption is that when $V_{Bias} = \Delta_{eff}$, $V_C = \Delta_{SC}$. This gives the voltage drop across the sample as $V_S = \Delta_{eff} - \Delta_{SC}$, which allows R_S to be found by solving as a potential divider

$$V_S = \frac{V_{Bias}R_S}{R_T} \quad (3.6)$$

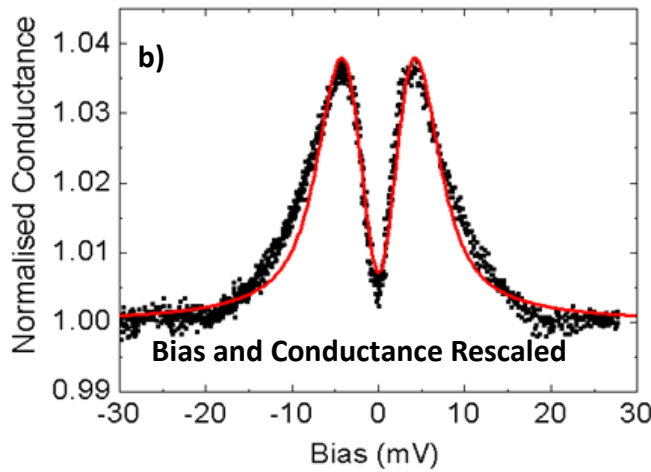


Figure 3.10: Rescaling of the spectrum in Figure 3.9b with both bias and conductance rescaled with fit parameters $\Delta = 2.39 \pm 0.16 \text{ meV}$, $Z = 0.20 \pm 0.06$, $P = 48 \pm 1.5\%$, $\omega = 1.65 \pm 0.09 \text{ meV}$

It is then possible to rescale the conductance, G_C , of the spectrum by

$$\frac{1}{G_C} = \frac{1}{G_T} - R_S \quad (3.7)$$

where $G_T = 1/R_T$.

This result of this rescaling has the effect of reducing Δ and ω from the fits but after the initial rescaling of the spectrum the process does not have a significant effect on the values of P and Z . However, after a few iterations rescaling the same spectrum in Figure 3.10, the results show that Δ approaches the value of $\Delta_{Nb} = 1.5\text{meV}$. The rest of the results of the rescaling are shown in Table 3.4. It is likely that rescaling the spectrum even further would show Δ approaching $\Delta_{Nb} (= 1.5\text{meV})$ due to the assumption made in rescaling the spectrum (that $\Delta = 1.5\text{meV}$). Z and P changes slightly by 0.15 and 9.5%, respectively, and the broadening is dramatically reduced from 3.18meV to 0.76meV (although still twice the thermal limit at 4.2K).

	Δ (meV)	Z	P (%)	ω (meV)
Original	2.84 ± 0.13	0.15 ± 0.05	51 ± 1	3.18 ± 0.05
1 st Rescaling	2.39 ± 0.16	0.20 ± 0.06	48 ± 1.5	1.65 ± 0.09
2 nd Rescaling	1.95 ± 0.11	0.24 ± 0.06	45.5 ± 2	1.04 ± 0.07
3 rd Rescaling	1.56 ± 0.12	0.30 ± 0.05	41.5 ± 2	0.76 ± 0.06

Table 3.4 The Values of the four fitting parameters of the Ho thin film spectrum in Figure 3.9b after three consecutive rescaling iterations.

An interesting example of spectra require rescaling because of high sample resistance are the PCARS measurements of Mn-Al doped ZnO oxide [108]. In Figure 3.11a, the spectra were taken using a Nb tip at 4.2K. The spectra were fitted using full-four parameter fit produced minima in $\chi^2(P)$, and the results are shown as black square data points (Figure 3.11b, 3.8c, 3.8d, 3.8e). The results give a value of Δ is higher than the bulk value Nb value at $R_C < 59\Omega$. These films have a magnetically dead surface layer that needs to be punctured by applying increasing tip pressure. As R_C is decreased, Z drops from 2-3 to 0.3-0.4 and P increases from 2% to ~46% - 52%. Additionally, ω is also considerably high reaching ~1.2meV at high R_C but then decreases at low R_C . This data is interesting as it provides us with a good example of what happens as a surface layer is punctured. However in the original work [108], series resistance was not taken into account.

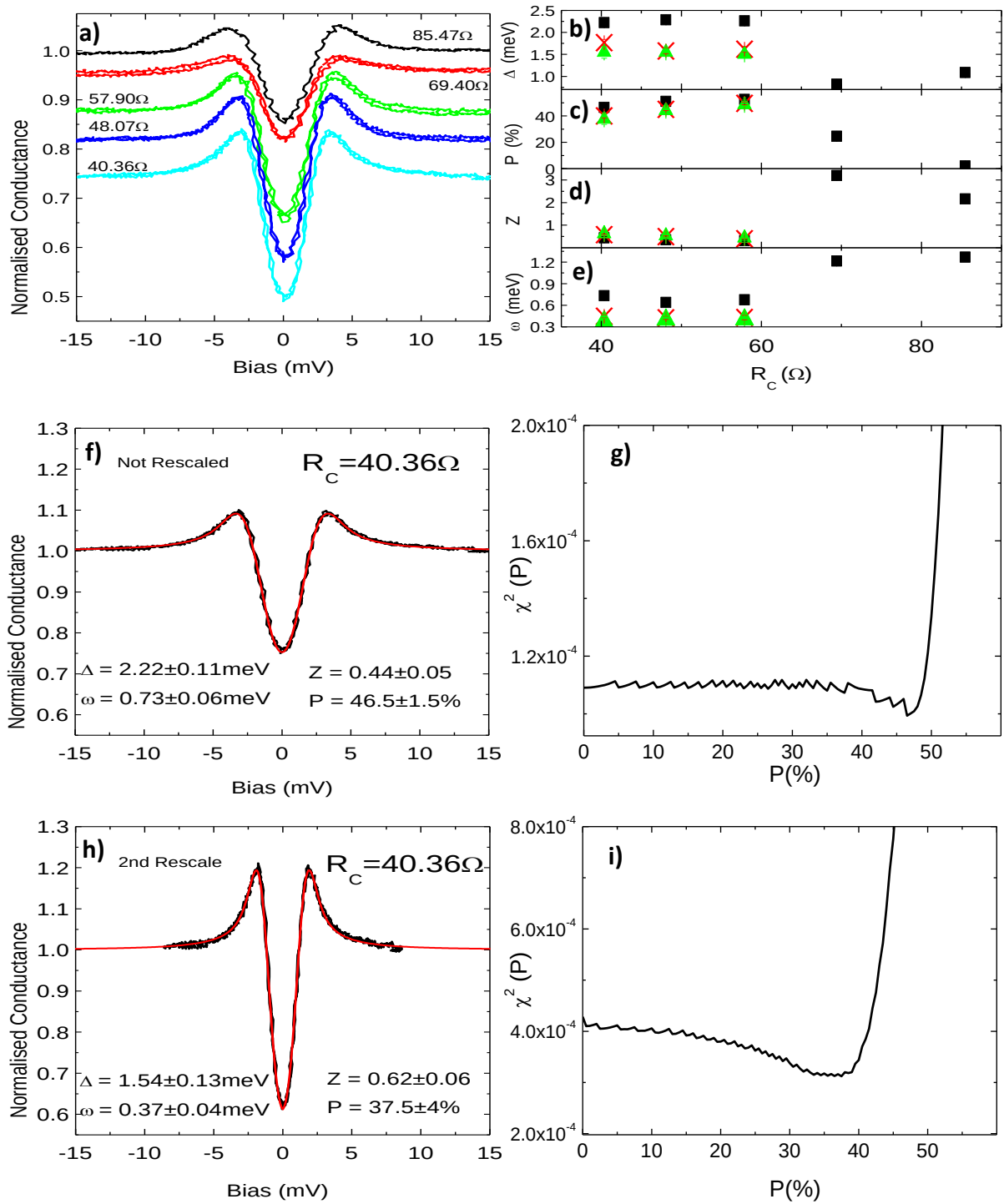


Figure 3.11: a) Spectra for Mn-Al doped ZnO normalised at 15meV with an offset. In b), c), d) and e) the black square, red cross and green triangle data points are values for the original, 1st rescaling and 2nd rescaling of the spectra respectively. f) and h) are the original and 2nd rescaling spectrum respectively, with the $\chi^2(P)$ of the full four-parameter fit in g) and i)

The increasing P and drop in Z is the behaviour one would expect when the tip penetrates an interface barrier. [109] However the high gap values may be a result of the film's resistance. Therefore the spectra in Figure 3.11a was also subjected to the same rescaling treatment as mentioned earlier in this chapter but since the last 3 data points below $60\ \Omega$ have high Δ , these are the only ones that can be rescaled. The result after rescaling once and twice are indicated by the red cross and green triangle data points respectively in Figure 3.11b, 3.8c, 3.8d, 3.8e. They show a decrease in Δ that almost reaches $\Delta=1.5\text{meV}$ and a decrease in ω to a value that of $\sim 0.38\text{meV}$, close to the thermal limit at 4.2K . Although the rescaling changes the ω significantly, the P and Z parameters do not change significantly greatly when compared to the original values. Rescaling the data has not significantly affected the conclusions of the study [108]; revealing that when the tip breaks through a barrier layer it reveals a highly polarised material beneath.

With the effects of broadening and sample resistance in mind, the following section considers the reliability of fixed gap fits and what information, if any, they give to individual spectra or series of spectra.

3.2.6 The effects of Fixed Gap ($\Delta = 1.5\text{meV}$) fit

The fixed gap fit performed in chapters 4 and 5 rely on the assumption that at the SC/FM interface the gap value is constant for a particular contact even as a (function of tip pressure). However Δ can be suppressed or enhanced (see section 3.2.5) at the interface so in order to understand how much error is introduced and how reliable these fits are, a series of spectra with suppressed and enhanced Δ (with respect to $\Delta_{Nb} = 1.5\text{meV}$) are generated and then fitted with a fixed Δ .

Theoretical spectra were generated with varying P_{THEO} . In Figure 3.12a the parameters are $\Delta_{\text{THEO}} = 1\text{meV}$, $\omega_{\text{THEO}} = 0.7\text{meV}$ (high broadening) and $Z_{\text{THEO}}=0.3$, while in Figure 3.12b $Z_{\text{THEO}}=0.5$. This is to simulate spectra with a 'suppressed' Δ taken from PCARS measurements. The value of $\omega_{\text{THEO}} = 0.7\text{meV}$ was chosen so that it would represent spectra that have broadening comparable to Δ_{THEO} (this was chosen as 100% of $\Delta_{\text{THEO}}/\sqrt{2}$). Additionally theoretical spectra were generated with similar Z and P but with an 'enhanced'

$\Delta_{\text{THEO}} = 2\text{meV}$ and $\omega_{\text{THEO}} = 1.41\text{meV}$ (this is also 100% of $\Delta_{\text{THEO}}/\sqrt{2}$). This may simulate the effects of sample resistance. The different sets of spectra are in Table 3.5. These ‘suppressed’ and ‘enhanced’ Δ spectra were fitted with a fixed gap of $\Delta = 1.5\text{meV}$.

	$\Delta(\text{meV})$	Z_{THEO}	P (%)	$\omega_{\text{THEO}} (\text{meV})$
Set 1	1	0.3	0 to 60%	0.7
Set 2	1	0.5	0 to 60%	0.7
Set 3	2	0.3	0 to 60%	1.41
Set 4	2	0.5	0 to 60%	1.41

Table 3.5: The theoretical set of spectra with suppressed and enhanced gap (with respect to $\Delta_{Nb} = 1.5\text{meV}$) and the values of Z_{THEO} , P and ω_{THEO}

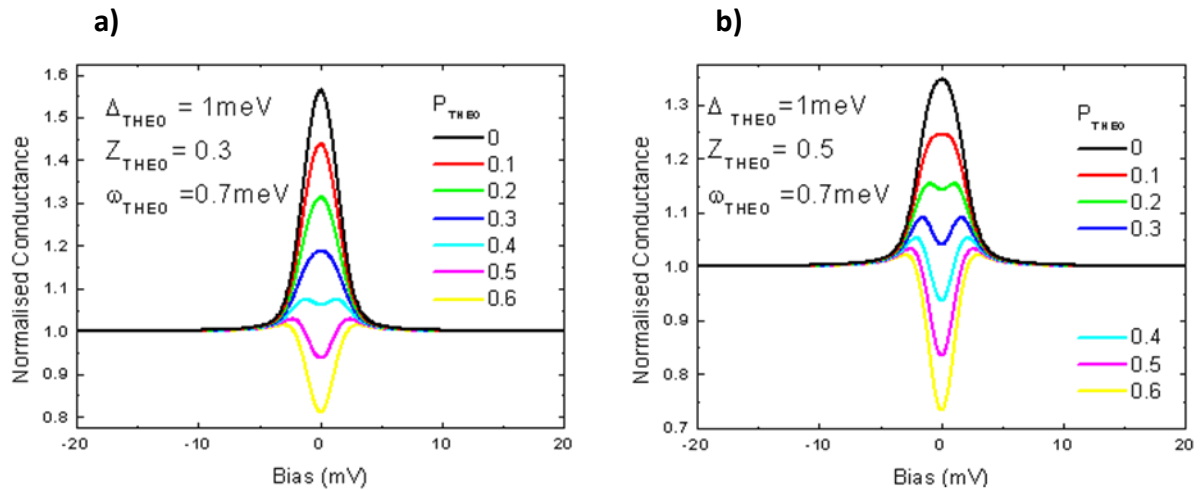


Figure 3.12: Theoretical spectra to simulate suppressed gap spectra with $\Delta_{\text{THEO}} = 1\text{meV}$, $\omega_{\text{THEO}} = 0.7\text{meV}$ with a) $Z_{\text{THEO}} = 0.3$ or b) $Z_{\text{THEO}} = 0.5$.

The results are shown in Figure 3.13a, 3.13b and 3.13c where the parameters, P, Z and ω , respectively are plotted against the theoretical values of P (i.e. P_{THEO}). The data points in Figure 3.13a, 3.13b and 3.13c, with $\Delta_{\text{THEO}} = 1\text{meV}$, contain results for fits to $Z_{\text{THEO}} = 0.3$ (filled red data points) and $Z_{\text{THEO}} = 0.5$ (filled blue data point). Included in the figure are the fits to the enhanced $\Delta_{\text{THEO}} = 2\text{meV}$, for $Z_{\text{THEO}} = 0.3$ and $Z_{\text{THEO}} = 0.5$ (the hollow square and triangle data points respectively).

In Figure 3.13a, the fixed gap fits of ‘suppressed’ $\Delta=1\text{meV}$ spectra shows that the fitting procedure is able to obtain the correct value of P for $P_{\text{THEO}} = 60\%$, for both $Z_{\text{THEO}} = 0.3$ and $Z_{\text{THEO}} = 0.5$ data sets and with high broadening. However it then starts to deviate for lower P_{THEO} and in the case of $P_{\text{THEO}} = 0$, the fitted value of P gave a result of $P = 30\%$ (blue data point) and 23% (red data point) (an artificial polarisation of 30% and 23% respectively). The enhanced $\Delta_{\text{THEO}} = 2\text{meV}$ fits also show a similar trend but P is underestimated for P_{THEO} below 60% and reaches zero at $P_{\text{THEO}}=30\%$.

Although the correct value of P is found for spectra with $P_{\text{THEO}} = 60\%$, the fitted Z parameter is considerably underestimated for $\Delta_{\text{THEO}} = 1\text{meV}$ (‘supressed’), Figure 3.13b. Such that for fits to spectra with $Z_{\text{THEO}} = 0.5$, the value obtained for $P_{\text{THEO}} = 60\%$ is $Z = 0.25$ and decreases with decreasing P_{THEO} . Similarly for $Z_{\text{THEO}} = 0.3$, the fitted value gives $Z = 0.15$ when $P_{\text{THEO}} = 60\%$ and also decreases as P_{THEO} decreases. However in the range $P_{\text{THEO}} = 0\%$ up to $P_{\text{THEO}} = 40\%$ the value of Z is zero. In the $\Delta_{\text{THEO}} = 2\text{meV}$ case (‘enhanced’), if $Z_{\text{THEO}} = 0.5$ then Z is overestimated in the range $P_{\text{THEO}} = 20\%-60\%$. If $Z_{\text{THEO}} = 0.3$ then it is also overestimated in the range $P_{\text{THEO}} = 30\%-60\%$. Z then falls below the value of Z_{THEO} at low P_{THEO} in both cases.

The result of the broadening parameter ω on the fixed gap fit is similar to Z in that its value is less than the expected ω_{THEO} for $\Delta_{\text{THEO}} = 1\text{meV}$ data points. However, as P_{THEO} decreases the value of ω also decreases for $Z_{\text{THEO}} = 0.3$ from $\omega = 0.66$ to $\omega = 0.49$. For $Z_{\text{THEO}} = 0.5$ there is a decrease in ω from 0.6meV down to 0.45meV between $P_{\text{THEO}} = 60\%$ to $P_{\text{THEO}} = 30\%$ after which ω starts to increase as P_{THEO} decreases. For $\Delta_{\text{THEO}} = 2\text{meV}$ the broadening is overestimated for all P_{THEO} but it is much higher in the range $P_{\text{THEO}} = 0\%$ to $P_{\text{THEO}} = 30\%$ for both $Z_{\text{THEO}} = 0.3$ and $Z_{\text{THEO}} = 0.5$.

In the case of $\Delta_{\text{THEO}} = 1\text{meV}$, as you move from low Z to high Z , P changes subtly but also moves from high to low. For $\Delta_{\text{THEO}} = 2\text{meV}$ as Z goes from high to low, P hardly changes but also goes from high to low. (These changes in P , with Z , are indicated by the arrows. in Figure 3.13).

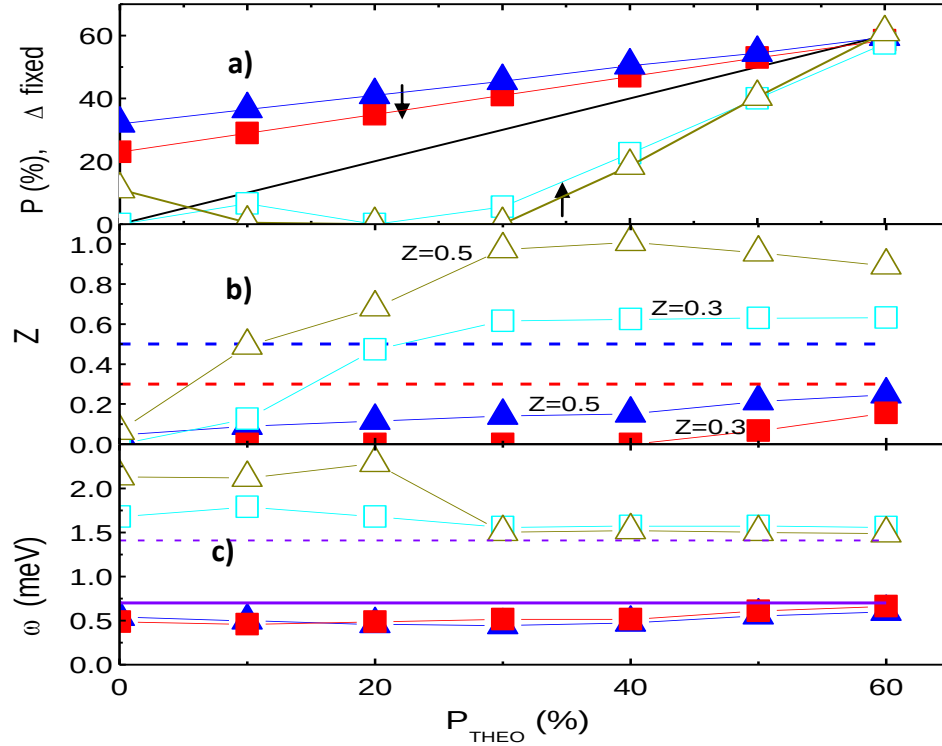


Figure 3.13: Results of the fixed $\Delta = 1.5\text{meV}$ fit, to theoretical spectra with suppressed $\Delta_{\text{THEO}} = 1\text{meV}$; the filled square and triangle data points are for $Z_{\text{THEO}} = 0.3$ and $Z_{\text{THEO}} = 0.5$ respectively. The theoretical spectra with enhanced $\Delta_{\text{THEO}} = 2\text{meV}$ is shown as hollow squares and triangles for $Z_{\text{THEO}} = 0.3$ and $Z_{\text{THEO}} = 0.5$ respectively. The solid line in a) is a guide to show how much the fitted P value has deviated from the theoretical P. the dashed lines in b) mark $Z_{\text{THEO}} = 0.5$ (blue dash line) and $Z_{\text{THEO}} = 0.3$ (red dash line). In c) the solid line is $\omega_{\text{THEO}} = 0.7\text{meV}$ and the dashed line is $\omega_{\text{THEO}} = 1.41\text{meV}$. Arrows indicate how P moves from high Z (0.5) to low Z (0.3)

This modelling informs us that caution has to be taken in interpreting data from fixed gap fits when the actual Δ of a spectrum could be either smaller or greater than the value used for the fixed Δ fitting. In the suppressed $\Delta = 1\text{meV}$ case high P values can be obtained for samples which may actually have low P and this would cause the fitting procedure to reduce ω to compensate for having a low Δ spectrum fitted with a higher Δ . This in turn will have an effect that will reduce Z and increase the P so that zero bias conductance can be fitted. This is important especially in the case of the fixed gap fitting of $\text{Ni}_{0.03}\text{Pd}_{0.97}$, in chapter 5, where a polarisation value of $\sim 40\%$ is obtained from fixed Δ fits; for a sample where the Ni concentration and T_{curie} is low then it is likely that the true P is close to zero.

In simulating 'enhanced' $\Delta = 2\text{meV}$, it was found that P is underestimated and rapidly drops to zero between $P_{\text{THEO}} = 60\%$ to $P_{\text{THEO}} = 30\%$ and the Z trend decreases with P_{THEO} and ω is high for all but more so at low P_{THEO} .

3.2.7 Dip features

Dip features in the conductance spectra may appear at $V \gg \Delta$, Figure 3.4, and vary in shape and bias position but always appear in both negative and positive bias. There are several reasons as to why these dips in the conductance would appear and they include Josephson junctions in series[110] with the contact, the proximity effect[19] and the critical current being exceeded in the contact region.[3] Shan et al. [110] measured PCARS of PtIr/MgB₂ and they observed dips in the spectra that they related to the grains of the superconductor forming SC/I/SC Josephson junctions in series with the PtIr point contact (i.e. an intergrain Josephson effect). At low bias the total conductance is dominated by the point contact, then as the bias is increased it will approach the Josephson critical current. At this point the normal state current will flow across the Josephson junction and so the total conductance drops. This drop would be apparent in the form of conductance dips on the conductance spectra. At higher voltages the conductance will depend on the normal state resistance of the point contact and Josephson junction. However, in an experiment involving a SC/Metal (NM or FM) interface, in which the tip is a SC, it is unlikely that the point contact will be in series with an intergrain Josephson junction. Therefore it is also unlikely that this is cause of the dips.

The proximity effect (section 2.3) and the role it has in the appearance of the dips have been investigated by Strijkers et al. [19]. The proximity effect in section 2.3 defines the probability in which Andreev reflection can occur in the normal metal side within a distance from the SC/NM interface described as the length ξ_{NM} and it reduces the superconducting gap value in the superconductor within a distance ξ from the interface. The model that Strijkers et al. used to fit the conductance spectra involved using two gap values, Δ_1 and Δ_2 . Δ_1 is the gap value of the proximity layer in the normal metal side and Andreev reflection takes place at the metal/proximity-layer interface. Δ_2 is the gap in the superconductor side and is the minimum energy for quasiparticle transport into the superconductor. The theoretical curves

fit quite well to the dips in the conductance spectra, although small peaks above the dips appear on the theoretical curve as result of this model. Their results also indicate that the appearance of the dips was more pronounced at lower values of Z . In the Strijkers et al.'s model the dips occur within the values Δ_1 and Δ_2 . Since superconductivity is suppressed at the SC/NM interface then $\Delta_1 < \Delta_2 < \Delta_{SC}$, where Δ_{SC} is the expected gap value of the superconductor. However, the dips that typically appear in the spectrum in this thesis, an example of which is in Figure 3.4b, cannot be a result of the proximity effect as the position of the dips (at ~ 20 meV) are above the expected superconductor gap value of Nb (1.5 meV). However the proximity effect, as explained in section 2.3.3, would be suppressed at a SC/FM interface and so these dips would not be present.

Not discussed in this thesis in the whole body of work on tunnelling spectroscopy. [111-113] One of the early highlights was the use of d^2I/dV^2 to provide information on the density-of-states of phonons using the Eliashberg α^2F , function. Point-contact spectroscopy can also be used to extract similar information.[37] In the study of Ho-Ho point contacts by Akimenko et al.[96], d^2I/dV^2 spectra indicated that Ho has magnon states at 4-5 meV and phonon states at 6-7 meV. However there is no indication of any states at higher biases e.g. at around the 20 meV. The presence of the 4-5 meV and 6-7 meV states in Ho are not identifiable from the dI/dV spectrum in Figure 3.4b which may be dominated by broadening of the Andreev spectrum. If this is the case, then it is not possible to distinguish any phonon/magnon states above 7 meV and therefore the dips seen in Figure 3.4b are not due to these states.

Another possible reason for the appearance of the dips, and may be the cause of the dips seen in this thesis, is if the critical current at the point contact interface is being exceeded.[114, 115] Theoretical modelling of the effect that these dips have on the fit results has been done by Dr. Fridrik Magnus.[3] The model assumes that the critical current is reached in a piece of wire (modelled as an additional resistance) in series with the interface resistance. Theoretical spectra were generated with parameters $\Delta = 1$ meV, $Z = 0.3$, $P = 30\%$ and $\omega = 0.3$ meV and varying critical current parameter I_C , Figure 3.14a. I_C is dimensionless and ranges from 0 to 8.

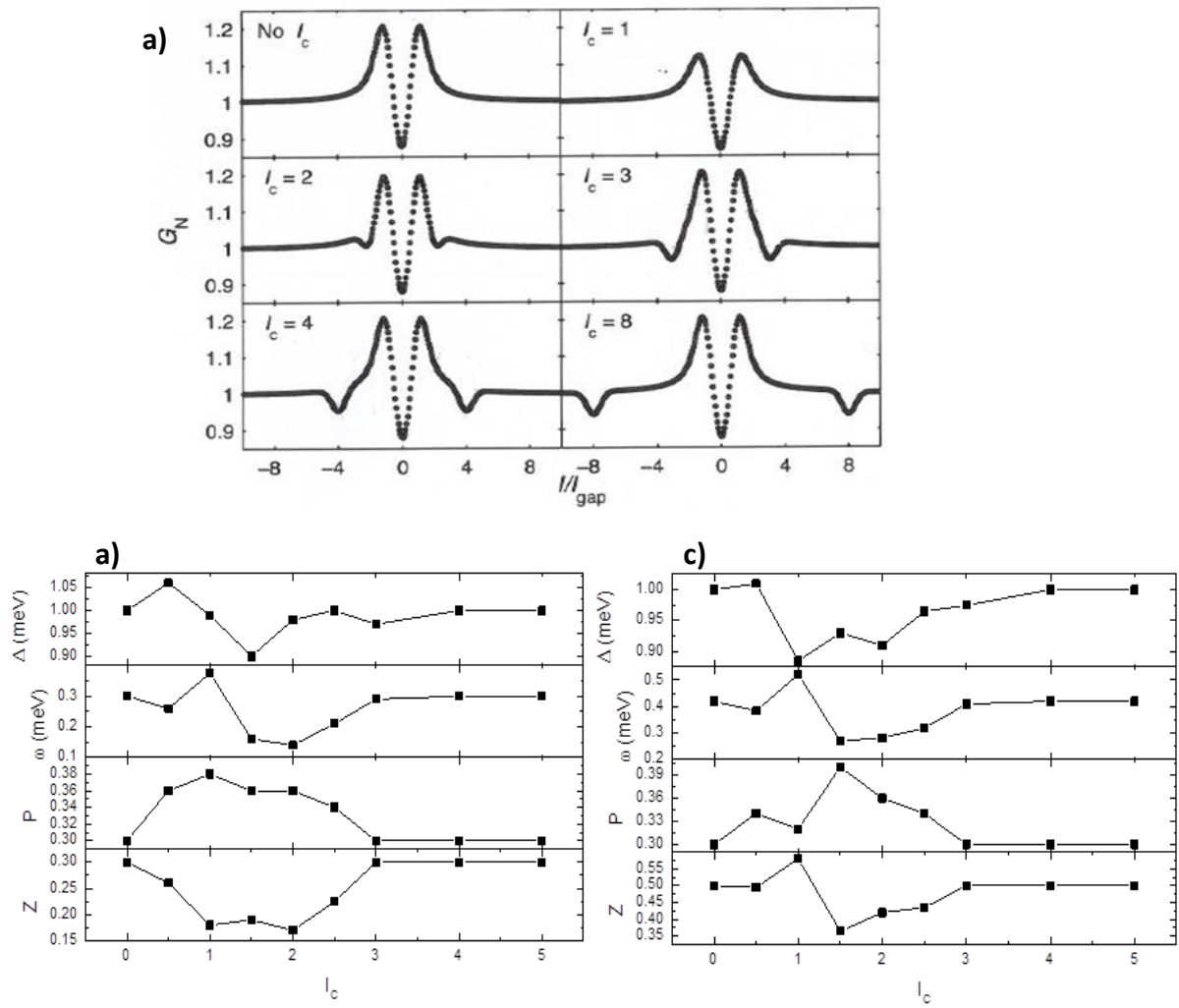


Figure 3.14: a) Generated spectra with the critical current dips, I_c , at various positions on the spectra. G_N is normalised conductance and the current axis is normalised to the current of the superconducting gap, I_{gap} . The results from a four-parameter fit to spectra with $\Delta = 1\text{meV}$, $P = 30\%$, $\omega = 0.3\text{meV}$ and b) $Z = 0.3$ or c) $Z = 0.5$. Adapted from ref [3]

The fitting procedure was done within I/I_{gap} (analogous to normalising the voltage scale by Δ) range of ± 2.5 so for a spectrum with high critical current parameter (i.e. $I_c = 5$) the dip features were ignored and this produced accurate results, Figure 3.14b. However for low critical current values (i.e. $I_c = 0.5-2.5$) the dips would start to affect the fitting procedure and overestimate the parameters P by up to 10% and underestimate Z by up to 30% at $I_c = 1$. Another set of spectra were generated with similar parameters but with $Z = 0.5$. The results, Figure 3.14c, from these spectra also showed P being over estimated by up to 10% at $I_c = 1.5$ and Z underestimated by up to 30% at $I_c = 1.5$, however at $I_c = 1$ the value Z is

overestimated by 20%. Realistically however these dips have variation in depth, width and bias position so these additional fitting parameters would need to be taken into account if the BTK were to be modified further. The reliability of the fitting would be reduced by the addition of more parameters.

3.2.8 The Two-Channel Model

At a SC/FM interfaces it is possible to have magnetic stray fields either intrinsically from the FM or by pressing the tip onto the sample. In either case the out-of-plane magnetic moments could induce vortices at the interface. Therefore the BTK model[42] would need to be modified to take this into account and this was first considered by Miyoshi et al.[1, 93, 116]. Here we analyse what happens when a fixed gap fit is used to fit theoretical spectra that are generated using this model (i.e. how does a fixed gap fit deviate from the theoretical parameters of the spectra?). This analysis is important in determining whether the trends seen from fitting the holmium spectra (discussed in section 4.7) are due to stray fields at the SC/FM interface.

The two channel model developed by Miyoshi et al.[1, 116] takes into account the field-dependent density of states of a type-II superconductor in the mixed state. In a PCARS experiment with a type-II SC and a NM (at an SC/NM interface) vortices will appear at the interface on the application of an external magnetic field. The model assumes the direction of the field is perpendicular to the interface. In this orientation the conductance across the interface will be through two different channels; one Ohmic, with conductance G_N (due to the number of vortices) and the other superconducting, with conductance $G_S(V)$. The model assumed that G_N is proportional to H [116] allowing the conductance to be weighted by a dimensionless factor $h = H/H_{C2}$ which scales with the contribution from the vortex cores. This means at a field of H_{C2} the conductance is completely Ohmic (e.g. $G(H=0)=G_S$ and $G(H=H_{C2})=G_N$), the equation used in the model is,

$$G(V) = hG_N + (1 - h)G_S(V) \quad (3.8)$$

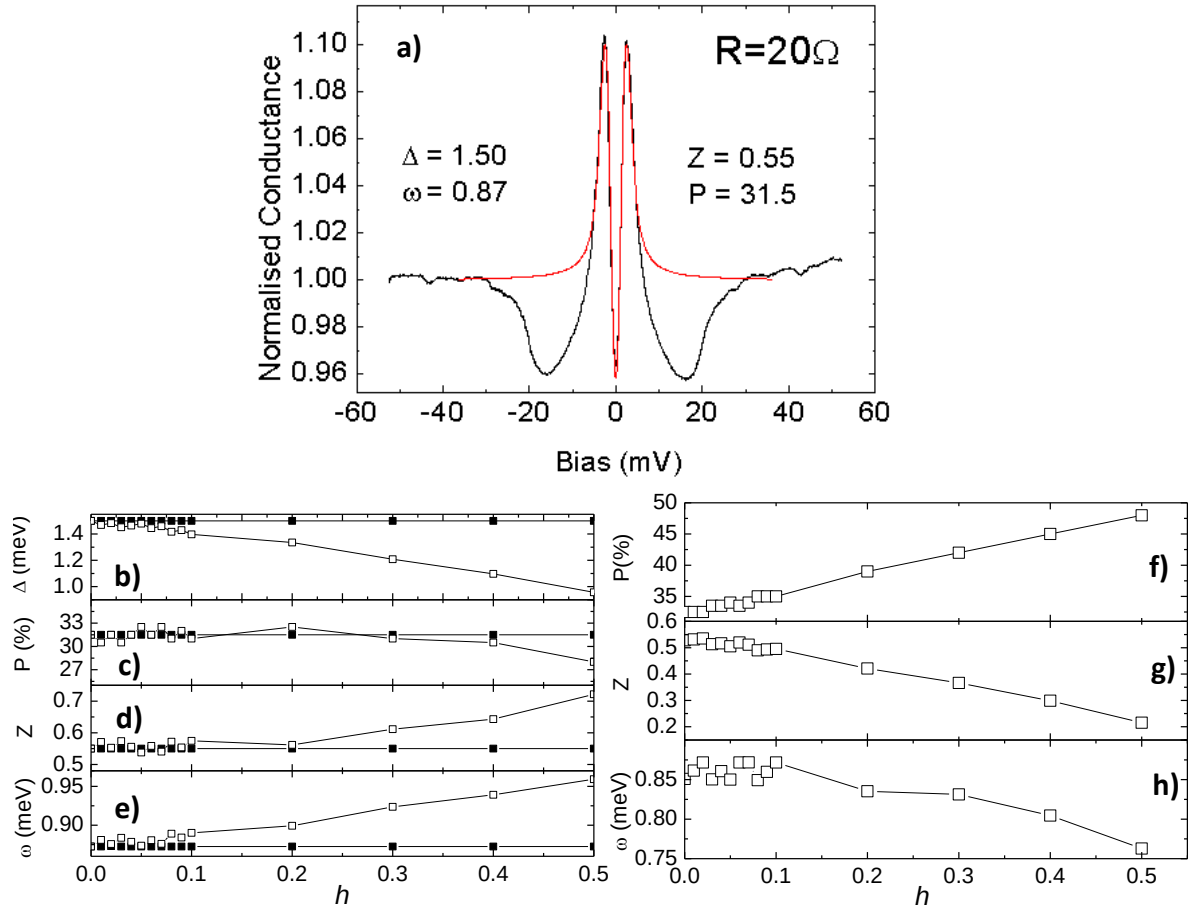


Figure 3.15: a) The spectrum for data point $R_{CB}/R_{CB-Peak} = 1$ in Figure 4.15a. The dependence of b) Δ , c) P , d) Z and e) ω on the field parameter h for full four-parameter 1-channel (hollow) and 2-channel (filled) fits. The dependence of f) P , g) Z and h) ω on h for full four-parameter 1-channel (hollow) with a fixed $\Delta=1.5$ meV

To see how the parameters behave with h , a full four-parameter fit, was performed on theoretical spectra with the parameters $\Delta=1.5$, $Z=0.55$, $P=31.5\%$, $\omega=0.87$ meV with varying h . The Δ , Z , P , ω parameters are from the data point at $R_{CB}/R_{CB-Peak} = 1$ (R_{CB} is the contact resistance) of Figure 4.14a, in chapter 4, shown here in Figure 3.15a. In Figure 3.15b, Figure 3.15c, Figure 3.15d, Figure 3.15e the fits are a result of full four-parameter 1-channel ($h=0$) fits (filled squares) and 2-channel fits (hollow squares). The parameters were taken from the minima of $\chi^2(P)$. We see that the 1-channel four-parameter fit produces a trend of decreasing Δ , increasing Z , slight decrease in P and increasing ω . On the other hand the 2-channel finds the theoretical parameters. However, a 1-channel fixed $\Delta=1.5$ meV fit, Figure

3.15f, Figure 3.15g, Figure 3.15h, produces the opposite trend compared to the full four-parameter fit. It is used in section 4.7 to negate any stray field effects.

A similar theoretical simulation was conducted by Dr. Y. Miyoshi[1], with spectra ($\Delta = 1.5$, $Z = 0.5$, $P = 30\%$, $\omega = 0.5\text{meV}$) that also varied with h . A full four-parameter 1-channel fit to the spectra showed that Δ decreases slowly with h and at $h = 0.5$, $\Delta \sim 1.3\text{meV}$. In Figure 3.15b, however, the value is much less with $\Delta \sim 1\text{meV}$ at $h = 0.5$. There are slight differences in the theoretical parameters (Δ, Z, P) between the spectra used by Dr. Y. Miyoshi and the ones used here (i.e. $\Delta = 1.5$, $Z = 0.55$, $P = 31.5\%$, $\omega = 0.87\text{meV}$). However, it is likely that the difference in broadening ($\omega = 0.87\text{meV}$ and $\omega = 0.5\text{meV}$) would result in the difference of Δ at $h = 0.5$. The reason being that increasing h has an effect that is similar to broadening and would increase ω for a 1-channel (i.e. if an exterior magnetic field is not taken into consideration). Therefore the fitting to a 1-channel model would primarily incorporate any increase in h by increasing ω , Figure 3.15e, and this would be compensated by decreasing the value of Δ . As ω of the spectra is increased, the apparent Δ is progressively reduced.

3.3 Chapter 3 Conclusion

In conclusion the method used to obtain conductance spectra for this thesis was PCARS. This chapter has outlined the experimental and electrical set up used to take the data. The conductance spectra obtained via PCARS have been analysed using the BTK model modified by Mazin et al.[42].

This chapter analyses how sample resistance may affect the fitting parameters by using a possible rescaling method that could be applied to a spectra affected by such a resistance. Other pre-fitting procedures such as normalisation by dividing the spectra to a background will be dealt with in chapter 4 in which they occur.

In the case where broadening is significant and causes the fitting routine to produce degenerate fits in $\chi^2(P)$ then fixing the Δ to a known value such as the bulk superconducting Nb tip gap value (i.e. $\Delta = 1.5\text{meV}$) is an option that can be taken. However as the parameters from the fit are not quantitative, it would be more suitable to perform this fit on a spectra set. This is so that any changes in the parameters can be understood in terms of the how that spectra set evolves e.g. as a function of temperature/contact resistance. This deviation from the 'real values' of the parameters, for a fixed Δ fitting, is demonstrated with theoretically generated spectra that had suppressed or enhanced Δ . In chapter 4 and 5 I shall implement and discuss if the parameter trends, rather than the absolute values, from the fixed Δ fitting give reliable indication of the underlying physics as a function of tip pressure.

4 Holmium

It was discussed earlier that spin mixing and spin scattering at the SC/FM interface is key in generating the $m = 1$ LRSTPE, section 2.3.8. Interfaces with intrinsic or artificial magnetic inhomogeneity have been studied theoretically with predictions on the spatial amplitude and oscillation of the spin singlet and triplet pair components in the FM.[47, 63, 69] A material that has intrinsic magnetic inhomogeneity is Ho and therefore may induce both spin mixing and spin scattering, section 2.3.8. Several experiments have shown signatures of the LRSTPE using Ho in multilayer thin films.[28, 29]

In this chapter we shall briefly give a description of Ho in terms of its magnetic structure. For this thesis, measurements (see section 3.1) were made on Ho single crystal and thin film samples using PCARS, however magnetometry and Hall imaging were also used to understand the possible magnetic structure of the samples.

In the analysis of the spectra from the Ho single crystal, unusual background features that are present on the Ho single crystal PCARS were removed (normalised), although spectra on the thin film sample do not show such features. The fitting procedure used on the experimental spectra was a three-parameter fit with a fixed Δ value of Nb (1.5meV). I find that there is reason to believe that although a fixed gap fit may not retrieve accurate P , Z and ω values, the trends are reliable. Trends in P and Z particularly suggest the presence of a spin active (mixing and/or scattering) interface.

4.1 Magnetic Properties of Ho

Holmium is a rare earth element with the magnetic easy axis oriented in the crystal a, b (basal) plane and the hard axis along in the c -axis. The magnetic phase diagram of Ho has been studied extensively [8, 27, 117, 118] particularly by Koehler et al.[8, 27, 117] where neutron scattering and magnetometry measurements were used to construct the complex magnetic phase transition of Ho, Figure 4.1a. In zero magnetic field, cooling Ho to temperatures below 133K ($T_{N\acute{e}el}$) causes it to undergo a transition from a paramagnetic

(PM) to an antiferromagnetic (AFM) phase with the magnetic moments parallel to the basal plane. In the AFM phase, moments between consecutive basal planes are usually rotated by 50° producing a spiral along the c-axis[117] with τ of $0.28c^*$. [8, 12, 119] (τ is the wave vector of the spiral in reciprocal lattice units of $c^* = 2\pi/c$, where c is c-axis lattice parameter of Ho which varies from $5.607\text{\AA}$ at $T_{N\acute{e}el}$ to $5.642\text{\AA}$ at T_{Curie}). [120] Further cooling below 19K (T_{Curie}) causes Ho to switch from a spiral structure to a spiral that has moments canted 20° from the basal plane. This gives a ferromagnetic component along the c-axis direction, shown schematically in Figure 4.1b, with $\tau = 0.167c^*$. [8, 12, 119]. In Ho crystal the length of the cone spiral, λ_s , is 3.5nm and the electron mean free path, λ_{mfp} , is 1.3nm.[121] In Ho thin films λ_s has been reported to be 1.1nm and λ_{mfp} is 1nm[70].

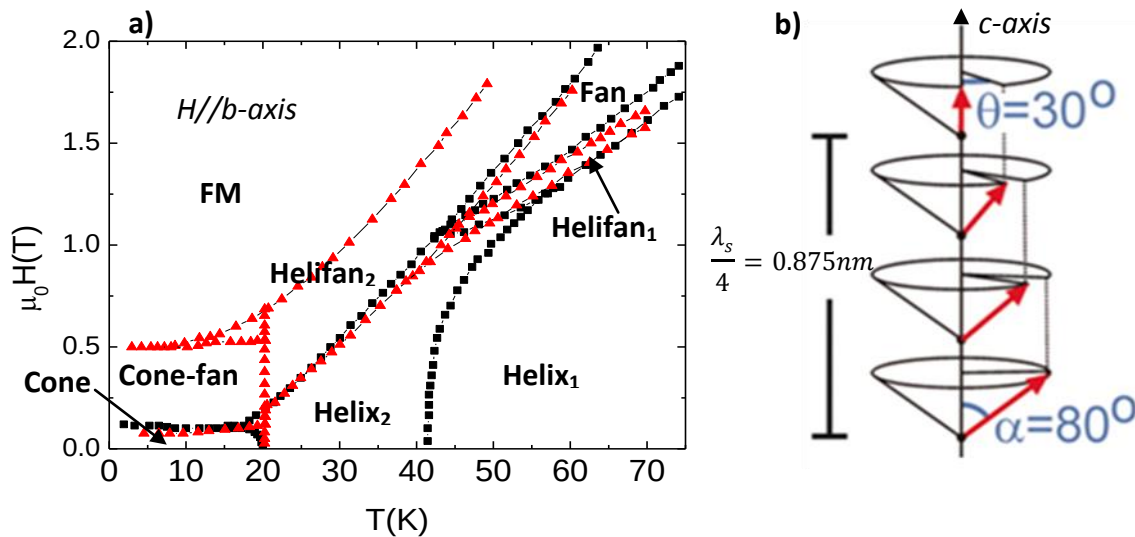


Figure 4.1: a) H-T Diagram of the phase of holmium measured by neutron diffraction (red data points, ref. [8]) and magnetoresistance (black data points, ref.[27]). The magnetic field was applied parallel to the b-axis. The phase labels are adapted from ref. [27], the subscript indicates it's a different τ but has the same magnetic structure. b) The magnetic cone spiral structure of Ho below 19K, from ref. [28], but with $\lambda_s/4 = 0.875\text{nm}$.

However below T_{Curie} the moments that lie between consecutive basal planes are not homogenous, i.e. they are not separated by a constant angle, but rather the hexagonal anisotropy of the crystal causes the moments of every two consecutive layers to be paired and bunched around the b-axis. The angle between the each moment and the b-axis, in a paired bunch, ranges from 5.8° at 4.2K and increases with temperature to 15° at 75K. [12,

117] The structures at 4.2K and various other temperatures can be seen on Figure 4.2a. The bunching of moments at 4.2K means that the angle between moments alternate from 12° and 48° . This gives the *average* rotation of 30° between each moment layer (which appears in some literature).[12, 117, 119, 122] This pairing of moments, with each pair separated by 60° , is repeated every 12 layers.[12]

Gibbs et al., [123] showed that the change in the magnetic structure (and τ) with temperature was not smooth and instead went through a series of lock-ins and spin-slips (i.e. structures in which paired layers are replaced by a single layer see Figure 4.2b). For example by introducing a spin-slip every 4 pairs of layers to a spiral structure that repeats every 12 layers the resulting structure that repeats every 22 layers instead (i.e. $\tau = 0.181c^* \Rightarrow \lambda_s = 3.1nm$). [123]

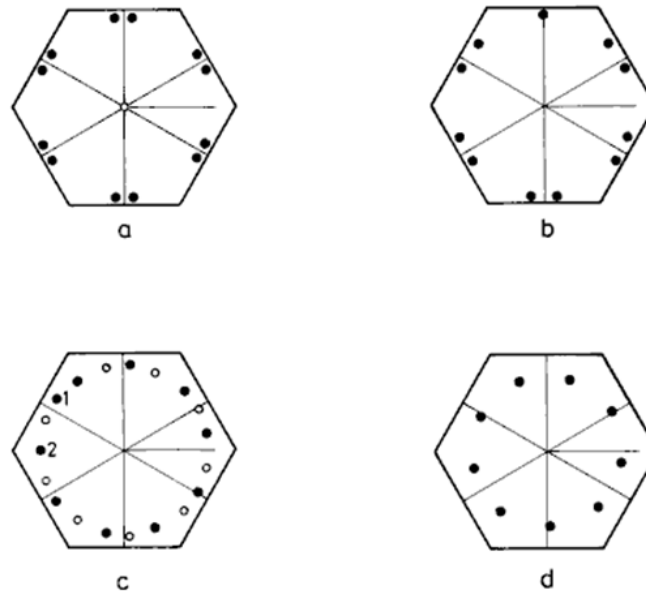


Figure 4.2: The periodic structures in Ho at different temperatures. Each circle represents the magnitude and direction of the moment in a specific plane, relative to the size of the moment at absolute zero ($10 \mu_B$), indicated by the length of the horizontal lines. The orientation of moments in adjacent planes is depicted by the positions of neighbouring circles. From ref. [12]

(a) The 12-layer zero spin-slip structure at 4K. The open circle in the centre indicates the ferromagnetic component in the cone structure.

(b) The 11-layer one-spin-slip structure at 25K.

(c) The 19-layer structure at 50 K. To understand the orientation of the moments, first start from '1' and follow the filled circles in an anticlockwise direction and then the open circles after '2'.

(d) The 9-layer structure at 75K. This may be viewed as a three-spin-slip structure, but the bunching is so slight that it is more useful to regard it as an almost regular helix, in which every third plane aligns its moments close to an easy axis.

The cone structure in holmium is due to the combination of interactions involving the crystal field, at low temperatures, causing instability of the helix structure [12, 119] and the dipole-dipole interaction favouring a c-axis ferromagnetic orientation.[12, 119] It has also been shown that Ho crystals exhibit thermal lattice deformation [120, 124] in which the a,b axis contracts and the c-axis expands with decreasing temperature. This would explain the FM cone in terms of lattice deformation resulting in the canting of moments in the c-axis.

At low temperatures (below 19K), due to hexagonal anisotropy, the transition from AFM spiral to cone spiral is first order and has no intermediate phases.[12] Additionally the cone structure is stable at zero field. Under an applied magnetic field in the basal plane, with the cone angle independent of the field, there is still a c-axis component of the moment but this disappears at the ferromagnetic transition. This FM transition begins at 0.1T and Ho becomes fully ferromagnetic at 0.5T, Figure 4.1a. It has also been reported that Ho exhibits giant magnetostriction [125, 126] under an applied field influenced by magnetoelastic coupling. [123] Therefore a field study of PCARS may present difficulties if the SC/FM contact is perturbed by a change in magnetic field.

In Figure 4.1a there is a discrepancy in the phase diagram at low temperature (with a magnetic field applied to the b-axis) between the results obtained using magnetoresistance (black data points from Gebhardt et al. [27]) and ones using neutron diffraction and magnetisation (red data points from Koehler et al.[8]). The main difference is the absence of a second transition point at 0.5T on the magnetoresistance phase diagram. Measurements of the magnetoresistance of Ho single crystal as a function of temperature from Gebhardt et.al. [27] do not indicate any transition at 0.5T. At the first transition point (magnetic field of 0.1T at 4.2K), Figure 4.1a, the moment still has an angle of 20° from the basal plane, i.e. the c-axis component is still present, only the basal plane component of the moment would align itself to parallel to the field. [12] The second transition would then be when the moments are fully parallel to the field. Since the cone angle is 20° from the basal plane it is possible that the second transition to a full in-plane moment may be small such that magnetoresistance measurements are not sensitive enough to detect the change.

4.2 Samples

Two types of Ho samples, single crystal and thin film, were measured using PCARS, magnetisation and Hall imaging. Later in chapter 5, the results are compared with thin film $\text{Ni}_{0.19}\text{Pd}_{0.81}$ to identify possible differences between SC/FM interfaces that have moment inhomogeneity (Ho) and one that is homogenous (NiPd) [10]. The Ho single crystal sample was made by Vladimir Zverev in Ames laboratory using strain annealing. [118] The dimensions of the crystal sample were 2.44mm x 1.82mm x 0.9mm with the c-axis perpendicular to the large area of the sample, Figure 4.3a. The thin film sample was made by Dr Jason Robinson at Cambridge University and had a 300nm Ho layer prepared in an Ultra-high vacuum (UHV) system by dc magnetron sputtering onto a 200nm thick Nb buffer on 5mm x 5mm c-plane axis oriented sapphire, Figure 4.3b. The substrate was heated to 873K during deposition. The Ho target was pre-sputtered for 15mins prior to film growth and the systems base pressure was better than 10^{-8}Pa . The thin film was epitaxial(c-axis oriented, i.e. c-axis perpendicular to the surface of the thin film), as confirmed by Dr Jason Robinson, and has a 10nm gold capping layer to protect the surface of Ho from oxidation.

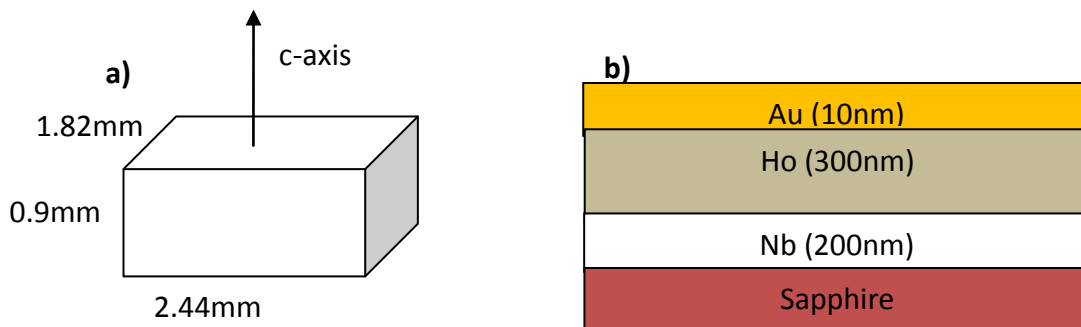


Figure 4.3: a) Holmium crystal with the c-axis direction and b) the thin film layers.

4.3 Magnetometry and Hall imaging

4.3.1 Magnetometry

Initial studies of Ho samples were done with magnetometry and Hall probe imaging (See section 3.1) to characterize the single crystal and thin film samples. In the magnetometry measurements, the sample was cooled from room temperature down to 5K and isothermal M-H measurements were taken at the temperatures shown in Figure 4.4a, for Ho crystal, and in Figure 4.4b for Ho thin film (for clarity only selected M-H curves are shown in Figure 4.4b). Up-field curves and down-field curves are the bottom and top parts of each M-H curve respectively. Between each isothermal M-H measurement the temperature was raised above, $T_{N\acute{e}el}$ and then cooled back down. The reason for this was to remove any remnant magnetisation and return the single crystal to its initial state before each M-H measurement.[117] The magnetic field was applied parallel to the ab-plane, for Ho crystal, and parallel to the thin film surface, for Ho thin film.

To compare Ho crystal and thin film saturation moment we shall compare the 10K M-H curves from Figure 4.4a and Figure 4.4b. The magnetisation saturation for Ho crystal for temperatures at 10K is $\sim 10.1\mu_B/\text{Ho}$, which is close to the value indicated by Koehler et al., $10.6/\text{Ho}$. [117] However the thin film reaches a saturation of $1172 \text{ emu}/\text{cm}^3$ at 10K and this would equate to $\sim 4 \mu_B/\text{Ho}$. This is assuming that the mass density of Ho for the crystal and thin film are the same, i.e. $8.531\text{g}/\text{cm}^3$ (this was obtained by weighing the single crystal sample. It is possible that there is a magnetic dead layer such that the calculation of the active Ho layer of the Ho thin film is miscalculated by approximately a factor of 2.

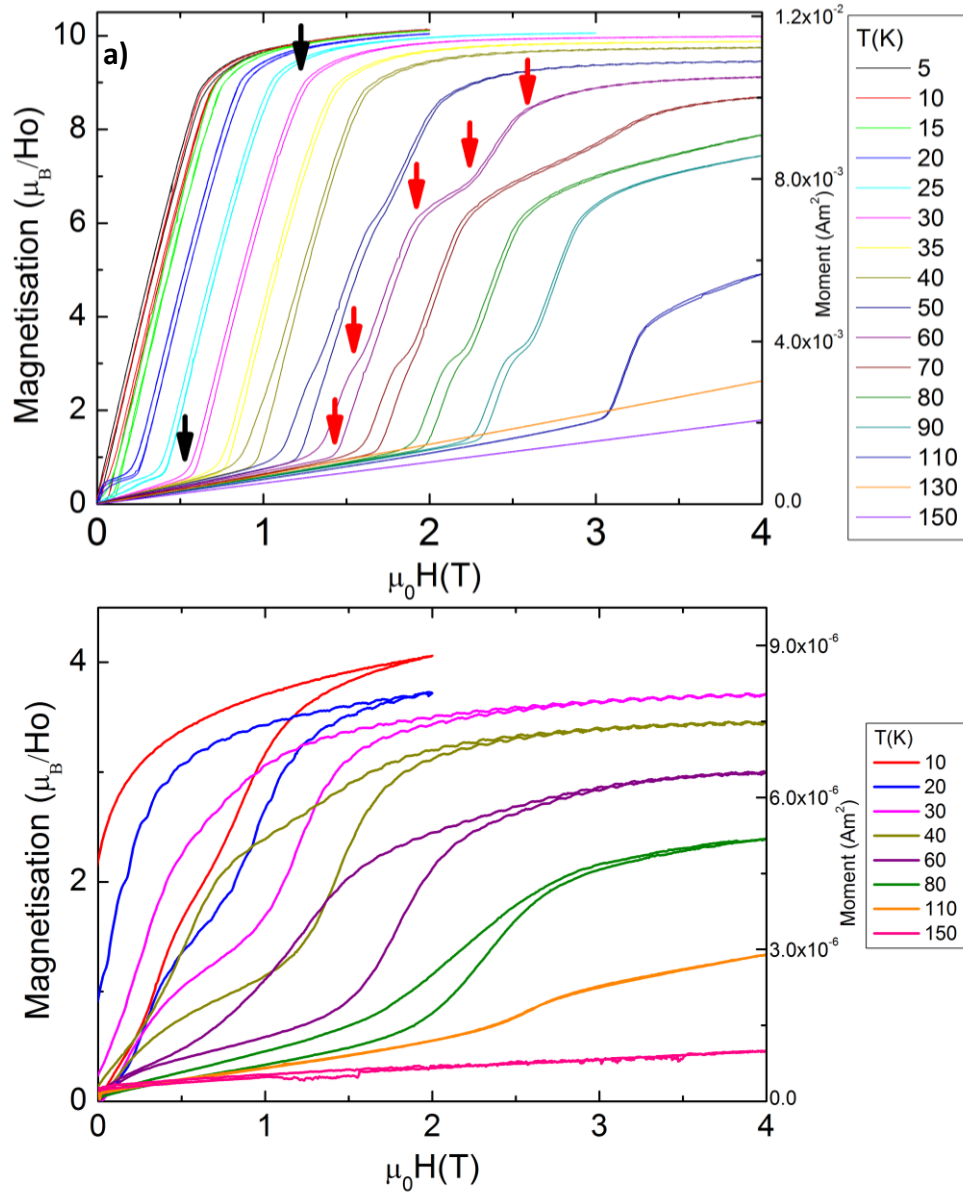


Figure 4.4: a) The MH as a function of temperature for the Ho crystal from magnetometry with H parallel to the ab-plane and moment measured parallel to the ab-plane. b) The MH as a function of temperature for the Ho thin film from magnetometry with H parallel to the surface of the thin film and moment measured parallel to the surface. The axis on the right is the moments taken from the experiment in units of emu. Arrows indicate where a transition point could be extracted.

On Figure 4.5 the phase transition points of the Ho single crystal and thin film are compared to the magnetic phase diagram from Koehler et al. [8]. The transition points of Ho crystal (green data points in Figure 4.5) and thin film (circle points in Figure 4.5) are taken from the M-H curves where the gradient changes, shown by the arrows in Figure 4.4a. For Ho crystal,

between 5K to 40K, there are two transition points that are plotted, then as the temperature increases an extra phase transition appears in the AFM phase (red arrows in Figure 4.4a). They are in agreement with that of Koehler et al.[8] However the thin film transition points do not match that of the Ho crystal and have various magnetic field transition points within the cone-spiral region (i.e. below 19K). There are four transitions that persists (0.3T, 0.6T, 0.8 and 1.1T) up to ~20K but then diverges at higher temperatures. This divergent trend above 20K is similar to the Ho crystal which may indicate that there may still be a similar transition taking place at ~19K (i.e. from a magnetic spiral to a cone spiral). The 0.3T and 0.6T transition below 20K may be related to the 0.1T and 0.5T phase transitions, respectively, of Ho crystal but shifted to higher magnetic fields possibly caused by strain in the epitaxial Ho thin film. [127] However, the unusual extra transitions (0.8T and 1.1T) below 20K would indicate the cone spiral entering extra transition phases before its FM phase. Although theory and experiments have been done on the suppression of $T_{N\acute{e}el}$ on ultra-thin Ho films [128-130] and the magnetic structure of Ho thin film [127], the full H-T phase diagram is not well understood and so the phases presented here would require further investigation.

The inset in Figure 4.5b shows M-H measurements of the Ho thin film taken at 10K with the field applied parallel and perpendicular to the plane of the film. With the field applied in-plane the saturation of the moments is reached at a much lower field (1T) compared to the out-of-plane M-H measurement. This is an indication that the easy axis is in the plane of the film.

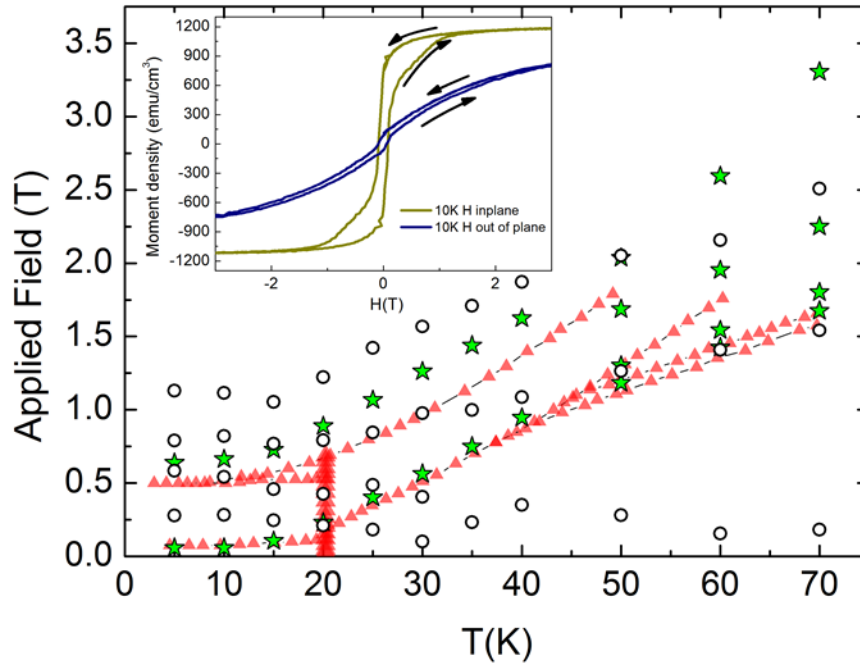


Figure 4.5: Plots of the magnetic transitions points extracted from Figure 4.4a (green star) and Figure 4.4b (circle) mapped over the (red data) phase diagram on Figure 4.1. Insert: M-H curve of the Ho thin film at 10K with the magnetic field in plane (Green curve) and the field out of plane (Blue curve) arrows indicate the direction the field was ramped for a curve.

4.3.2 Hall probe imaging of Ho c-axis single crystal

Hall probe imaging (see chapter 3.1.3) was used to probe the surface of the Ho samples and characterize the magnetic inhomogeneity that the SC-tip, used in PCARS, would experience. The samples were cooled down to 6K in zero applied magnetic field and images were taken at various applied fields from 0T to 2T.

Isofield Hall images showing the magnetic transitions of the Ho single crystal surface are shown in Figure 4.6. The direction of the magnetic field is parallel to the ab-plane and direction of the field with respect to the images is shown at the top of Figure 4.6. The bright regions indicate magnetic moments pointing up along the c-axis and the dark areas are magnetic moments pointing down. At the initial state, 0T, the surface presents magnetic

domain structures which are later (in section 4.3.4) compared to chiral domains found by Lang et al. [22]

As the external magnetic field is increased along the b-axis, the magnetic image changes dramatically and at 40mT the domains are barely detectable. As the field is increased past the first transition point at 0.1T the image shows a surface that is 'magnetically smooth' at 1.0T and doesn't show any trace of inhomogeneity. As the magnetic field is ramped down the moments do not seem to change and as the field returns to 0T, the initial 0T image is not recovered. This would be attributed to the remnant magnetisation of Ho. The virgin state can be recovered by warming to temperatures above $T_{N\acute{e}el}$ before cooling back down to 4.2K. [8, 117] The evolution of the magnetisation of the surface in Figure 4.6 is understood to be associated with magnetostriction effects[131] as the application of a magnetic field can change the lattice of Ho. For performing PCARS in a magnetic field the main concern would be maintaining a constant resistance as the surface of the Ho crystal may change.

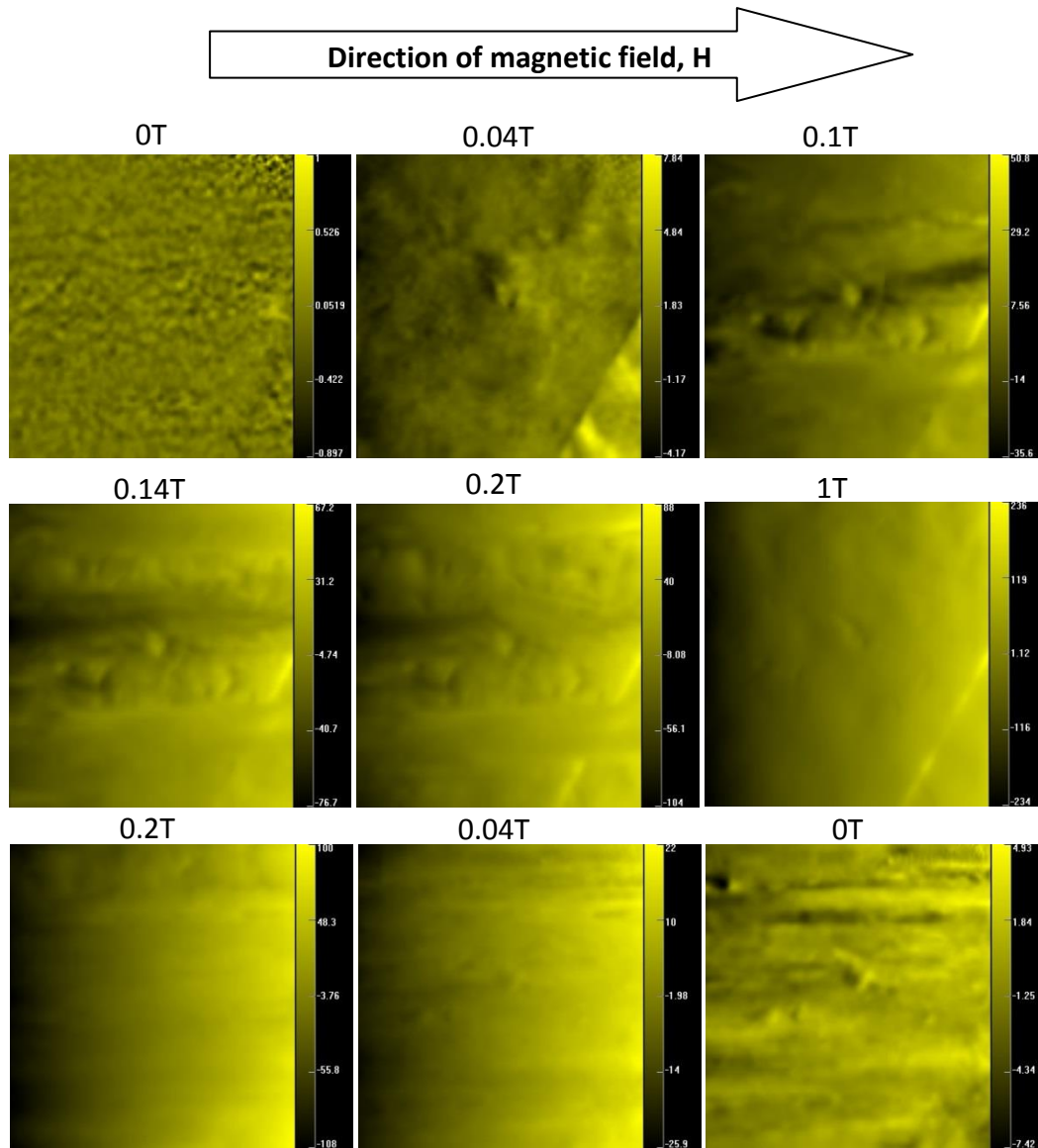


Figure 4.6: Hall images at 6K showing the surface magnetisation of Ho crystal parallel to the c-axis. Ho Single crystal with the field applied parallel to the basal plane as indicated by the arrow above. Each image is 1mm x 1mm. Black regions represent negative induction and bright represents positive induction. Ho crystal contrast is scaled by dividing by $1.281 \times 10^{-5}\text{V}$ (the highest value in the first 0T image).

4.3.3 Hall probe imaging of the Ho 300nm Thin Film

The Hall images in Figure 4.7 show the magnetic surface transition for the Ho thin film at 6K. The initial zero field image shows little sign of the domain structure that was apparent in

the Ho single crystal. At a field of 50mT there is a slight deformation of the magnetisation at the surface. As the applied field is increased past a saturation field of 1T, no change is observed in the magnetisation of the surface. However as the field is brought back down to 0T the surface structure is visibly different than the initial 0T image. The change in the surface structure is unlikely due to the Hall sensor as it is suspended above the surface.

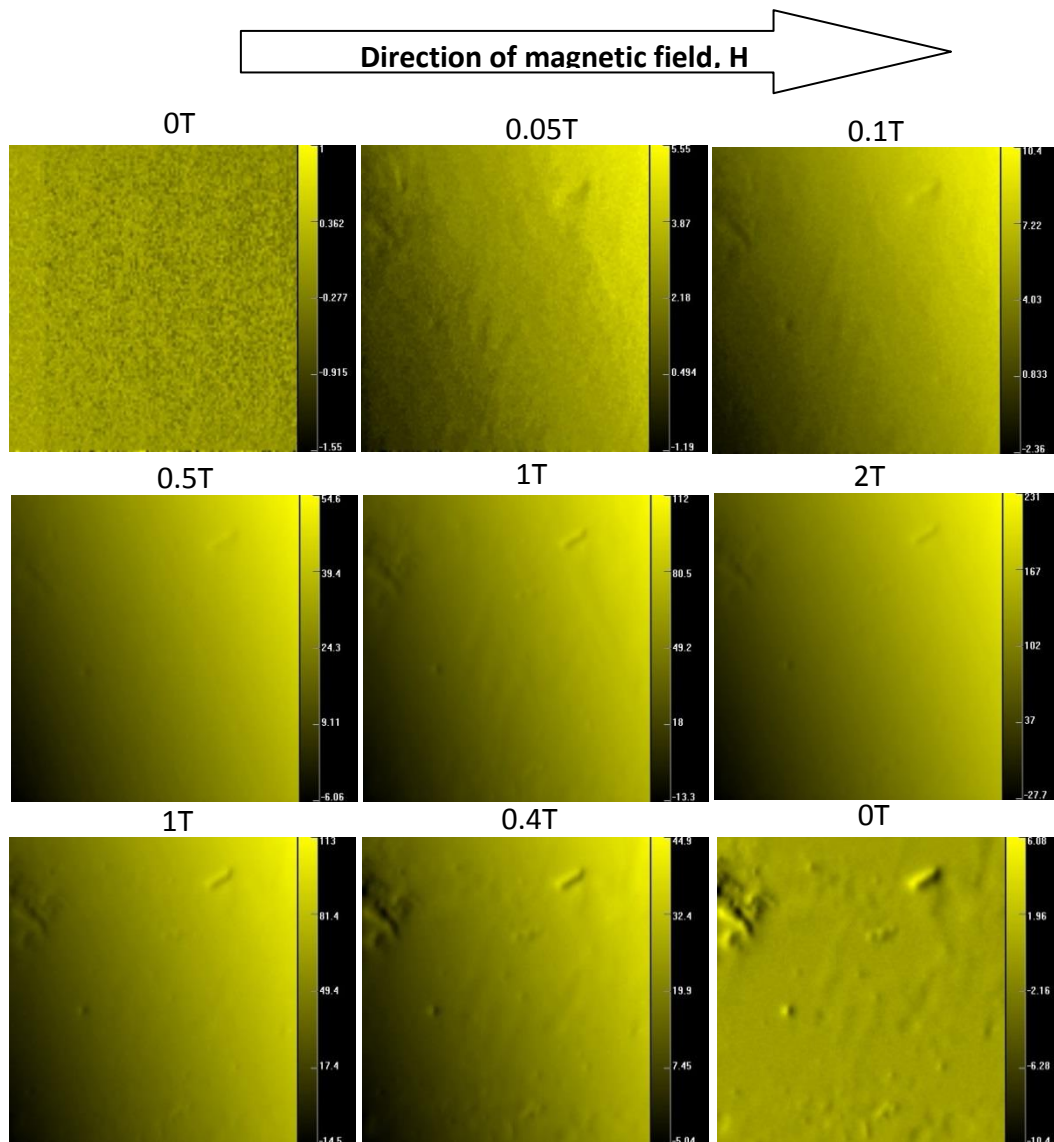


Figure 4.7: Hall images at 6K showing the surface magnetisation of the Ho thin Film with the Field applied parallel to the basal plane as indicated by the arrow above. Black regions represent negative induction and bright represent positive induction. Ho film contrast is scaled by dividing by $2.295 \times 10^{-6} \text{V}$ (the highest value in the first 0T image).

4.3.4 Hall image comparison of Ho single crystal and thin film

In this section the zero field images of the surface of the Ho single crystal and thin film, Figure 4.8a and Figure 4.8b, respectively, are compared. The images are taken at 6K, in zero field and with an area of 1mm x 1mm with the c-axis normal to the image. The contrast scale for both images in Figure 4.8 is the same to allow direct comparison.

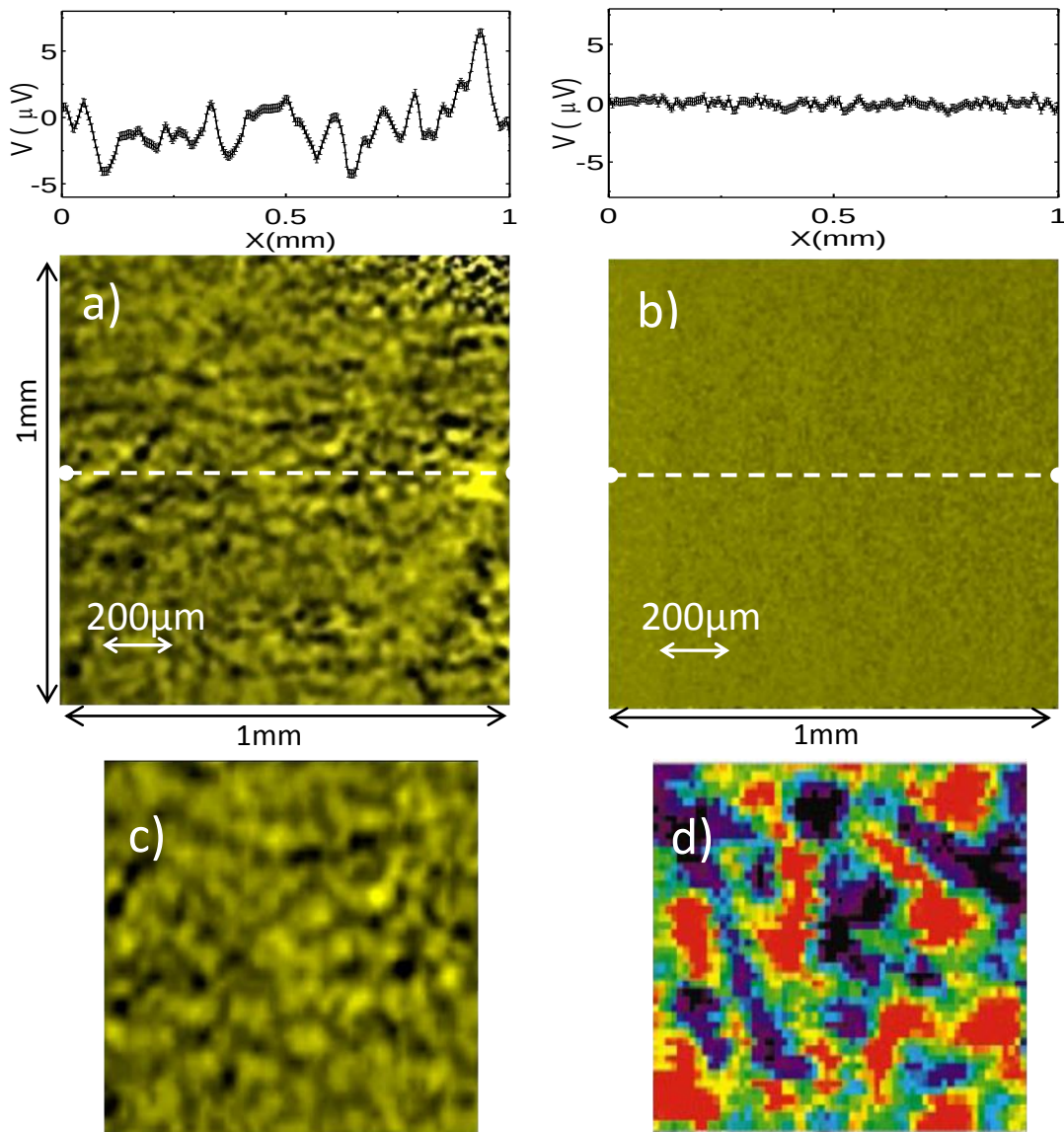


Figure 4.8: Hall images of a) single crystal and b) thin film Ho at $H = 0T$ and 6K, cooled from above $T_{N\acute{e}el}$. Black regions represent negative induction and bright represent positive induction. Line scans across the centre of the images (white dashed lines) are shown in the top panels. c) a $600\mu m \times 400\mu m$ image of the central region in a). d) a $600\mu m \times 400\mu m$ surface of Ho crystal taken with circularly polarised x-ray, at 60K.[22]

It is clear that the single crystal has domain structures with moments pointing in directions parallel and anti-parallel to the c -axis. The domain size and distribution on the surface of Ho, Figure 4.8c, is slightly smaller compared to the results obtained by using circularly polarized x-rays by Lang et al. [22] seen in Figure 4.8d. However, Lang et al. took their image at 60K which is where Ho is in the AFM and it is known that the lattice contracts in the a,b plane when cooling. [120, 124] Unlike circularly polarised x-ray diffraction, Hall imaging does not provide information on the surface chirality of the Ho samples, so only the direction of the out of plane moment is known. The characteristic sizes of these domains on the Ho sample are $\sim 25\mu\text{m}$ and so a SC/FM interface less than this would sample a single domain (i.e. field is inhomogeneous). Typically individual contacts would be much less than $25\mu\text{m}$, (contacts are $\sim 10\text{nm}$). In contrast, similar magnetic domains cannot be identified in the thin film image, which would suggest that the out-of-plane moments are suppressed at the surface of the film and consequently the absence of the magnetic cone spiral. However, the noise floor of the $5\mu\text{m}$ Hall probe is $\sim 0.3\mu\text{V}$ and the line scans across the centre of the Ho image of Figure 4.8a show that the signal measured for the thin film is limited by the noise floor. However the signal from the thin film, Figure 4.8b, is 10^3 times smaller than the crystal (see Figure 4.4) and with the addition of the noise it is not possible to identify any domains or out of plane moments from the Hall image of the thin film. It is also possible that as $T_{\text{Néel}}$ is suppressed to lower temperatures in Ho thin films, the cone-spiral phase would also be suppressed at 4.2K. Therefore we would not expect any out-of plane moment. [127]

The phase diagram from magnetometry (section 4.3.1) and neutron diffraction measurements of Ho single crystal, green stars and red triangles respectively in Figure 4.5, show similar transition points. This may also indicate similar magnetic (cone) spiral structures at 4.2K. We can infer from this and the Hall imaging that a PCARS tip could sample a single magnetic cone spiral domain at 4.2K. However the thin film phase diagram is unusual at temperatures below 19K (i.e. the magnetic cone spiral region), circles in Figure 4.5. This may need further investigation to understand the possible change in the magnetic structure of Ho with an applied magnetic field.

Hall images of the Ho thin film were not conclusive to determine whether domain structures similar to this were present in the Ho crystal due to the weak magnetic signal. X-ray

diffraction on the thin film by the Cambridge group confirms that the films are epitaxial and *c*-axis oriented.

The transition from a magnetic cone spiral to a cone-fan magnetic structure at 0.1T below 19K, Figure 4.5, has been observed in both neutron diffraction and magnetoresistance measurements. This suggests that there is a possibility that the PCARS tip will be able to measure the transition as a magnetic field is applied in the *b*-axis (i.e. measure the transition when the *c*-axis moment reduces to zero). The most interesting phase transition is from the magnetic cone-fan structure to the collinear FM at 0.5T as suggested by the neutron diffraction measurement in Figure 4.1. Applying the magnetic field, in the *b*-axis, to observe a high field transition would require a SC tip that has an upper critical field, H_{c2} , greater than 0.5T. Although Miyoshi et al.[132] have shown that SC tips can have an increase in H_{c2} for certain PCARS contacts, a SC with an intrinsically high H_{c2} would be more practical. The intended approach was to use NbTi which has $H_{c2} = 11.5T$ [133] and (T_c is 9.8K). The characterisation of this tip with field is presented in Chapter 3. However an observed change in the tip/sample contact and even a break in contact, (i.e. caused by applying a magnetic field from magnetostriction) would make PCARS in the magnetic field challenging. In the next section, results from zero field PCARS $T=4.2K$ are discussed.

4.4 Point Contact Andreev Reflection Spectroscopy

4.4.1 Nb tip Results

Measurements using a mechanically cut Nb tip were taken at 4.2K on Ho single crystal and thin film are shown Figure 4.9a and 4.7b, respectively. Point contacts on the Ho sample were made with the tip parallel to the crystal c-axis which is the direction of spin inhomogeneity (spin spiral), the ideal direction. Spectra were taken as a function of contact resistance R_{CB} , which is taken to be the value of the resistance of the spectrum at 30mV.

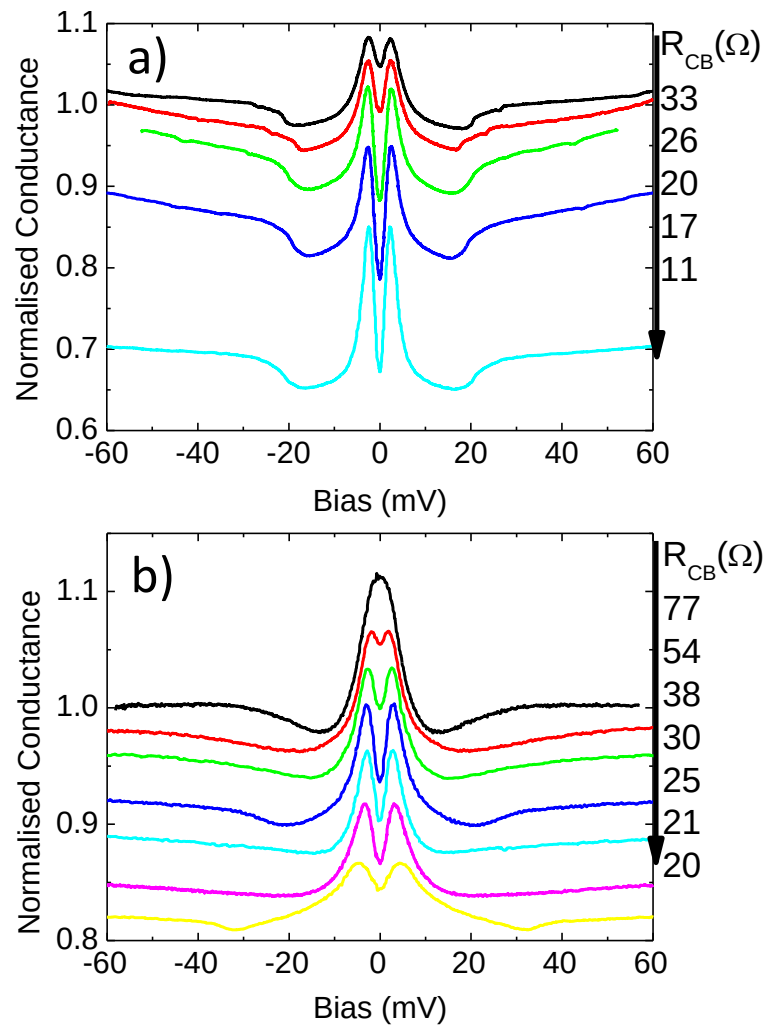


Figure 4.9: Point contact Andreev reflection data at 4.2 K for a) Normalised (differential) conductance spectra as a function of R_{CB} for the Ho crystal and b) Normalised (differential) conductance spectra as a function of R_{CB} for the Ho film. The arrows in a) and b) indicate decreasing contact resistance. All curves are normalised by the conductance value at 30mV and offset in the vertical scale for clarity.

Experimental spectra that are fitted using the BTK model modified by Mazin. et al.[20, 42] (section 3.2) require the data to be normalised. Usually this normalisation is done by taking the conductance at high bias ($V \gg \Delta$) which is usually flat. However for the Ho single crystal, non-flat backgrounds, such as that seen in Figure 4.9a, were observed. These require special consideration in the normalisation procedure and will be analysed in the next section. The spectra on the Ho thin film, Figure 4.9b, at $V \gg \Delta$ indicate a background conductance that is featureless and flat and therefore the normal conductance at high bias can be used.

4.4.2 Normalisation of the high bias Background for Ho Single Crystal

The unusual non-flat background conductance (Figure 4.9a) on the Ho single crystal spectra at $V \gg \Delta$ makes the normalisation point for the fitting procedure become unclear. These background features persist above $V \gg \Delta$. To see whether it is related to the contact made with the SC Nb tip, a normal metal (gold and platinum) point-contact (PC) tip can be used instead of a SC tip. Measurements using these normal tips were taken at 4.2K and at various contact resistances to identify any general feature associated with background spectra. Background measurements were also taken using Nb tips at temperatures above the superconducting critical temperature. These backgrounds of Ho with different tips are shown in Figure 4.10a.

Early FM/NM point contact measurements have been made by Yanson et al. [134] and Naidyuk et al. [135] with Co as the FM and either Ag or Cu as the NM. However, these measurements took second derivative (d^2V/dI^2) spectra, at 4.2K, to show phonon and magnon signatures in NM and FM, respectively. Yanson et al. [134] and Naidyuk et al. [135] observed an unusually sharp d^2V/dI^2 peak at high negative bias. They indicated this to be a magnon signature from a diffusive or thermal contact, as the electrons experience strong impurity scattering. Akimenko et al.[136], however, measured the d^2V/dI^2 spectra of Ho-Ho contacts and recorded magnon excitation at 4meV and phonon excitations at 6-7meV. The appearance of magnons at low bias, unlike that of Yanson et al. [134] and Naidyuk et al. [135], may possibly be due to the contact being in the ballistic regime.

These magnon signatures from FM/NM spectra (termed as background spectra in this thesis), however, are not apparent, Figure 4.10a, and by taking the derivative, d^2I/dV^2 , the curves in Figure 4.10a did not give clear signatures of magnons or phonons at high or low bias. There were also no distinct correlation between contact resistance regimes (tip pressure) and the form of the background spectra. The common form of the background spectra may be described as as V – shaped. It is possible that these V – shaped background spectra in Figure 4.10a are tunnelling related, however the feature should then disappear as the contact resistance is decreased. Features related to heating effects are ones in which the conductance at high bias would decrease (the resistance increases as the sample temperature increases, for metallic samples).

The background spectra were then compared to the Ho single crystal spectra, Figure 4.9a, at $V \gg \Delta$ and then divided from the Ho spectra. An example of this is given in Figure 4.10b where the spectrum is divided by the 28Ω background to obtain a featureless conductance at $V \gg \Delta$, Figure 4.10c. The fits to the spectra in Figure 4.10c and 4.8e were done with a fixed Δ fit (a 3-parameter fit) which will be discussed in section 4.5.2. A single series of spectra, as shown in Figure 4.9a, is analysed by dividing by the same background, e.g. 28 Ω (these results are presented in section 4.5.2). However, here I shall simply make a comparison of the $R_{CB}=33\Omega$ spectrum divided/normalised by the 28 Ω background and 48Ω background (from a Pt tip), shown in Figure 4.10b and Figure 4.10d, respectively. Although the resulting spectra from the 48Ω background normalisation do not have flat backgrounds, Figure 4.10e, the parameters gives similar results.

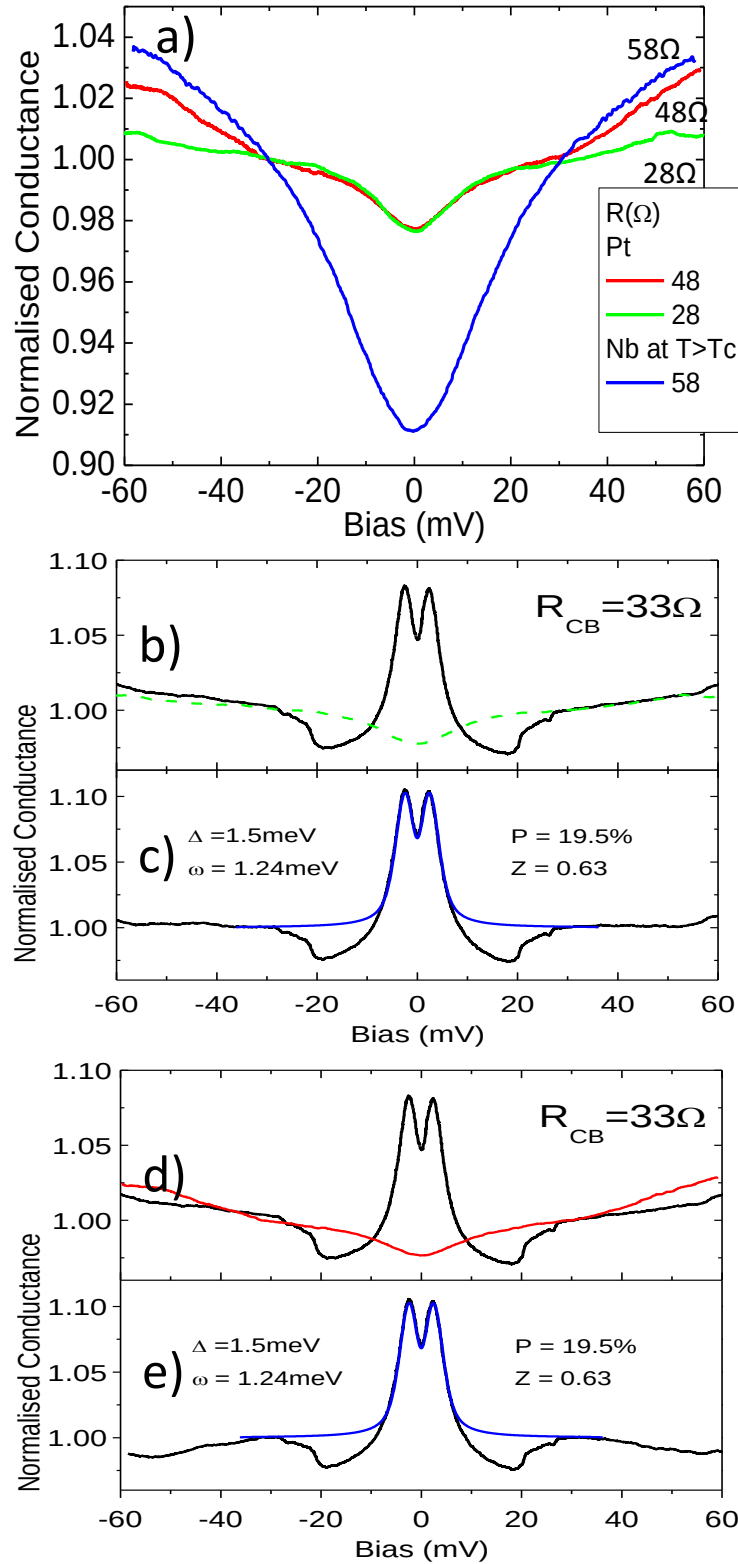


Figure 4.10: a) Normalised background conductance for the Ho single crystal taken using a Pt tip (Red and Dashed Green curve) and a Nb tip at temperature above T_c (11.7K) b) and d) show the $R_{CB} = 33\Omega$ spectrum (black curve) from Figure 4.9a with the 28 Ω (green) and 48 Ω (red) background, respectively, from Figure 4.10a. c) and e) are the theoretical fits, with fixed Δ for Figure 4.10b after background division.

The effect of the background is also tested by dividing with a linear curve. To do this, first the spectra are symmetrised from 0mV to 60mV then divided by a linear curve extrapolated from the slope of the spectra taken between 30mV to 40mV, Figure 4.11a. The result from a fixed Δ fit gives parameters which are slightly different to the fits in Figure 4.10c and Figure 4.10e.

Dividing by the backgrounds taken at 28 Ω and 48 Ω doesn't seem to give significant difference in the extracted parameters, P , Z and ω . There is a difference however when compared with the parameters using a linear background for the normalisation procedure. With respect to the parameters in Figure 4.10 the result in Figure 4.11 shows an increase in P by 11%, decrease in Z by 0.12 and an increase in ω by 0.08meV. We shall see later that although the values are different the trends are the same for a spectra set which we shall see in section 4.5.2.

In the next section I analyse the Ho spectra in Figure 4.9a divided by the 28 Ω , 48 Ω and linear using a fixed Δ fit (section 3.2.4) to understand whether the trends in the parameters as a function of R_{CB} , would be more meaningful than their values.

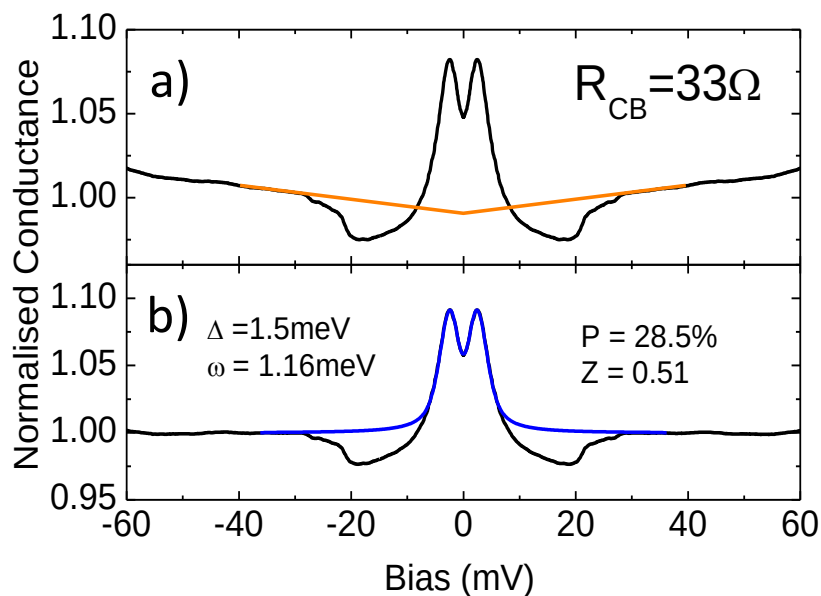


Figure 4.11: a) The $R_{CB}=33\Omega$ spectrum (black curve) from Figure 4.9a with an extrapolated linear background (orange curve). b) The spectrum after dividing by the linear background. The blue curves are the theoretical fits.

4.5 Extracting parameters from fits

4.5.1 Four-Parameter fitting

The choice of performing the fits in a particular regime, either a diffusive or ballistic (discussed in section 3.1.2) depends on whether the radius of the contact radius, a , is less or greater than λ_{mfp} , respectively, in the holmium. The Sharvin resistance, R_{Sh} in equation (2.1), can be used to estimate the point in which resistance goes from ballistic to diffusive. If it is assumed that $\rho=4.5 \times 10^{-7} \Omega\text{m}$ and $\lambda_{\text{mfp}}=1.3\text{nm}$ (this is at $T_{\text{Néel}}$) [121], by assuming the crossover from ballistic to diffusive is when $\lambda_{\text{mfp}} = a$, then $R_{\text{Sh}}=147\Omega$. All of the Ho spectra have contact resistance less than 100Ω and it therefore suggests a diffusive fit is appropriate. However, both diffusive and ballistic full four-parameter (Δ, Z, P, ω) fit of the Ho crystal spectra in Figure 4.9a show degenerate fits in $\chi^2(P)$ allowing only an *upper limit* of the value of P to be extracted. The upper limit of P is where the $\chi^2(P)$ diverges and it is indicated by the arrows in the Figure 4.12a (for Ho single crystal spectrum with $R_{\text{CB}} = 33\Omega$, Figure 4.9a, divided by 28Ω background).

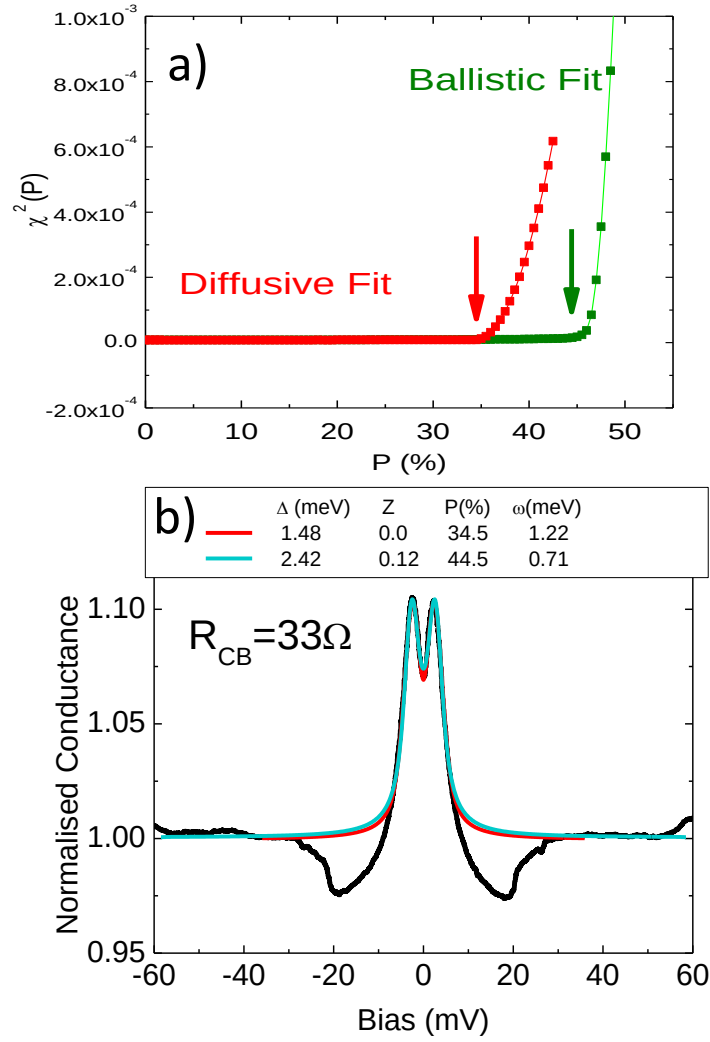


Figure 4.12: a) $\chi^2(P)$ of a four-parameter fit to the Ho single crystal spectra with $R_{CB} = 33\Omega$, from Figure 4.9a, where the red and green curves are the upper limit P from a diffusive and a ballistic fit, respectively. b) A full-four parameter fit to the spectrum for the ballistic (cyan) and diffusive (red).

The upper limit P and the associated fit parameters, using both ballistic and diffusive fits, for the $R_{CB}=33\Omega$ spectrum are shown in Figure 4.12b. In the ballistic case the upper limit P has parameters $\Delta = 2.42\text{meV}$, $Z = 0.16$, $P = 44.5\%$, $\omega = 0.71\text{meV}$. Given that the Fermi velocities of Holmium and Niobium are $1.56 \times 10^8 \text{cm s}^{-1}$ and $2.17 \times 10^8 \text{cm s}^{-1}$ respectively, [137] the minimum value for Z from the Fermi velocity mismatch (see section 2.1.3) would be $Z_{\min}=0.16$. This is close to the $Z=0.12$ value from the upper limit of P for the ballistic case. However, also in the ballistic case, Δ is higher than the expected value of $\Delta_{Nb} (= 1.5\text{meV})$, which is also unphysical. In the diffusive fit the upper limit P would give the parameters

$\Delta = 1.48\text{meV}$, $Z = 0$, $P = 34.5\%$ $\omega = 1.21\text{meV}$; $\Delta = 1.48\text{meV}$ is reasonable for a Nb tip however $Z=0$ is unphysical. This highlights the issue of degenerate fits, due to broadening of the spectrum, affecting the fitting procedure's ability to distinguish the effects of P and Z on a spectrum.[20] Due to this problem, a robust way of obtaining values of P , Z and ω would then be to use a fixed $\Delta=1.5\text{meV}$, this is discussed in the next section.

4.5.2 Fixed $\Delta_{\text{Nb}}=1.5\text{meV}$ fit

In this section the Ho single crystal spectra in Figure 4.9a will be used to explore fitting with a fixed $\Delta_{\text{Nb}}=1.5\text{meV}$. The spectra divided by the 28Ω background were fitted in both the ballistic (black square) and diffusive limits (black triangle), Figure 4.13. The results for ballistic fits of Ho spectra divided by the 48Ω background or the linear background are also shown in Figure 4.13 (yellow triangle and red cross data points, respectively).

The general trend that the fixed Δ fit has on the values of P , Z and ω , in both ballistic and diffusive limits, is that Z increases, P decreases and ω decreases with decreasing R_{CB} . However, the diffusive fit gives a Z parameter value of zero for all fits except at the lowest R_{CB} where it shoots up to 0.21, but otherwise the trends for each parameter are the same as in the ballistic fit.

In section 3.2.4 the errors involved in using a fixed Δ fitting to spectra with suppressed Δ or enhanced Δ were discussed. Here, although the absolute values of the parameters vary, the trend does not, for ballistic and diffusive fits. Since the fitting is systematic for each spectra, the error would, similarly, be the systematic within a set. So although the values of the parameters are not reliable, the trends may be more robust. In the following section I compare results of Ho single crystal and thin film PCARS.

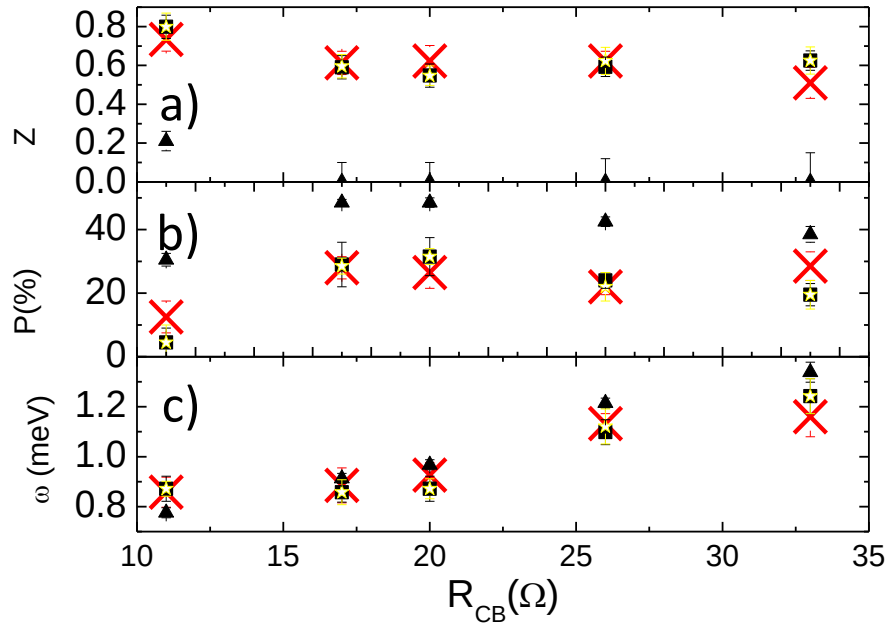


Figure 4.13: The a) Z , b) P and c) ω for ballistic (black square) and diffusive (black triangle) fit to Ho single crystal spectra in fig 4.6a, with the spectra divide by the 28Ω background in Figure 4.10a. The yellow star and red cross are the ballistic fit to the spectra divided by 48Ω and a linear background, respectively.

4.6 PCAR Results of Ho single crystal and thin film

4.6.1 Spectra as a Function of Contact Resistance

In this section we present the result following from a fixed $\Delta=1.5\text{meV}$ fit to the Ho single crystal and thin film spectra. The $P(Z)$ trend, Figure 4.14, show the common trend that is observed of low P with high Z and vice versa.[19, 30, 91, 116] Although the P - Z relation is not understood very well, it is thought, as discussed in section 2.3.10, that a high Z at a SC/FM interface that leads to a decrease in P is due to spin scattering.

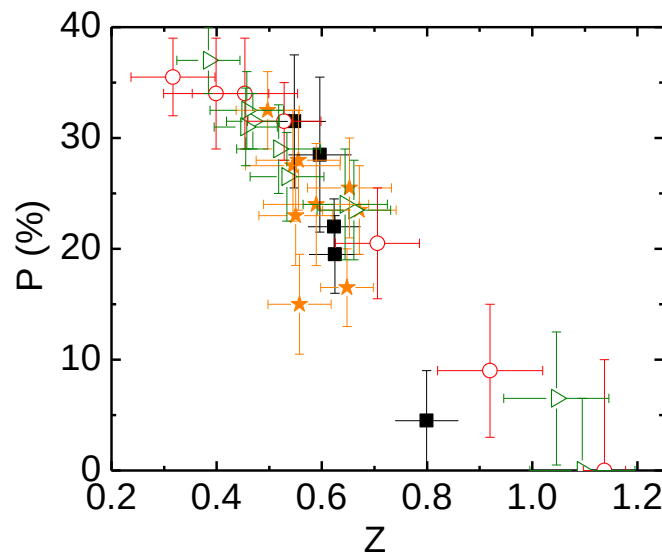


Figure 4.14: The $P(Z)$ trend for Ho single crystal (filled data points) and thin film (hollow data points)

In general, with all the caveats discussed above, it seems that the data hints at the interesting relationship between P and Z at low contact resistance R_{CB} in both the single crystal, Figure 4.15a, Figure 4.15b, Figure 4.15c, and thin film, in Figure 4.15d, Figure 4.15e, Figure 4.15f. For the Ho single crystal there appears to be a peak and dip feature in $P(R_{CB})$ and $Z(R_{CB})$, respectively. In PCARS, R_{CB} can decrease either from a cleaner interface or due to an increase in the physical size of the contact [19, 108, 138]. Therefore for different contacts on the single crystal the absolute contact resistance depends on the tip because there are many micro-contacts in one tip-sample contact. Hence it is the reason why the peak/dip in the trends does not appear at the same contact resistance for each dataset. Therefore by normalising each trend to its $R_{CB-Peak}$ ($R_{CB-Peak}$ is defined in caption Figure

4.15), and by plotting $P(R_{CB}/R_{CB-Peak})$ and $Z(R_{CB}/R_{CB-Peak})$, it is possible to compare the changes between trends with respect to this peak/dip. However, for the Ho thin film data in Figure 4.15d and Figure 4.15e, a peak or dip in P or Z is not apparent and instead the P and Z are constant at high R_{CB} and then decreases with decreasing R_{CB} .

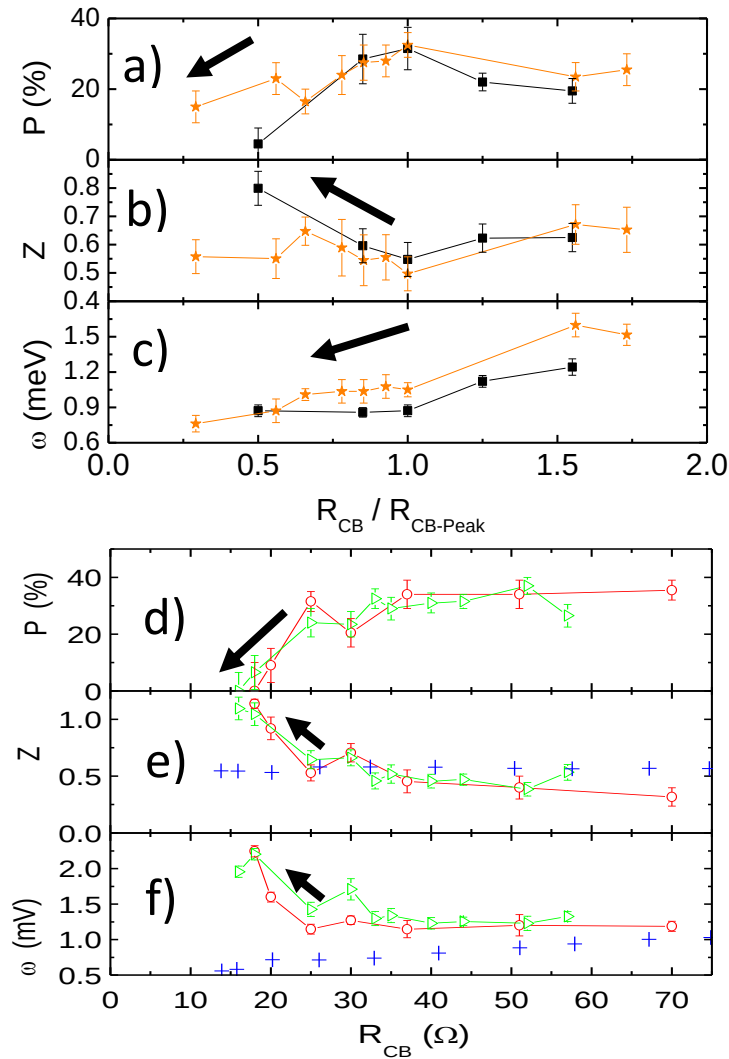


Figure 4.15: Dependence of (a) P , (b) Z and c) ω for the Ho crystal as function of $R_{CB}/R_{CB-Peak}$, where $R_{CB-Peak}$ is the value of R_{CB} at the peak in the polarization with $R_{CB-Peak} = 20\Omega$ and 41Ω for the squares and stars in a) and b), respectively. The dependence of P (d), Z (e) and f) ω on R_{CB} for the spectra taken on the Ho thin film (unfilled symbols) and copper foil (cross symbols). The arrows indicate the trend of the parameters with decreasing R_{CB} . Each trend is one contact from different tips. The sample used for a) to c) is the same for each trend the same goes for d) to f).

The ω and Z trends obtained when a Nb tip is pressed into a copper foil is shown in Figure 4.15e and Figure 4.15f (crosses), and suggests the behaviour of the Ho samples is anomalous. In the case of Cu (where $P=0$), there is a small decrease in Z as R_{CB} is reduced which is attributed to the increasing transparency of the tip-sample interface[20] and hence the absence of P for Cu Figure 4.15d). In the next chapter we attempt to study these trends with R_{CB} in other ferromagnetic systems.

4.6.2 Modelling the Effect of stray field on the spectra

It is important to understand whether these trends can be an artefact of the Nb/Ho contact. Hence in this section I model to see if stray magnetic fields, due to the out-of-plane moment of the cone spiral, might affect the tip properties.[116] It was seen in section 3.2.8 that, for a 1-channel fit with fixed $\Delta=1.5\text{meV}$, as the reduced magnetic field (h) increases, Z decreases, P increases, and ω decreases, seen here in Figure 4.16 . By assuming that h would increase as R_{CB} decreases (such that pressing the tip down causes the interface to experience more stray field) a comparison can be made of the P , Z and ω trends from the experiment, Figure 4.15, and the model Figure 4.16. The trend in $\omega(R_{CB})$ for the single crystal is similar to the model but this trend, also seen in Cu [20], is more likely a result of the tip experiencing a cleaner interface as R_{CB} decreases. [20] However, the trends in P and Z in Figure 4.15, for both the single crystal and Ho thin film, are contrary to the model. Therefore it is unlikely that the $P(R_{CB})$ and $Z(R_{CB})$ trends in Figure 4.15 can be explained by stray fields and it is possible that the trends are a result of the tip experiencing some form of additional scattering at the interface as R_{CB} decreases, for the single crystal results.

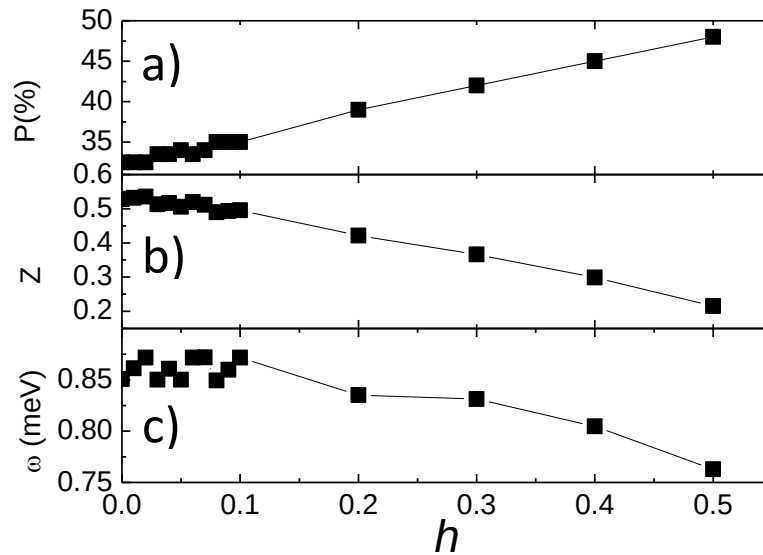


Figure 4.16: Dependence of (a) P , (b) Z and (c) ω on stray field at the tip. This is simulated using, as the initial parameters, the black square data point at $R_{CB}/R_{CB-Peak}=1$ from Figure 4.15a, Figure 4.15b, Figure 4.15c and then seeing how the field parameter, h , as described in chapter 3 affects the fitted parameters.

4.6.3 Series Resistance Effects

Although stray field may not be the cause of the trend in $P(R_{CB})$ and $Z(R_{CB})$ trends, there is still the $\omega(R_{CB})$ that needs to be examined. In the previous section I already explained that, for Ho single crystal, the $\omega(R_{CB})$ trend, Figure 4.15c, is caused by the tip experiencing a cleaner interface. However for the Ho thin film there is an unusual trend in $\omega(R_{CB})$, Figure 4.15f. For thin film Ho the broadening parameter is constant at high R_{CB} but then increases dramatically at low resistance, this high broadening may be related to sample (series) resistance, as R_{CB} which has the identical effect of increasing the broadening parameter.[101]

However, the behaviour of P and Z in Ho cannot be explained purely by an increase in the broadening parameter with decreasing R_{CB} , as both the Ho crystal and the Cu sample show the same trend of decreased broadening as R_{CB} is reduced.[20] Furthermore a Van der Pauw four-point contact measurement on the thin film showed a resistance that was negligible. At room temperature the Van der Pauw resistances were $R_1 = 0.31\Omega$ and

$R_2 = 0.19\Omega$, giving a sample resistance of $\sim 1\Omega$. This sample resistance is numerically calculated using the equation $\exp(-\pi R_1/R_S) + \exp(-\pi R_2/R_S) = 1$ where R_S is the sample resistance. [139] At low temperature ($\sim 10\text{K}$) the resistances were even lower, taking values of 0.081Ω and 0.051Ω , giving a sample resistance of $\sim 0.29\Omega$. Therefore a sample resistance effect can be ruled out as the cause of this increasing broadening for the Ho thin film in Figure 4.15f. A possible cause of this broadening could be the top 10nm Au layer. Chalsani et al. [99] fabricated Co/Pt/Pb and Co/Pb nano-contacts and observed broadening of their Co/Pt/Pb spectra that, unlike their Co/Pb spectra, it could not be simply fitted by adjustment of the scattering parameter Z . They also found that their spectral broadening had no dependence on the thickness of the Pt layer. It was suggested that inelastic scattering causes pair breaking effects via the Pt layer or through some intermixing at the Pt/Co interface, which results in the broadened spectra. Their solution was to include a broadening parameter Γ (instead of ω) and found that their model fits to the experimental conductance curve if there is finite Γ (increasing initially from $\Gamma = 0$) and an increase in Z but with a decrease in P . The results of Chalsani et al.[99], therefore offer an explanation of the unusual behaviour of $\omega(R_{CB})$ observed for the Ho thin film.

4.6.4 Understanding the Trends of $P(R_{CB})$ and $Z(R_{CB})$

We have so far attempted to rule out causes of the trends. However in this section I describe the phenomenological scenario to provide a possible interpretation of the results in $P(R_{CB})$ and $Z(R_{CB})$. The dependence of $P(R_{CB})$ and $Z(R_{CB})$ can be understood qualitatively using a simple schematic, as shown in Figure 4.17. The behaviour of Z at high R_{CB} in the Ho crystal implies the existence of a surface layer, probably an oxide, as proposed for other systems [108]. As the Nb tip first approaches the Ho (Figure 4.17a), the surface layer acts as a spin scattering layer resulting in a low P (and high Z) in the conventional way. As the tip is pushed further into the crystal surface (Figure 4.17b), the Andreev reflection probes the spin alignment of the Ho with a Z parameter that is indicative of a clean interface and P reaches a maximum. Finally, as the tip goes through this surface layer completely (Figure 4.17c), the spin-mixing/spin scattering of the Ho becomes dominant (Z increases) and so P is once again reduced.

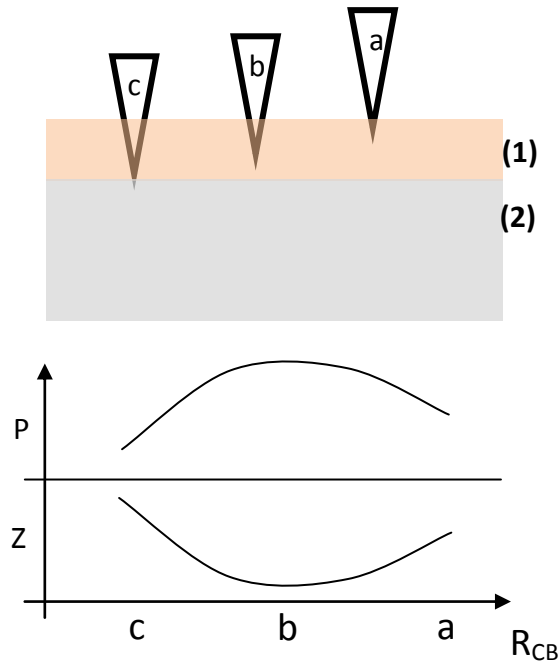


Figure 4.17: Schematic illustrating the behaviour of P and Z as a function of tip pressure for a system with a surface scattering layer. Layer (1) is a thin surface oxide and layer (2) represents bulk Ho.

In the thin film case, the thin Au capping layer prevents the oxide from forming, so as the tip first approaches the capped film surface, the intrinsic P of the Ho is preserved through the thin metallic capping layer and P is approximately constant with R_{CB} . As the tip further punctures the capping layer it will probe the Au/Ho interface which would result in the decrease of P but at the same time increase in the broadening.[99] This explains the similarity of the P (and Z) of the crystal and thin film at low R_{CB} .

In section 2.3.9 the theory presented by Grein et al. [24] showed how spin mixing can be observed by the formation of conductance peaks near the gap value (see Figure 2.16a and 2.16b). The development of the conductance peak, as R_{CB} decreases, can be clearly observed in Figure 4.9a. The peaks can be usually characterised by the Z parameter and we have seen that the trend in $Z(R_{CB})$ does suggest increased Z , using the BTK fit. We have also mentioned how an increase in Z can lead to P decreasing in the presence of spin scattering, section 2.3.10. Therefore this complements our explanation of the schematic in Figure 4.14 if we assume that a suppressed P with enhanced Z could be due to some spin active interface (spin mixing/scattering). Whether the LRSTPE is present or not could not be

concluded, from these experiments. It is worth noting that Zutic and Das Sarma[140] (in a SC/Semiconductor also showed that PCARS conductance peaks would become more pronounced with increased spin-flip scattering.

4.7 Chapter 4 Conclusion

In conclusion the Holmium single crystal and thin film samples were characterised using magnetometry and Hall probe imaging. Hall probe images in zero field showed that the Ho crystal had domain features with out-of-plane moment in parallel to the c-axis. The sensitivity of the Hall probe imaging however meant an out-of-plane component of the moment in the film would be below the detection limit.

PCARS was done on both the Ho single crystal and thin film samples with the Nb tip parallel to the c-axis (i.e. in the direction of the spiral axis inhomogeneity). It was shown, from fixed Δ fit to the Ho PCARS spectra, that there is an anomalous dependence of P and Z on the contact resistance, R_{CB} , in the magnetically inhomogeneous Ho. Similarities in the results of both single crystal and thin film Ho suggest a common scattering mechanism at low R_{CB} . This scattering results in reduced P and suggests increased spin scattering/mixing, a fundamental precursor to the LRSTPE effect or conversion of $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ to $(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$.

However the requirement to fix Δ to obtain results would suggest that most valuable message from this chapter is the realisation that the BTK model is too restrictive to explain the complex interactions at SC/FM interfaces.

5 PCARS of Ni Alloys

In chapter 4, fixed Δ fit to Ho single crystal and thin film PCARS spectra showed anomalous trends in P , Z as a function of tip pressure. In this chapter, the motivation was to study “simple” FM metals, as a function of tip pressure. The best example of the performance of a FM as a function of tip pressure is the Mn-Al doped ZnO (section 3.2.5) which shows what happens when you puncture through a barrier, after which the parameters are constant. The attempt to repeat this with other less exotic metals has been very challenging.

Results on $\text{Ni}_{0.19}\text{Pd}_{0.81}$ are presented along with data on $\text{Ni}_{0.03}\text{Pd}_{0.97}$ to evaluate the possibility of determining the fitting parameters for low T_{Curie} samples. Recently these alloys have been used in complex SC/FM/SC Josephson junctions (chapter 2) in which the $m=1$ spin triplet proximity effect (LRSTPE) is generated, although they are not thought to generate the LRSTPE of themselves.

In this chapter we first introduce the case of NdNi_5 as reported in the literature of Mukhopadhyay et al. [16, 141] We digitize the data and confirm that the four-parameter fitting produces results that are consistent with those reported in the literature.

We then examine systems designed to have low Curie temperatures. First we look at the magnetisation data and discuss the expected Curie temperature and the apparent super paramagnetic blocking temperature, suggestive of clusters in our films. We review evidence for clusters in similar films in the literature.

Before studying these films we review the difficulties with fitting data on the films with low polarisation, using Cu and Ni as examples. We then attempt to fit $\text{Ni}_{0.19}\text{Pd}_{0.81}$ data as a function of tip pressure and $\text{Ni}_{0.03}\text{Pd}_{0.97}$ as a function of temperature. This last section is ,perhaps, the most interesting because the data seems be complementary to Mukhopadhyay et al. [16, 141]

This chapter also analyses the possibility of observing spin fluctuation in weak FM materials such as $\text{Ni}_x\text{Pd}_{1-x}$ alloys, which have a T_{Curie} that varies with Ni content.[10] The interest in performing PCARS on $\text{Ni}_{0.03}\text{Pd}_{0.97}$ is the possibility that spin fluctuation at temperatures close

to T_{Curie} would provide the condition for triplet generation i.e. an inhomogeneous magnetic interface. Therefore it is possible that at $T \sim T_C$ signs of spin fluctuations may be visible in the parameters P and Z as a function of T .

5.1 Spin Fluctuation in NdNi₅

NdNi₅ is a ferromagnet with a Curie temperature, $T_{Curie} \sim 7.7K$. [16, 141] The moment of the NdNi₅ compound is localised at the Nd sites and induces a small moment on the Ni sites. [16, 142] PCARS of NdNi₅ were measured by Mukhopadhyay et al. [16, 141] as a function of temperature that passed through T_{Curie} , and our interest in this material is the anomalous broadening that they attributed to spin fluctuations. Due to the low T_{Curie} of the sample it was possible to observe the change in the parameters Δ (meV), Z, P(%) and Γ (meV) as a function of temperature, where Γ is the broadening parameter, attributed to the quasiparticle lifetime (see section 3.2.2). The interesting result of the fits to the spectra from Ref. [16] is that despite having a low T_{Curie} (a weak exchange field), the moment is sizeable and despite the absence of appreciable spin splitting in the density of states [143], the observed P is high. Additionally P(T) decreases to zero as T_{Curie} is approached and Mukhopadhyay et al. [16, 141] shows that P(T) is proportional to magnetisation M(T), Figure 5.1c.

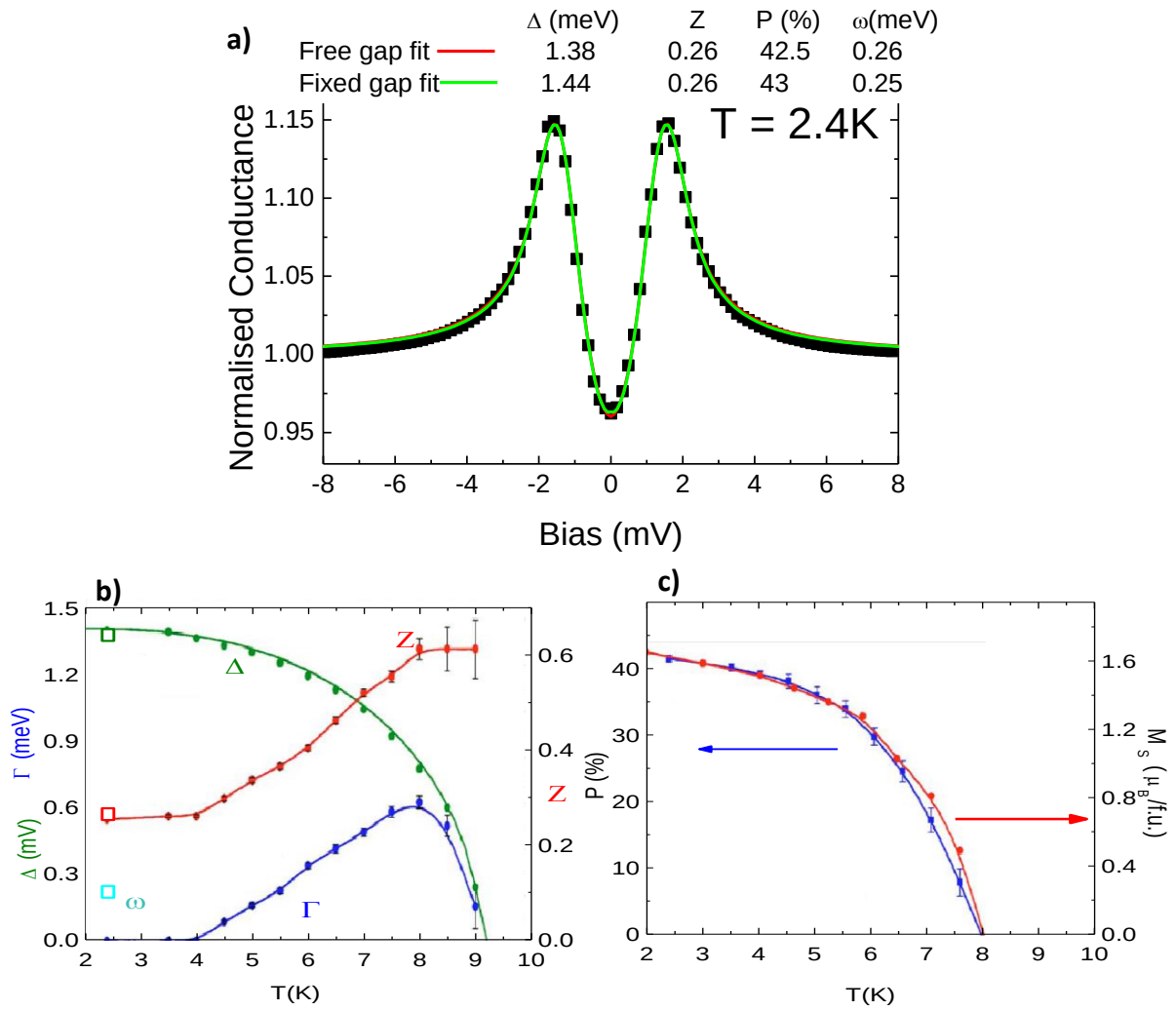


Figure 5.1: a) The digitised spectrum from ref. [16] at 2.4K with a full four-parameter (free) and fixed gap fit. b) the filled data points are from ref. [16] showing Δ , Z and ω vs. temperature and the $\square$ data points are from our BTK fit c) P (blue) and Magnetisation (red) vs. temperature. from ref. [16]

In order to verify if their interpretation and fitting parameters were realistic, the 2.4K spectrum shown in fig.3a of ref.[16] was digitised and fitted using a four parameter fit. This result is shown in Figure 5.1a. The parameters obtained by Mukhopadhyay et al. in ref. [16] were $\Delta = 1.44\text{meV}$, $Z = 0.27$, $P = 42\%$ and $\Gamma = 0\text{meV}$, while our four-parameter fit obtained $\Delta = 1.38\text{meV}$, $Z = 0.26$, $P = 42.5\%$ and $\omega = 0.26\text{meV}$ (red curve in Figure 5.1a). Thermal smearing ($k_B T$) at 2.4K is 0.21meV so a value of $\omega = 0.26\text{meV}$ means that our fit is quite reasonable. However the results presented in ref.[16] are from fits that only allow the gap to vary within 5% of the expected BCS gap of Nb at each temperature (effectively it is a fixed

gap fit). This reduces the number of free parameters to the remaining three (P , Z and Γ). A fixed gap fit to the same curve with $\Delta = 1.44\text{meV}$, the value used in ref.[16], (green curve in Figure 5.1a) also gives similar results to Mukhopadhyay et al. (hollow square data point at 2.4K on Figure 5.1b). Reassuringly using either fitting method reproduces similar results for Δ , Z and P .

However the broadening parameter that was used in Ref.[16] is related to the quasiparticle broadening parameter Γ [97] [98] and therefore would have captured non thermal smearing. On the other hand ω captures both thermal effects ($k_B T$) and inelastic scattering (i.e. Γ), and it was also suggested by Magnus et al.[144] that the contributions can follow a sum rule. Hence in the absence of inelastic scattering ($\Gamma = 0$), as indicated by Mukhopadhyay et al. at 2.4K [16], our measured $\omega = 0.26\text{meV}$ is mainly due thermal broadening. Furthermore we see in Figure 5.1b that there is an increase in broadening parameter Γ with temperature, which is, phenomenologically speaking, a result of increasing inelastic scattering.[3, 144] The unusual peak in $\Gamma(T)$ at 8K, Figure 5.1b, was explained by Mukhopadhyay et al. [16] as a result of spin fluctuations near T_{Curie} causing inelastic scattering of carriers and decreasing quasiparticle lifetime.

The trend in $Z(T)$ was suggested by Mukhopadhyay et al. to be due to the evolution of the Fermi velocity of the FM spin-up and spin-down bands with temperature[16] that would contribute to an increase in Z with increasing temperature. Phenomenologically speaking, an increase in elastic scattering should reduce the interface transparency, resulting in an increase in Z . It was only stated by Mukhopadhyay et al. that spin fluctuations could also have an effect on an increasing Z , but would require a more detailed theoretical understanding on the contribution of spin fluctuation to Z .

P and Z have entirely opposite trends as a function of temperature in Figure 5.1b; P decreases as Z increases with increasing temperature. This would show a $P(Z)$ relation (high P with Low Z or Low P with High Z) similar to Ho (section 4.6.1) and some commonly seen $P(Z)$ trends of FM materials [19]. The $P(Z)$ trends is also discussed in section 2.3.10. Mukhopadhyay et al.'s result [16] suggested a relation between $P(T)$ and $M(T)$, Figure 5.1c, however their $P(Z)$ is similar to that discussed in section 3.2.8 and scales with temperature. This may indicate a scattering effect that causes High Z and low P at $T \sim T_{Curie}$

5.2 Clusters in Ni Alloys

Unlike the study of Mukhopadhyay et al. in which the magnetisation is essentially localised to the Nd atoms [16, 142], the films used in this study were $\text{Ni}_x\text{Pd}_{1-x}$ and $\text{Cu}_{1-x}\text{Ni}_x$. These alloys may be expected to be ferromagnetic if they are homogenous.[10] Nonetheless there are problems growing these films and so before presenting results on $\text{Ni}_x\text{Pd}_{1-x}$ alloys, a discussion on magnetic clustering of Ni atoms in alloys may be important in understanding the results presented in later sections.

In a study of $\text{Pd}_{1-x}\text{Fe}_x$ and $\text{Ni}_x\text{Pd}_{1-x}$ alloys, Crangle et al.[145, 146] stated that a common feature in the magnetic measurements of the dilute FM alloys is the large μ_B per FM atom. This is usually associated with the element in its normal FM state (bulk Ni has $0.6\mu_B$ per Ni atom. The large μ_B per Ni atom is because of the Ni polarising the Pd matrix via the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[146]

Aldred et al.[147] suggested that these large moments of Ni in $\text{Ni}_x\text{Pd}_{1-x}$ alloys may be caused by clustering. They used elastic magnetic diffuse neutron scattering to measure the forward scattering cross section due to Ni impurities in $\text{Ni}_x\text{Pd}_{1-x}$ samples. They found that the minimum concentration (critical concentration, c_0) in which there is ferromagnetism in the alloy, $\sim 2.5\%$ Ni, was because Ni atoms alone are not magnetising i.e. it could not polarise the Pd matrix. The giant moments observed in $\text{Ni}_x\text{Pd}_{1-x}$ (with $x = 3\%, 3.4\%, \text{ or } 4.7\%$) as explained by Aldred et al. was from the magnetic interaction of nearest Ni neighbours or groups (i.e. clusters) polarising the Pd rather than individual atoms.

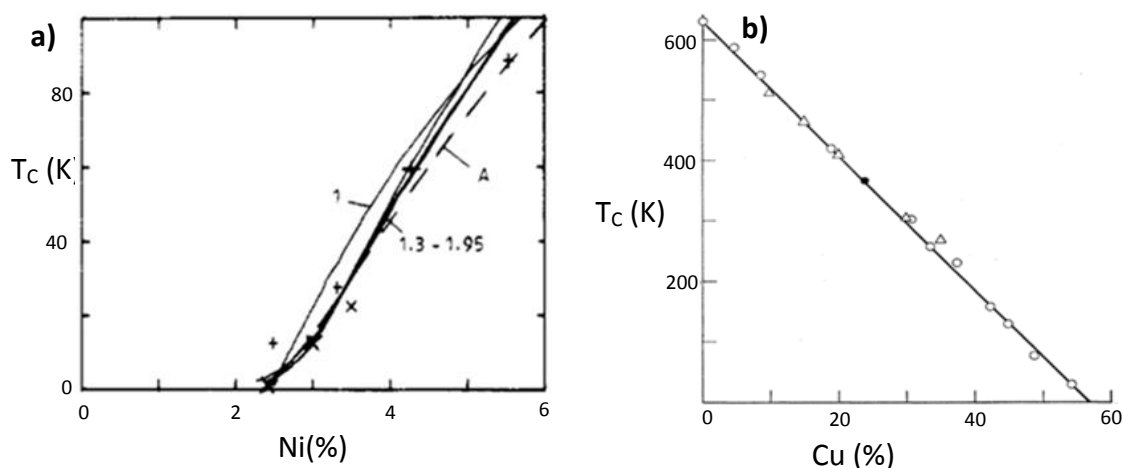


Figure 5.2: T_{Curie} versus a) Ni concentration for Ni_xPd_{1-x} alloys in % of Ni [10] and b) Cu concentration for CuNi alloys in % of Cu.[25]

Experimental results and analysis as presented by Chouteau et al.[148] Chouteau[149], Sain and Kouvel[150] and Cheung et al. [151] support the view that magnetic clusters are present in Ni_xPd_{1-x} alloys. These clusters were shown to be also present in low Ni concentration samples of Ni_xPd_{1-x} [149-151]. Chouteau et al. [148] Chouteau [149], Sain and Kouvel [150] and Cheung et al. [151] analysis of Ni_xPd_{1-x} modelled magnetisation by splitting it into contributions from magnetic impurities, such as the clusters, and nonmagnetic impurities, such as single Ni atoms. It was found that above $\sim 1.85\%$, the experimental and theoretical magnetisation disagreed. The discrepancies indicate that the magnetisation of Ni triad clusters is greater in the experimental results compared to the theoretical calculation. [151] Cheung et al. [151] proposed that these discrepancies can be taken into account if magnetic Ni pairs form clusters in close proximity to other pairs or single Ni atoms. This was also suggested from the results of neutron diffraction on Ni_xPd_{1-x} samples with 2.5% and 3% Ni concentration.[152]

In the analysis of Chouteau et al. [148] and Chouteau [149], it was shown that a cluster of three Ni atoms could have a polarising sphere that extends up to a radius of R_F ($\sim 10\text{\AA}$) in which the Pd matrix is polarised. However not only is the Pd polarised but it was also believed that there are distances from the cluster centre, R_1 and R_2 , [148, 149] in which isolated Ni atoms or Ni nearest neighbour pairs, respectively, will become polarised and have a moment of $2.4\mu_B$. Ododo [152, 153] explained that the long-range interaction of the

clusters, i.e. the polarising sphere, in the $\text{Ni}_x\text{Pd}_{1-x}$ samples below c_0 was via the RKKY coupling. This leads to cluster glass formation, which is similar to spin glass but only the impurities that are magnetic, in this case the clusters, are involved in “freezing-in” instead of individual Ni atoms. Therefore, this would mean that the alignment of the Pd and Ni atoms in the polarisation sphere of one cluster would be different to that of another cluster. As the concentration increases the RKKY coupling gets stronger and at c_0 the polarising spheres start to overlap, the sample becomes ferromagnetic. The conclusions of all these results indicate that clustering of Ni is always present in $\text{Ni}_x\text{Pd}_{1-x}$ samples which are therefore magnetically inhomogeneous.

However Loram et al.’s [10] analysis on the experimental data of Chouteau et al.[148] Chouteau[149], Sain and Kouvel[150] and Cheung et al. [151] would argue that dilute $\text{Ni}_x\text{Pd}_{1-x}$ alloys are homogenous and individual Ni atoms are magnetic. The reason why individual Ni atoms appear to not have a moment at low concentrations and low temperatures is due to intrinsic spin fluctuations of the individual Ni moments related to the spin orientation lifetime of Ni $\hbar/kT_S$ where $T_S(=55\text{K})$ is the spin fluctuation temperature.[10] Loram et al. showed that by taking this into account, the effective moment per Ni atom is $5.8\mu_B$ at $T=0$ and $3.4\mu_B$ at $T=700\text{K}$ and shows giant moments due to the fluctuating moments of Ni atoms. As the concentration of the Ni increases, the distance between Ni atoms decreases and the onset of ferromagnetism is due to the exchange interaction between the fluctuating moments of individual Ni atoms. The conclusion of Loram et al. was that the magnetic behaviour of dilute $\text{Ni}_x\text{Pd}_{1-x}$ is not actually due to clusters. However Loram et al. did point out that for Ni concentrations below 2% the saturation magnetisation that happens at low fields from results of Chouteau et al.[148] and Chouteau[149] cannot be explained with their spin fluctuation model and this may indeed indicate giant magnetic clusters.

It is possible that the techniques by which samples are made could determine the formation of clusters.[154] In the experiments of Chouteau et al.[148] Chouteau[149], Sain and Kouvel[150] and Cheung et al. [151] the $\text{Ni}_x\text{Pd}_{1-x}$ were bulk samples prepared by annealing. A recent measurement of $\text{Ni}_{0.14}\text{Pd}_{0.86}$ thin film alloys [155] which were prepared by sputter deposition, showed signs of clustering and an effective moment of $4.6\mu_B$ per Ni atom, which is seven times more than usual (i.e. $0.6\mu_B$) .[155] Therefore a possibility is that although bulk

$\text{Ni}_x\text{Pd}_{1-x}$ samples may be homogenous as explained by Loram et al.[10], clusters could be present in NiPd thin films.

However it also is possible that both views on spin fluctuations and giant moments of Ni clusters are correct and can explain $\text{Ni}_x\text{Pd}_{1-x}$ alloys if they are understood to be superparamagnetic. In superparamagnetic materials the FM particles are small enough such that they have a single magnetic domain.[154] These particles have giant magnetic moments (due to the sum of individual FM atoms that form the particle, i.e. a cluster) and their magnetisation is subject to thermal fluctuations. Due to this, in zero magnetic field, the net magnetisation averages to zero but if a field is applied then the moments of the particles will tend to align to the field, although thermal energy will tend to misalign them. [154] The time in which they fluctuate (i.e. reverse in spin direction) is temperature dependent. Below a certain temperature called the blocking temperature, T_B , the fluctuation time will be long such that the magnetisation appears to be stable with the moments of each FM particle 'blocked' in a particular direction. We shall see later that this blocking temperature is indeed observed not just in $\text{Ni}_x\text{Pd}_{1-x}$ but also in $\text{Cu}_{1-x}\text{Ni}_x$.

5.3 Thin Film Nickel Alloys

In section 5.1 we discussed Mukhopadhyay et al.'s results [16] and suggested that the spin fluctuations occurring at temperatures close to T_{Curie} may cause some form of scattering that increases the Z parameter. However, if spin fluctuations also occur in Ni_xPd_{1-x} thin films then it may also provide a similar condition that would produce similar P and Z trends as a function of temperature; since spin fluctuations are temperature dependent.[154] This was the initial motivation to study dilute FM alloys with low T_{Curie} , as it is possible that spin fluctuations near T_{Curie} of the dilute FM alloys could also provide a magnetically inhomogeneous interface that results in the LRSTPE being generated.

The dilute FM alloys discussed in this chapter, $Ni_{0.03}Pd_{0.97}$ in particular, had low T_{Curie} so the polarisation of carriers, P, is expected to be very low, and in the following we address whether it is feasible to make meaningful measurements of low P systems. If the absolute values are difficult to determine, then the trends with tip pressure or temperature may give some insight into the spin fluctuations at SC/FM interface.

The thin film $Cu_{0.43}Ni_{0.57}$ sample was fabricated by Dr Nadia Stelmashenko of the Device Materials Group at the University of Cambridge. The $Cu_{0.43}Ni_{0.57}$ was deposited in ultra-high vacuum (UHV) using DC magnetron co-sputtering onto Si(100) substrates with a 250nm thick oxide layer. The exact composition was controlled by the distance between the substrate and the magnetron. The samples were measured with EDX (Energy dispersive X-ray) analysis which irradiates $5\mu m^2$ of the thin film using an electron beam. The EDX measurements give an accuracy of 5% to the composition of the alloys. $Ni_{0.03}Pd_{0.97}$ and $Ni_{0.05}Pd_{0.95}$ samples were also fabricated by the same group at Cambridge using the same techniques of co-sputtering and composition characterisation. Both Ni_xPd_{1-x} and $Cu_{1-x}Ni_x$, were fabricated with thickness greater than 100nm to ensure that the samples would have negligible series resistance effects. The thicknesses of these alloys were 175nm ($Cu_{0.43}Ni_{0.57}$), 176nm ($Ni_{0.03}Pd_{0.97}$) and 186nm ($Ni_{0.05}Pd_{0.95}$). The expected T_{Curie} of these Ni alloys are 151K, 13K and 80K respectively (taken from Figure 5.2b[10] and Figure 5.2a[25]). A polycrystalline $Ni_{0.19}Pd_{0.81}$ thin film alloy (108 nm thick) was also fabricated by Tim Verhagen from Leiden University. This film was also grown by sputter deposition in a UHV chamber on

to a Si substrate as described by Cirillo et al. [156]. The T_{Curie} of Cirillo et al.'s $Ni_{0.19}Pd_{0.81}$ alloy was measured to be 210K. [156]

SQUID measurements of the $Cu_{0.43}Ni_{0.57}$ samples were taken by Dr. Olga Kazakova and Katharina Zeissler using an MPMS XL 5, Quantum Design instrument driven by MPMS MultiVu Application Software at the National Physical Laboratory, UK. Zero field cool (ZFC) magnetisation measurement was taken by first cooling down from 390K to 2K without an applied field. Then a 0.1T field was applied and the magnetisation measured while warming the sample up to 390K. For the field cool warm (FCW) magnetisation, the sample was first cooled from 390K to 2K with a field of 0.1T, then the measurement was taken as the sample was warmed up to 390K also in 0.1T. Each measurement point is the average of 5 measurements and is repeated 3 times. The magnetisation as a function of temperature for $Cu_{0.43}Ni_{0.57}$ is shown in Figure 5.3e.

Magnetisation of the Ni_xPd_{1-x} samples was taken using the VSM (section 3.1.3). The ZFC and FC magnetization measurement for these samples follows the same method described previously. For $Ni_{0.19}Pd_{0.81}$ liquid nitrogen was used to cool to 80K and the ZFC and FC magnetization measurements were taken up to 280K, shown in Figure 5.3a. The $Ni_{0.03}Pd_{0.97}$ sample was cooled using liquid helium to 4.2K and warmed to 60K, shown in Figure 5.3c. The T_{Curie} for $Ni_{0.19}Pd_{0.81}$ in Figure 5.3a appears to be at 230K, which is slightly higher than a previously measured value of 210K. [156] However, this may be due to a small change in surface composition of the target during sputtering.[157] Similarly for $Ni_{0.03}Pd_{0.97}$ the T_{Curie} in Figure 5.3c seems to be at 50K, which is higher than the expected 13K. A T_{Curie} of 50K would mean that, from Figure 5.2a, the Ni content is 4% and this 1% difference may also be caused by a small change in surface composition of the target during sputtering.

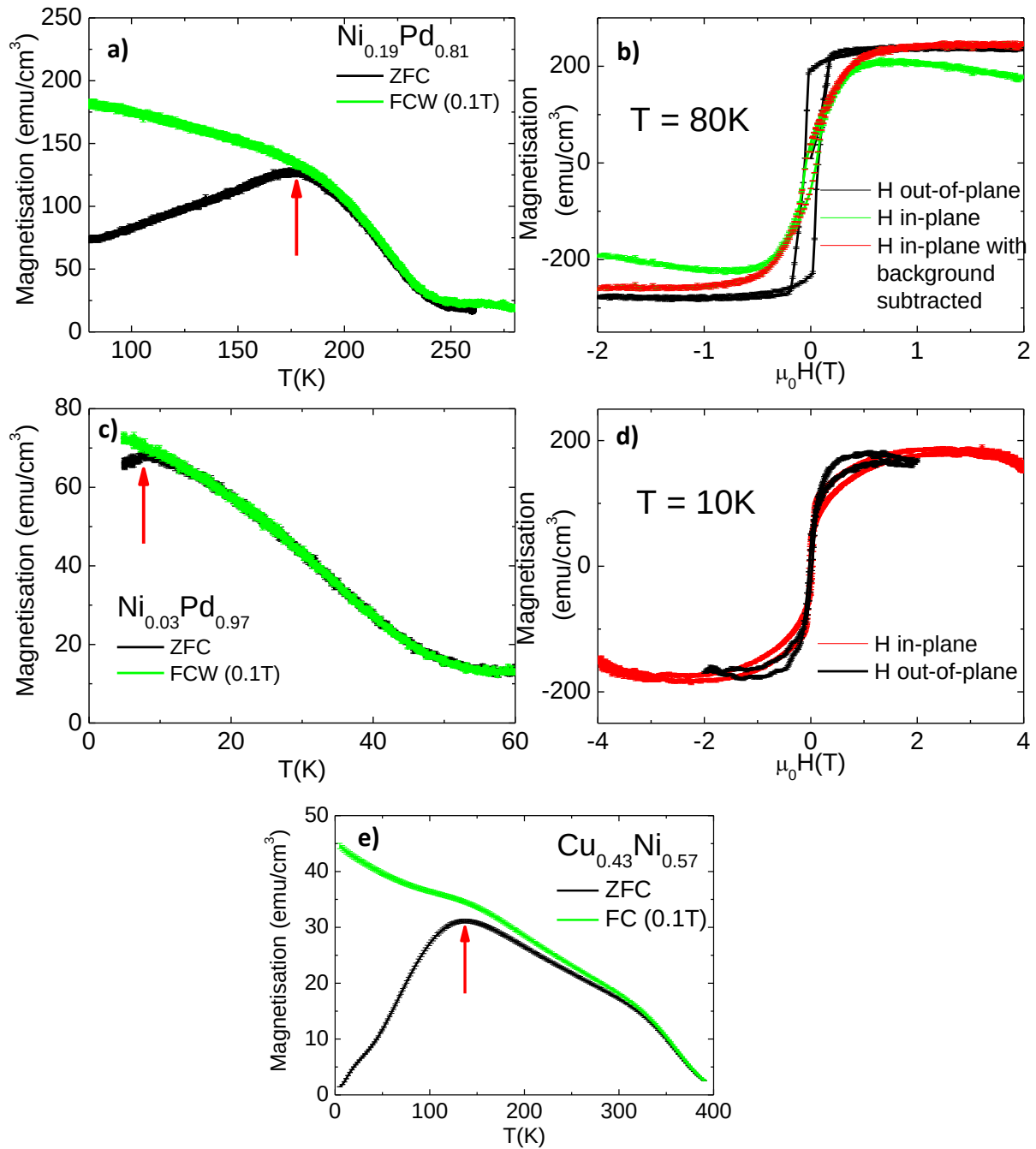


Figure 5.3: a) Magnetisation vs. temperature (M-T) for the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ sample. b) the isothermal M-H measurement of $\text{Ni}_{0.19}\text{Pd}_{0.81}$ taken at 80K indicates an out of plane moment. c) The M-T measurement for $\text{Ni}_{0.03}\text{Pd}_{0.97}$. d) the isothermal M-H measurement of $\text{Ni}_{0.03}\text{Pd}_{0.97}$ at 10K. e) The magnetisation vs. temperature for the $\text{Cu}_{0.43}\text{Ni}_{0.57}$ film. The red arrows in the figures mark the peak (i.e. the blocking temperature) which is at 176K, 7.5K and 138K for $\text{Ni}_{0.19}\text{Pd}_{0.81}$, $\text{Ni}_{0.03}\text{Pd}_{0.97}$ and $\text{Cu}_{0.43}\text{Ni}_{0.57}$ respectively.

M-H measurements of the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ sample at 80K, Figure 5.3b, indicate an easy axis perpendicular to the sample surface and would therefore imply the thin film has an out-of-plane moment, which is similar to the samples from ref.[76] and ref.[9]. Spin-orbit coupling may induce the out-of-plane moment in the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ thin film if there was uniform strain in the plane during film growth.[25] For the $\text{Ni}_{0.03}\text{Pd}_{0.97}$, Figure 5.3d, it is unclear whether the moment is parallel or perpendicular to the surface, however the saturation magnetisation is reached at a lower magnetic field for the out-of-plane M-H measurement; an indication of an out-of-plane easy axis.

The M-T magnetisation measurements on all samples show a peak in the ZFC curve, which is indicated by the arrows in Figure 5.3a, 5.3c and 5.3e. The temperature at which the peak appears is referred to, in the case of superparamagnetic behaviour, as the average blocking temperature, T_B . [158] These peak features have been attributed to the clustering of Ni in the thin film and are an indication of superparamagnetic behaviour of the samples.[159]

It is possible to use the M-H and M-T data of the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ film to estimate the size of the clusters using the relation[154]

$$V = \frac{25k_B T_B}{K} \quad (5.1)$$

Where V is the volume of the cluster, T_B is the blocking temperature and K is the magnetocrystalline anisotropy constant. For the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ film, K can be found by using $K = (M_s H_{co,0})/2$, where M_s is the magnetisation saturation that can be found in Figure 5.3b and $H_{co,0}$ is the coercive field at a temperature of 0K (approximated from [154] using the coercive field, H_{co} , in Figure 5.3b). In CGS units, with $M_s = 238 \text{ emu/cm}^3$ and $H_{co,0} = 2120 \text{ Oe}$, then $K = 2.53 \times 10^5 \text{ ergs/cm}^3$ (or $2.53 \times 10^4 \text{ J/m}^3$). Using the SI unit value of K and with $T_B = 176\text{K}$, the volume of the cluster is $2.40 \times 10^{-24} \text{ m}^3$. Then by assuming the cluster has a spherical volume, it follows that the radius of the cluster is $\sim 8.3\text{nm}$ ($\sim 230,000$ Ni atoms). Furthermore, the volume of the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ film is $4.32 \times 10^{-12} \text{ m}^3$, if we account 19% of that volume (8.21×10^{-13}) is Ni atoms and that the atomic radius of Ni is 135pm [160] then the number of Ni atoms is $\sim 7.97 \times 10^{16}$. Similarly, with an atomic radius of 140pm [160] for Pd, there are 3.04×10^{17} Pd atoms. It has been calculated for $\text{Ni}_{0.19}\text{Pd}_{0.81}$ alloys that the moment per Ni and Pd atoms is $0.6\mu_B$ and $0.2 \mu_B$, respectively.[161] Therefore this would mean that

the theoretical total moment, if all the atoms are polarised, is $1.09 \times 10^{17} \mu_B$ (with $4.78 \times 10^{16} \mu_B$ from Ni and $6.08 \times 10^{16} \mu_B$ for Pd atoms, respectively). Experimentally, from Figure 5.3b, the saturation moment is $8.30 \times 10^{16} \mu_B$ (7.7×10^{-7} emu) so even if all the Ni atoms are polarised, not all the Pd would be.

For $\text{Ni}_{0.03}\text{Pd}_{0.97}$ thin film, $M_s = 180 \text{ emu/cm}^3$, $H_{CO,0} = 2630 \text{ Oe}$ and using similar calculations $K = 2.36 \times 10^5 \text{ ergs/cm}^3$ (or in SI units: $2.36 \times 10^4 \text{ J/m}^3$). With $T_B = 7.5\text{K}$, the volume of the cluster is $1.09 \times 10^{-25} \text{ m}^3$. Then by assuming the cluster has a spherical volume, it follows that the radius of the cluster is 3nm ($\sim 10,000$ Ni atoms). The moment of this cluster would be $6,000\mu_B$ ($0.6\mu_B \times 10,000$). The volume of $\text{Ni}_{0.03}\text{Pd}_{0.97}$ is $1.45 \times 10^{-12} \text{ m}^3$ and with 3% of that volume is Ni ($4.35 \times 10^{-14} \text{ m}^3$) this means there are 4.22×10^{15} Ni atoms and 1.23×10^{17} Pd atoms. The moment from the Ni and Pd is then expected to be $2.53 \times 10^{15} \mu_B$ and $2.46 \times 10^{16} \mu_B$, respectively. However experimentally, Figure 5.3d, the saturation moment is $2.87 \times 10^{16} \mu_B$ close to the sum of the moments from Ni atoms.

In section 5.2 it was mentioned that a cluster of three Ni atoms had a polarising radius of at least 1nm ($10\text{\AA}$). Therefore we could assume that clusters with a radius of 8.3nm or 3nm and a moment of $138,000\mu_B$ ($\sim 230,000$ Ni atoms) and $6000\mu_B$ ($\sim 10,000$ Ni atoms), respectively, may have a longer polarising radius that will polarise the surrounding Ni and Pd atoms. However, from the saturation magnetisation of the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ and $\text{Ni}_{0.03}\text{Pd}_{0.97}$, it would seem the polarising radius of the clusters do not appear to be significant enough to polarise all Pd atoms in the thin films.

5.4 PCARS measurements of Cu, Ni and Ni_{0.19}Pd_{0.81} - Degeneracy of $\chi^2(P)$

In this section I first look at PCARS measurements in samples where degenerate fits to the spectra can occur. Then Ni_{0.19}Pd_{0.81} spectra taken at different contact resistances, R_{CB} , (i.e. varying the tip pressure) are presented. A unique fit may be difficult to obtain for a spectrum with significant broadening as broadening can make it difficult to distinguish the effects due to P and Z.[20] This problem has been modelled and discussed previously in section 3.2.3. Under these circumstances, I explore the validity of using a fixed gap fit, $\Delta = 1.5\text{meV}$, as discussed in section 3.2.8. The Ni concentration in the Ni_{0.19}Pd_{0.81} film would suggest that polarisation is low, but a fixed gap fitting routine gives an unexpected finite polarisation and this is discussed in the following sections.

5.4.1 Distinguishability of fits to Cu (P=0%) and an FM with Intermediate P

For a sample with expected zero spin polarisation like Cu, Figure 5.4a, broadening of the spectrum causes a divergent $\chi^2(P)$ from the full four-parameter fit, Figure 5.4b and puts an upper bound on polarisation of Cu, determined by the PCAR technique to be $P \leq 40\%$. In the previous chapter Ho spectra were fitted with a fixed gap to resolve issues of degenerate fits. The result of such a fit, with $\Delta_{Nb} = 1.5\text{meV}$, for Cu can be seen to give a finite value for P; not expected for a material with $P=0$ (green curve in Figure 5.4a). In section 3.2.4 we saw that a fixed $\Delta = 1.5\text{meV}$ fit to spectra that had a suppressed Δ would overestimate the value of P. However, since it is Cu, the spectrum can be fitted under the reasonable assumption that $P = 0$, the corresponding parameters are shown in Figure 5.4a (red curve). With $P = 0$ the Δ value is suppressed (0.91meV) and gives a $\omega = 0.54\text{meV}$.

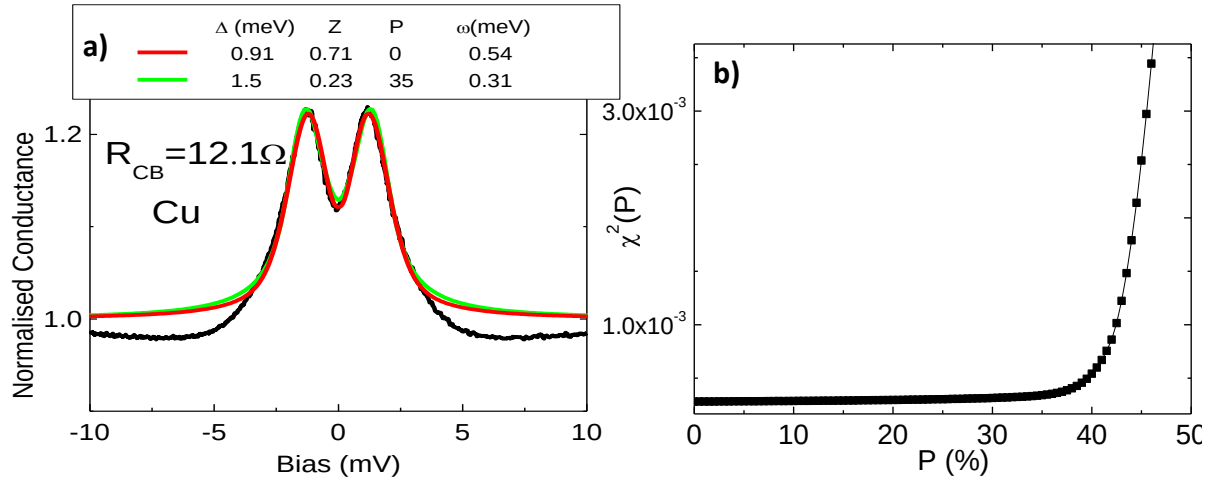


Figure 5.4: a) PCARS of Nb-Cu at 4.2K showing theoretical fits to the experimental data with $P=0\%$ and $\Delta=1.5$ meV and b) the $\chi^2(P)$ fit.

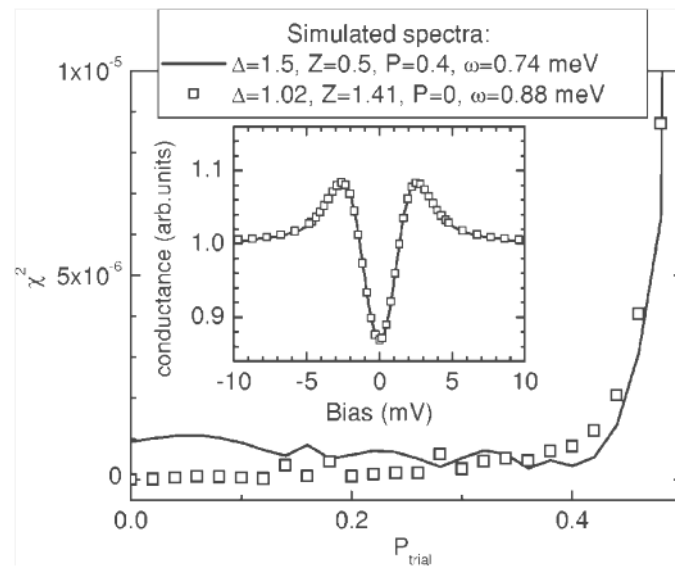


Figure 5.5: Results of a $\chi^2(P)$ fit for the two generated curves (shown in the inset) taken from ref.[20] showing how a full-four parameter fit can result in degeneracy. The two generated curves have polarisations of 40% (line) and 0% (square points), respectively with strong broadening.

Even for a FM with intermediate polarisation, such as Ni [19], broadening also causes the spectral resolution to be compromised [20] and the fitting procedure may fail to distinguish whether the dipcentral feature at zero bias (peak/dip in conductance) is due to P or Z . This was modelled in section 3.2.3. Dr. Fredrik Magnus has also modelled the effects of the Z parameter on broadened spectra and showed that even a high Z in the low broadening

regime can still have a significant effect on the ability to determine a reliable value of P . [3, 144]

An example of degenerate fits, from a full four-parameter fit, for Ni samples are given in Figure 5.6a and 5.6c for Nb-Ni and Pb-Ni contacts, respectively. Here, only an upper bound P can be determined (i.e. where $\chi^2(P)$ diverges). The method of identifying an upper bound would in reality be arbitrary but as long as the method is consistent then upper bound results may be comparable, although still not ideal. In this case in Figure 5.6b and 5.6d the upper bound is chosen at a point where $\chi^2(P)$ is twice the value of $\chi^2(P=0)$.

The parameters from the upper bound of the $\chi^2(P)$ fits are shown (green curves) in Figure 5.6a and Figure 5.6c. For both Pb-Ni and Nb-Ni, the Δ is large and unphysical. Therefore, for consistency, we apply the same method previously used in section 4.6.1, which is to use a fixed Δ fit. These parameters are also shown (red curves) in Figure 5.6a and Figure 5.6c.

We have shown that Both Cu and Ni spectra affected by significant broadening gave degenerate $\chi^2(P)$ fits. A $P=0$ and $P=35\%$ spectra can be used to fit a Cu spectrum while a $P = 38.5\%$ spectra can be used to fit a Ni spectrum with Nb tip. Bugoslavsky et al. [20]. Also demonstrated , by simulating spectra with high broadening, that it wouldn't be possible to distinguish a spectrum with $P = 40\%$ and $\omega = 0.74\text{meV}$ (70% of $\Delta/\sqrt{2}$) from a spectrum with $P = 0$ and $\omega = 0.88\text{meV}$ (122% of $\Delta/\sqrt{2}$), Figure 5.5 (from ref.[20]). Bugoslavsky et al. [20] have also confirmed from Nb-Cu PCARS measurements that significant broadening allows Cu spectra to be fitted with P up to 40%. This makes it exceedingly difficult to distinguish spectra of Cu from that of Ni. It is therefore unlikely that the P of a $\text{Cu}_{0.43}\text{Ni}_{0.57}$ sample will be able to be uniquely determined.

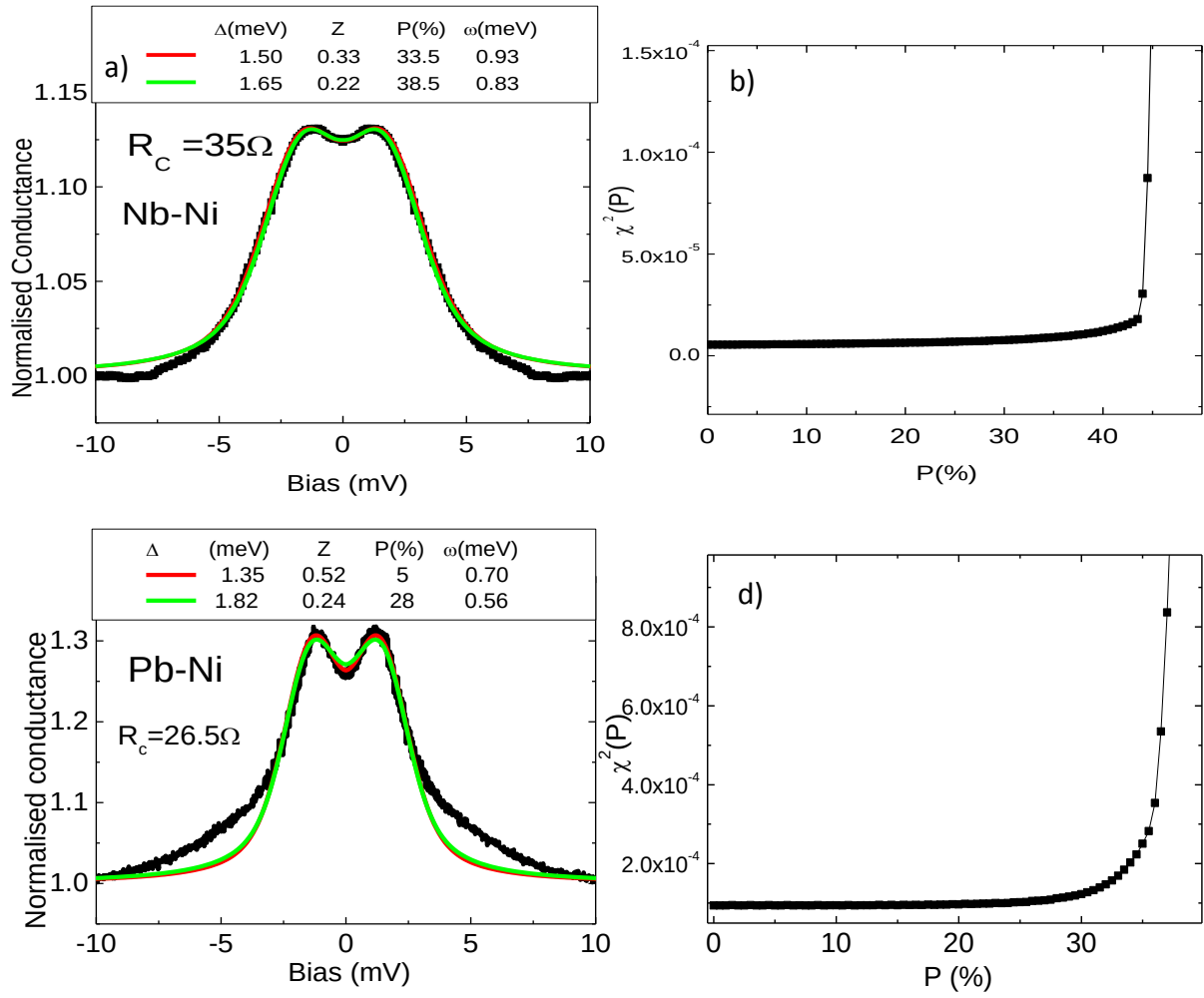


Figure 5.6: a) PCARS of Nb-Ni at 4.2K showing theoretical fits to the experimental data for upper bound $P=38.5\%$ (green curve) from b) $\chi^2(P)$. c) PCARS of Pb-Ni at 4.2K showing theoretical fits to the experimental data with upper bound $P=28\%$ (green curve) from d) $\chi^2(P)$. The red curve in a) and c) are obtained from fixed $\Delta_{Nb} = 1.5\text{meV}$ and $\Delta_{Pb} = 1.35\text{meV}$ fit [7].

5.4.2 PCARS of $\text{Ni}_{0.19}\text{Pd}_{0.81}$

The next few sections look at PCARS results for an alloy ($\text{Ni}_{0.19}\text{Pd}_{0.81}$) that has an out-of-plane moment to the sample surface. As was stated at the beginning of this chapter, $\text{Ni}_x\text{Pd}_{1-x}$ alloys are used in complex SC/FM/SC Josephson junction experiments to help generate the LRSTPE, although it does not generate the LRSTPE by itself.[15, 17, 28, 69]

As with the Cu and Ni fitting, the spectra for the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ sample, Figure 5.7a and 5.7 b, produce non-unique, degenerate $\chi^2(P)$ curves using a full four-parameter fitting and as such only an upper bound can be ascertained for the polarisation. An example of the degenerate fit and the corresponding $\chi^2(P)$ of a $\text{Ni}_{0.19}\text{Pd}_{0.81}$ spectrum is shown in Figure 5.7c and 5.7d respectively. The parameters from the upper bound of $\chi^2(P)$, like in the Ni case, gives an unphysical high value of Δ and alternatively the $P = 0$ parameter set has a reasonable energy gap value but yields $\omega = 0.81\text{meV}$ which is quite significant. In order to see if there were any systematic changes in P , Z and ω , fits were done with Δ fixed to 1.5meV . As was mentioned in section 4.5.2, although this method does not give reliable quantitative values in P , Z and ω , it is possible to identify trends in the parameters as a function of contact resistance even though the error in the values is unknown.

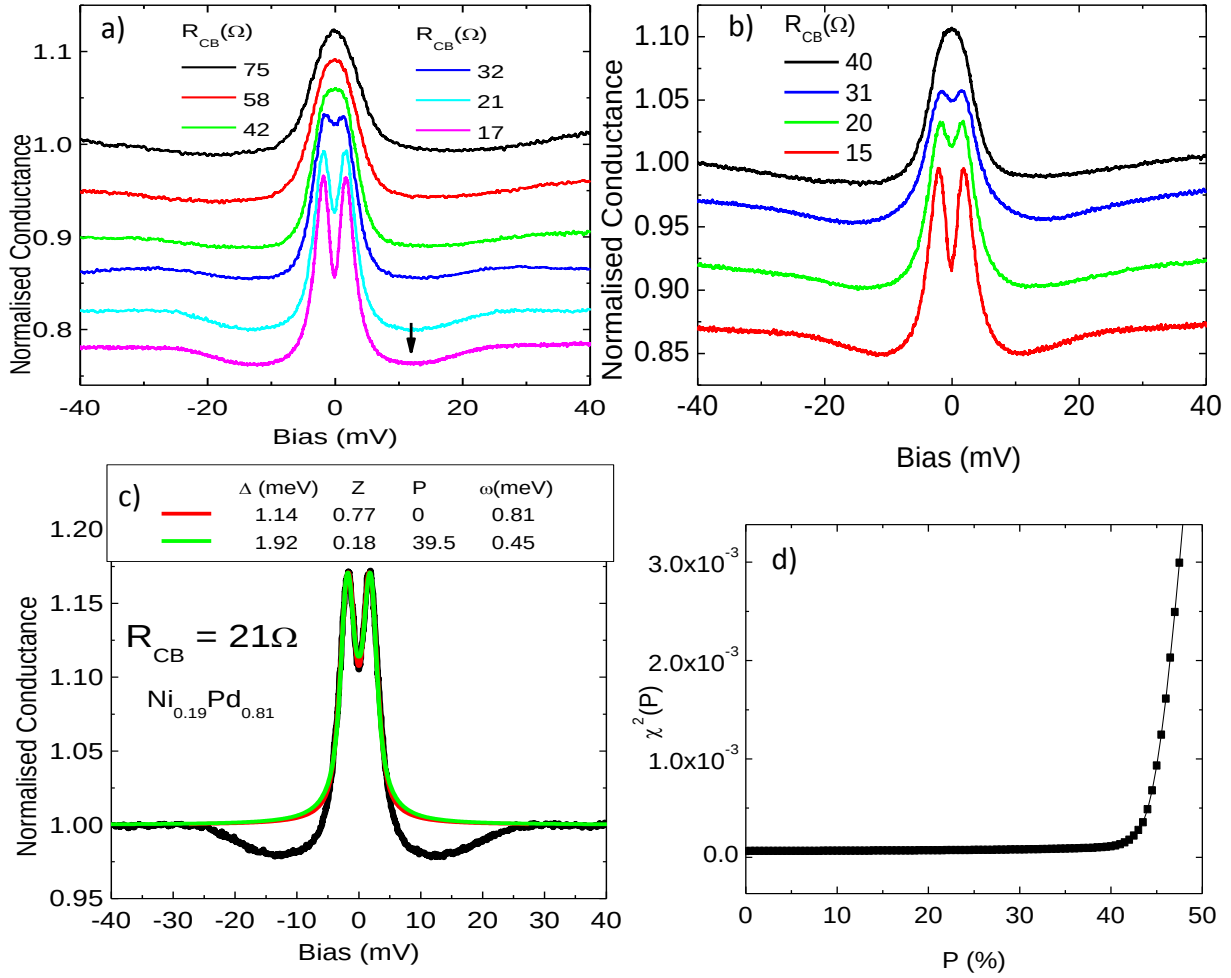


Figure 5.7: a) and b) are the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ spectra taken with a Nb tip at 4.2K as a function of R_{CB} defined in chapter 4. They are from two different contacts. The dip (marked by an arrow) comes in as the contact resistance decreases. The dips have has been discussed in section 3.2.7. Spectra have been normalised at 30mV and offset from highest R_{CB} at the top to lowest at the bottom. c) PCARS of $\text{Ni}_{0.19}\text{Pd}_{0.81}$ taken at 4.2K showing theoretical fits to the experimental data with $P = 0\%$ and an upper $P = 39.5\%$. These are taken from c) the degenerate $\chi^2(P)$.

5.4.3 Fixed Gap Fit Results

The spectra, as a function of R_{CB} , in Figure 5.7a and 5.7b were fitting using a fixed $\Delta = 1.5\text{meV}$ and $P(R_{\text{CB}})$, $Z(R_{\text{CB}})$, and $\omega(R_{\text{CB}})$ shown in Figure 5.8a, 5.8b and 5.8c, respectively. The P value from the fixed gap fit resulted in values of 25% - 40%. However, it is likely that the actual polarisation of the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ sample would be much lower, as it has low T_{Curie}

and low Ni content. Previously in section 3.2.8, theoretical spectra with suppressed and enhanced Δ were investigated to see how fits with fixed $\Delta = 1.5\text{meV}$ affects P , Z and ω values. It was found that for a generated spectrum with low P and a gap of $\Delta = 1\text{meV}$, a fixed $\Delta = 1.5\text{meV}$ fit overestimates the value of P by $\sim 20\% - 30\%$ for a spectrum with $P = 0$. Therefore, it is possible that the finite P value from the fits to the $\text{Nb-Ni}_{0.19}\text{Pd}_{0.81}$ spectra is an artefact from a fixed Δ fit.

In Figure 5.8a, 5.8b and 5.8c the Ho thin film data is also included to compare with the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ thin film as the initial intention was to compare PCARS of different FM materials as a function of tip pressure. The main difference between the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ and Ho thin film trends is that the Ho thin film show “sharp” changes in all three parameters as the contact resistance decreases. The $\text{Ni}_{0.19}\text{Pd}_{0.81}$ thin film, however, does not show similar signs that would indicate some change in scattering or mixing that was suggested for the Ho thin film.

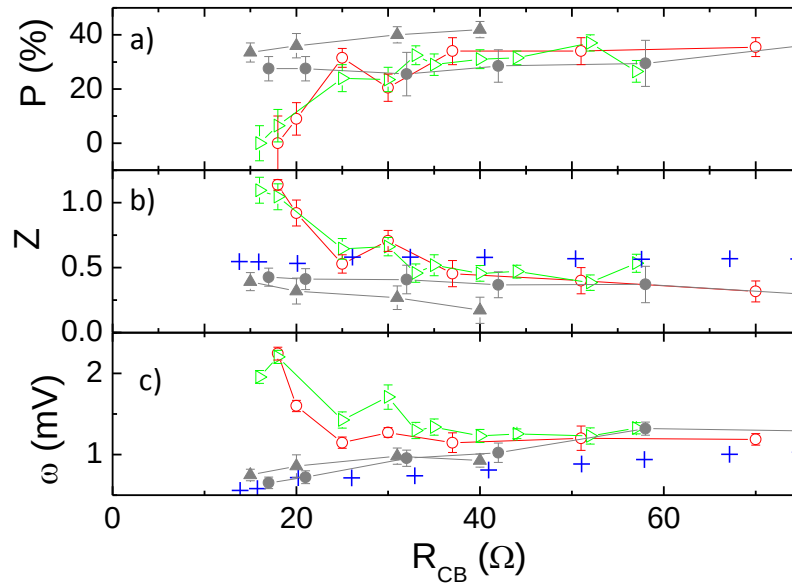


Figure 5.8: Dependence of a) P , b) Z and c) ω vs. R_{CB} for $\text{Ni}_{0.19}\text{Pd}_{0.81}$ (filled triangles and circles are two separate contacts) which were fitted with fixed $\Delta = 1.5\text{meV}$ and Cu Foil (blue cross ref. [20]) which were fitted with $P = 0$. The open symbols are from Ho thin film in Figure 4.14.

5.4.4 Is it possible the polarisation value is real?

It is known that ferromagnetic clusters can affect the measured polarisation of a sample.[77, 162, 163] In their experiments with Co/Pt and Co/Ir nanojunctions, Taddei et al.[77] showed how the magnetic moment at the surface of Co can be enhanced and that band structure mismatch at the interface leads to a surface polarisation value that is different to the bulk of the FM.[77] P was enhanced by 12%. The magnetic moment is enhanced because the orbital component of the magnetisation at the surface is not suppressed.[77, 164] At the surface, the symmetry of the cubic crystal is broken and so the charge distribution is reduced which means the orbital component is partially suppressed. [77, 164] This is contrary when in the bulk of the sample where the crystal fields from the distribution of electric charge density in the cubic crystal suppresses the orbital component of the magnetisation.

This enhanced magnetisation has also been seen by Billas et al. [162] in samples where small Ni clusters were shown to have moments greater than the bulk value of Ni, $1\mu_B$ per Ni atom, and as the size of a cluster is increased the moment became comparable to the bulk value of Ni. Billas et al.[162] explained that the moments can be affected by spatially oscillating spin density waves that propagate from the surface of the cluster into its centre. The moment of an atom in the cluster would depend on its distance from the surface, with the surface atoms having larger moments than the inner atoms.

Enhanced magnetisation was also found in Co clusters by Izquierdo et al. [163] They did a theoretical study of Co clusters grown on Cu(111) that formed triangular islands that didn't coalesce, with the sides of the islands having a length of $25.55\text{\AA}$. The local magnetisation of each triangular island was shown to have increased by 40% from that of Billas et al. [162] with the smallest increase found at the centre and the largest found at the corners of the Co islands due to reduced symmetry.

In Taddei et al.'s [77] case polarisation is defined in a similar way equation (2.7). However it has to be mentioned that the polarisations defined by Billas et al. [162] and Izquierdo et al. [163] are mainly the enhancement of the magnetic moment per atom in clusters and does not describe the polarisation of current going through a FM/SC contact. However, the main

emphasis here is that clusters can enhance magnetisation and may affect the polarisation of current going through the tip.

From Figure 5.9, the value of P between 20%-45% is similar to that of Ni as indicated by Strijkers et al. [19] with similar trend in the $P(Z)$ (open squares in Figure 5.9a) between $Z=0$ to $Z=0.5$. The effects of clusters may dominate and cause this enhanced polarisation effect, which could explain why the P values are similar to that found for Ni PCARS.[19] If we assume that Ni clusters in the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ and $\text{Ni}_{0.03}\text{Pd}_{0.97}$ thin film (calculated in section 5.3) are distributed homogenously then the volume per Ni cluster is $1.26 \times 10^{-23} \text{ m}^3$ and $3.63 \times 10^{-24} \text{ m}^3$, respectively. This means the radius per Ni cluster in the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ and $\text{Ni}_{0.03}\text{Pd}_{0.97}$ thin film is 14nm and 9.5nm, respectively and the distance between Ni clusters is 28nm and 19nm, respectively. Therefore it is possible that a PCARS tip in the order of nanometres may be able to sample the clusters that polarise the Pd surrounding it.

However the fitting of the spectra, and therefore the P values, are still subject to a fixed $\Delta = 1.5\text{meV}$ fit and would only be valid if the value of Δ of the Nb tip is also 1.5meV; only then the result seen in Figure 5.9 can be justified as an effect of FM clusters. However, since the superconducting gap is unknown for the PCARS experimental spectra, it can only be said that the finite polarisation is a consequence of the fixed Δ fitting procedure. So the focus of the analysis would rather be on the trends of the parameters rather than the values. The P and Z parameters plotted against the contact resistance, R_{CB} , shown in Figure 5.8a and 5.8b respectively would seem to show constant trend with decreasing R_{CB} for the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ sample. If the surface layer polarisation is enhanced compared to the bulk then by pushing the tip down, as suggested by Yates et al. [109], it is possible to penetrate the surface layer such that P changes as a function of R_{CB} . However, the absolute value of P is unknown and may have a considerable degree of error on its determination. Moreover, previously (section 3.2.4) it was mentioned that a $\Delta = 1.5\text{meV}$ gap fit to a suppressed gap contact ($\Delta = 1\text{meV}$) could involve an error of up to $P \sim 20\% - 30\%$ for spectra with low P . This would mean the apparent slight change of P and Z parameters in Figure 5.8a and 5.8b is not significant within error, and so it is not possible to say that there is any trend.

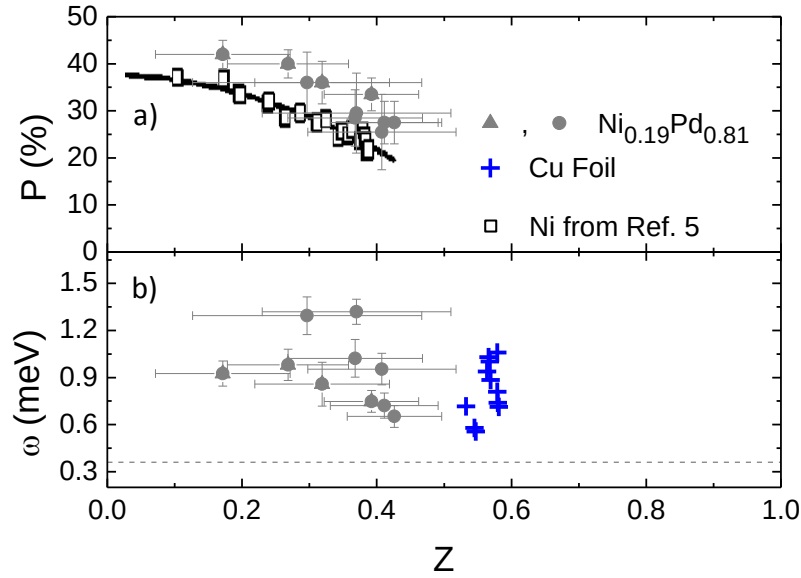


Figure 5.9: a) Dependence of a) P , and b) ω vs. interface scattering parameter Z for $\text{Ni}_{0.19}\text{Pd}_{0.81}$ (filled circles and triangles, from Figure 5.8) and Cu Foil (blue cross from ref. [20]). The open squares are $P(Z)$ of Ni from ref. [19]. The dashed line is $k_B T = 0.36 \text{ meV}$.

Comparison of $\omega(R_{CB})$ for $\text{Ni}_{0.19}\text{Pd}_{0.81}$ and Cu, filled triangles/circles and blue crosses, respectively, in Figure 5.8c, shows something that you would expect as you penetrate the surface of magnetic dead layers. These dead layers cause inelastic scattering at the surface which adds to the broadening.[144] In ref.[93] a correlation was observed that showed ω and Z can be correlated at NiMnSb-Nb and $\text{Co}_2\text{MnSi-Nb}$ contacts, indicating that increased interface scattering mechanism, in that case, also increases the broadening. However in Figure 5.9 there are no general trends for $\omega(Z)$ that can be identified.

5.4.5 Modelling the Effects of an Out-of-plane Moment on the PCARS spectra

Previously in section 4.6.2, the effect of an out of plane moment on the spectra was investigated, in order to rule out any possibility that the anomalous trends observed there were caused by the tip experiencing a strong stray field as it was pushed into the surface of the Ho sample. The effect was for a 3-parameter fit in which P increases while Z and ω decreases with increasing field parameter $h = H/H_{C2}$ (where H is the field, H_{C2} is the upper critical field of the superconductor, see section 3.3). The experimental spectra are

shown in Figure 5.7a and the experimental spectrum in which increasing h was applied is the spectrum with $R_{CB} = 21\Omega$. The results are shown in Figure 5.10a. The same results from section 3.2.9 also apply here, Figure 5.10b, that the stray field at the tip is not having the effect of changing P and Z seen in Figure 5.8a.

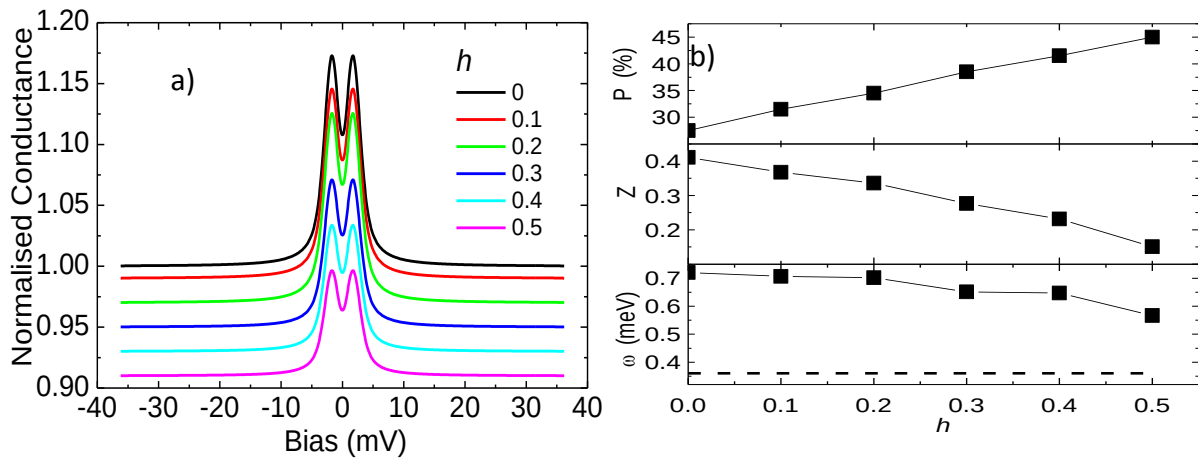


Figure 5.10: a) Theoretical spectra taken from the extracted fit parameters of the spectrum with $R_{CB}=21\Omega$ with varying magnetic field, h , added to simulate the tip experiencing stray magnetic field from the out of plane moment of the thin film. b) the fixed Δ fit to the spectra in a) showing the trend of the parameters with h . The dashed line is the thermal broadening at 4.2K (0.36meV).

5.5 Temperature Dependent PCARS of $\text{Ni}_{0.03}\text{Pd}_{0.97}$

In samples with low polarisation, systematic changes of parameters with external controls such as magnetic field and temperature can help validate the fitting procedure (the variation of Δ and ω). Study of these very dilute alloys proved too challenging to comment in detail on the variation of P and Z . Nevertheless in this section we examine examples of spectra taken as a function of temperature. The only sample that we had access to that had a T_B below the critical temperature of Nb (9.2K) was the $\text{Ni}_{0.03}\text{Pd}_{0.97}$ thin film. The purpose of this is to observe how spin fluctuation affects the parameters P , Z and ω . Temperature measurements were taken from 5K

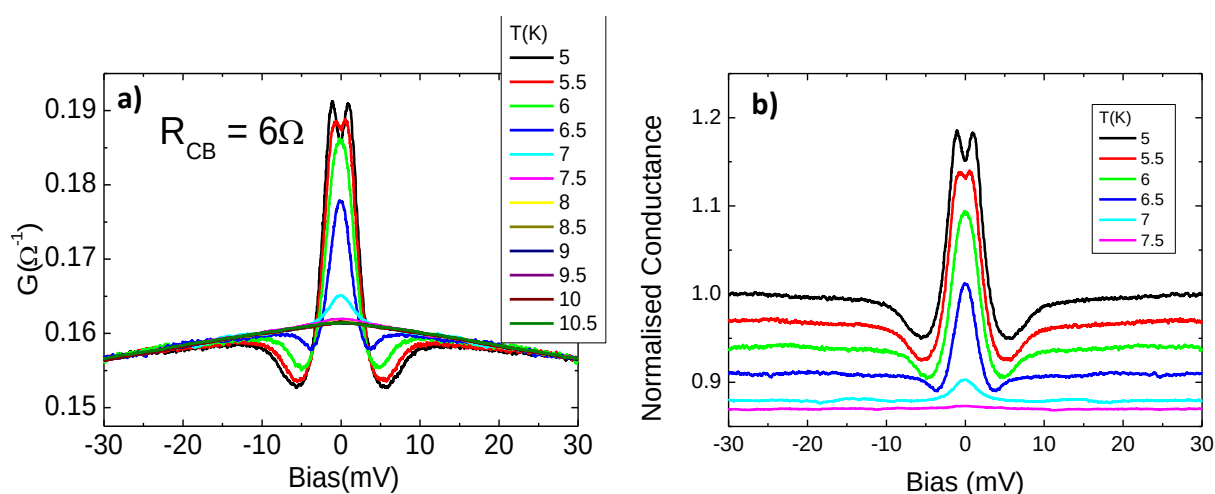


Figure 5.11: a) PCARS spectra of $\text{Ni}_{0.03}\text{Pd}_{0.97}$ taken as a function of temperature at $R_{CB} = 6\Omega$ with a Nb tip. b) the spectra of a) normalised to the background taken at 10.5K and with an offset.

The PCARS measurement of the $\text{Ni}_{0.03}\text{Pd}_{0.97}$ using a Nb tip from 5K to $T > T_C$, ($T_C = 9.2\text{K}$), is shown in Figure 5.11a. There is a linear inverse background that persists throughout the spectra as the temperature is increased. This background does not change significantly above a temperature, $T \sim 8\text{K}$, which could indicate a suppressed superconducting critical temperature of the Nb tip. The spectra in Figure 5.11a were normalised to the background taken at 10.5K to give the flat background spectra, shown in Figure 5.11b.

The superconducting critical temperature could be confirmed by plotting the conductance at zero bias (from Figure 5.11a) as a function of temperature, shown in Figure 5.12a. This $G(V = 0)$ vs. T plot suggests a suppression of the superconducting critical temperature at

8K which implies that $\Delta_{\text{Nb}}(T)$ is also suppressed. The fact that the background on the spectra shows a decreasing conductance with voltage (Figure 5.11a) is also consistent with heating at the tip interface which would result in the appearance of a suppressed T_C .

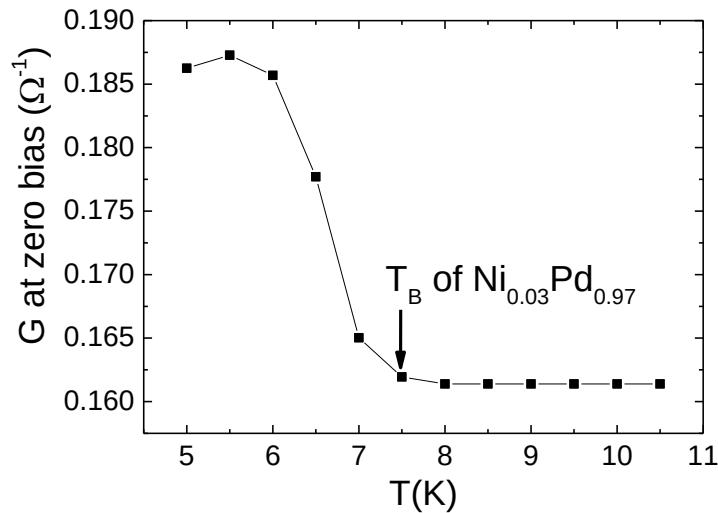


Figure 5.12: The zero bias conductance of Figure 5.11a plotted with temperature, to give the suppressed superconductor critical temperature of 8K.

5.5.1 Fitting with Fixed P=0%

Since the Ni concentration is only 3% then it is likely that P is closer to or even 0%. In Figure 5.13b the effect of fitting the spectra with fixed P=0 on the parameters is shown (black square data points). In this case the $\Delta(T)$ is suppressed way below the theoretical BCS values of Nb with $T_C = 9.2\text{K}$ (red triangle data points). However the theoretical BCS values of $\Delta(T)$ with suppressed $T_C = 8\text{K}$ (blue circle data points) are closer to but still exceed the black data points. The Z parameter however is constant up to 6K but dramatically increases above it and would reflect the decrease in transparency of the interface as the conductance (in Figure 5.12 starts to decrease at this point. The broadening parameter ω is also constant up to 6K but dips at 6.5K within error. The dramatic increase in Z above 6K is, interestingly, in the region of the blocking temperature (T_B) for $\text{Ni}_{0.03}\text{Pd}_{0.97}$ which has been identified to be 7.5K (see section 5.3, Figure 5.3c).

This increasing $Z(T)$ trend may be due to the tip approaching T_C of the Nb tip since T_C appears to be suppressed in this case. However this increase in $Z(T)$ also appears in a region where Mukhopadhyay et al. (as explained in section 5.1) saw an increase in Z in a region of spin fluctuations, which may be the reason for the increase in Z seen in $\text{Ni}_{0.03}\text{Pd}_{0.97}$, Figure 5.13.

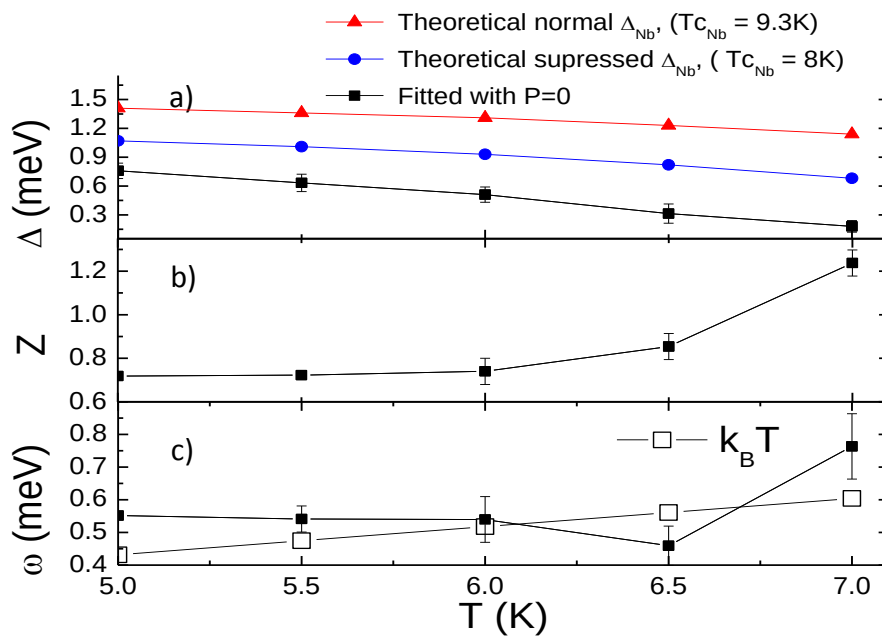


Figure 5.13: The black squares in a), b), c) are the Δ , Z and ω trends when the spectra are fitted with a fixed $P = 0$. The red triangle and blue circle data points are the BCS $\Delta(T)$ curve if we assume T_C is 9.2K and 8K respectively.

5.6 Chapter 5 Conclusion

We wanted to examine the behaviour of simple FMs as a function of the tip pressure. The simplest case was Mn-Al doped ZnO, all other systems have proved complicated to fit for a variety of reasons. We did make an interesting excursion to look in more detail at the low T_{Curie} films and we found that the P , Z trends with R_{CB} were flat (with a three-parameter fixed gap fitting) and the $Ni_{0.03}Pd_{0.97}$ thin film showed an interesting enhanced Z as T_B was approached.

It is worth noting that this increase in Z near T_B is mirrored by the increase in Z with decreasing R_{CB} (contact resistance) for Ho-Nb PCARS (section 4.6). The increase in Z may then be due to an increase in spin mixing or spin scattering at the interface in both cases. It is reasonable then to suggest that the $Z(T)$ trend observed from PCARS of $NdNi_5$ -Nb PCARS is related to spin mixing/spin scattering.

6 Conclusions and Future Work

6.1 Conclusion

The motivation of this thesis was to investigate SC/FM interfaces to see if signatures associated with spin mixing can be identified with Point-contact Andreev Reflection spectroscopy. The main experimental method chosen to obtain conductance spectra was from PCARS. Spectra obtained using PCARS were analysed with a fitting procedure developed by Dr. Yura Bugoslavsky[20] adapting Mazin et al.'s modified BTK model.[92] Holmium and $\text{Ni}_x\text{Pd}_{1-x}$ (the FM material that was investigated in chapter 4 and 5, respectively) have been used in previous experiments as components that induces spin mixing. Spectra were primarily taken as a function of tip pressure to observe any changes in the P and Z behaviour at the SC/FM interface.

Due to degeneracy of the full four-parameter $\chi^2(P)$ fits of the Ho and $\text{Ni}_x\text{Pd}_{1-x}$ alloys, explained in chapter 4 and 5 respectively, a fixed Δ fitting procedure was implemented for all the experimental spectra in this thesis. The result from these fits to the Ho spectra show anomalous behaviour of P and Z as the contact resistance decreases (equivalent to an increase in tip pressure). I interpreted this behaviour as the result of the tip experiencing different interface regimes as it is pressed onto the Ho sample. Usually when a tip penetrates a surface layer, a cleaner interface is experienced and Z should decrease and maximal P is observed. This effect is akin to the results on Mn-Al doped ZnO where P increases and Z decreases.[109] However, as the tip passes through the surface layer in Ho single crystal (e.g. a magnetic dead layer), then the tip experiences more of the Ho resulting in an increase in spin scattering or mixing (increasing Z) and P decreasing, although there is no means to differentiate. For Ho thin film capped with Au, P remains constant until the tip punctures the Au capping layer and experiences the intrinsic spin mixing of Ho which results in high Z and low P similar to the single crystal. However, similar fixed Δ fitting of $\text{Ni}_{0.19}\text{Pd}_{0.81}$ thin film spectra did not show a significant change in P and Z as a function of tip pressure.

PCARS measurements of $\text{Ni}_{0.03}\text{Pd}_{0.97}$ as a function of temperature was fitted with fixed $P=0\%$ produced results that showed increasing Z with temperature; similar to that of Mukhaphdayay et al.[16] I suggested that spin fluctuations may be causing the tip to experience an increase in scattering.

However, in this thesis the main problems that arose were to do with the fitting of conductance spectra. These included how to fit spectra with features such as backgrounds, dips, high smearing and possible effects of the sample series resistance on the spectra. A pre-fitting procedure to remove background features of the H_0 spectra was implemented to remove any ambiguity of the normalisation point during fitting. A problem of degenerate fits to a spectrum with significant broadening was also highlighted, which was the reason for the fixed Δ fittings. I show from fitting to theoretically generated curves in section 3.2.4 that the absolute values of the fitting parameter obtained using fixed gap fits are unphysical. However in section 4.5.2 it was discussed that, from a fixed Δ fit of spectra set, the trend of the parameters may have a valid significance, shedding more light on the interpretation of the underlying physics.

6.2 Future work

The future of studying the spin triplet proximity effect would be in fabrication of planar contact devices that will possibly allow control of inhomogeneity of the SC/FM interface and to an extent control of the spin triplet proximity effect. It is possible that different scattering layers between the Ho and Nb may have an effect on spin mixing. Therefore it worth investigating FM/SC interfaces of varying junction resistance or observe different scattering layer thickness between the FM and SC. A bonus of fabricating planar contacts would be the ability to compare results from many trials of the same contact; within similar conditions (e.g. thermal or magnetic field). To do this I would fabricate an array of Pb/FM contacts with various sizes, Figure 6.1. However I would start of first with fabrication of Pb/Au arrays to investigate if the size of the contacts can be easily reproduced including whether a clean/dirty interface can be reproduced.

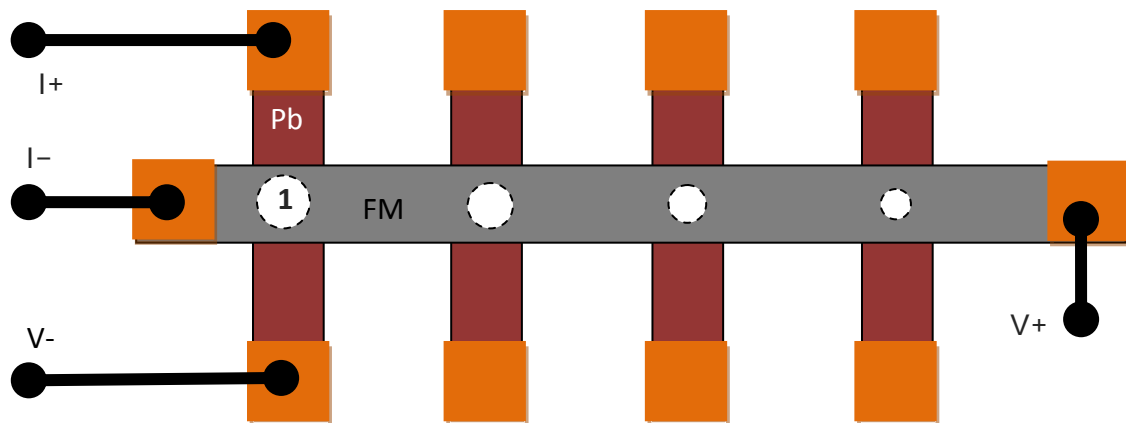


Figure 6.1: Array of Pb/FM contacts formed from strips of Pb (red) and FM (grey) with the varying contact sizes (circles). The orange are current and voltage pads. The black lines are the current and voltage leads for measuring a particular contact, i.e. '1'. Measuring other contacts requires simple rearrangement the current/voltage leads.

Another future work would be to further investigate the signatures of the spin triplet pair at a single FM/SC interface using a thin film structure such as the one in Figure 6.2. The wedge shape of the Ho layer allows a thickness gradient across the thin film so that the 'long range'

effect of the spin triplet pair can be tested. The Au contacts would then be patterned onto the Ho at different points to measure the conductance spectra at different Ho thicknesses. Notches would then be milled down to the Nb layer to ensure each contact is separated from each other.

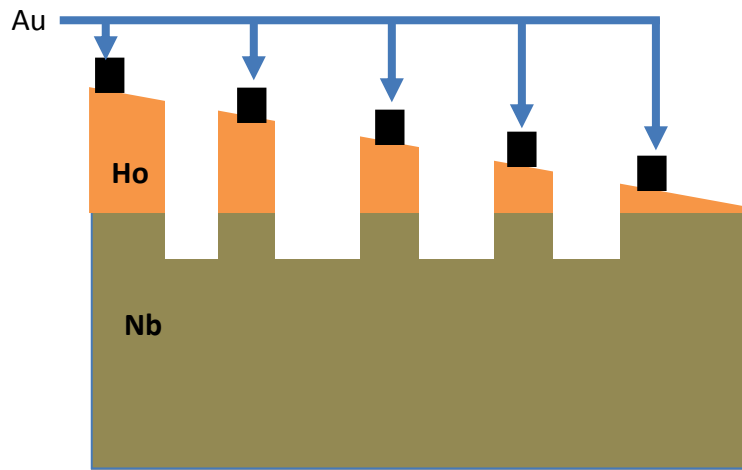


Figure 6.2: Ho-Nb thin film with a wedge shape Ho layer and Au contacts. The notches are there to ensure each contact is separated from each other.

In a recent experiment by Robinson et al.[165] SC/FM/SC junctions were investigated in which the FM included a Bloch domain wall made by using Ni-Gd-Ni layers. The domain wall rotation can be controlled by altering the thickness of the Gd and they found supercurrent signatures that were attributed to the conversion between spin singlet and triplet pairs (i.e. spin mixing). A way to possibly control inhomogeneity, and therefore the spin mixing, would be to control the moment alignment of the domain wall. However in the method used by Robinson et al.[165], it involved warming to room temperature followed by cooling after applying a field. A more direct approach would be if domain walls were controlled directly via a magnetic field. A possible method would be to use FM nanowires that have notches to pin domain walls[166] and by applying a magnetic field the domains can be move from one notch to another. This means it is possible to design planar device in such a way that the notch is placed within proximity or under a SC/FM interface, Figure 6.3. The domain wall would then act as the inhomogeneous interface. However this idea may not work, if there is a possibility of out-of-plane moments that can cause the SC to turn normal as the SC/FM interface.

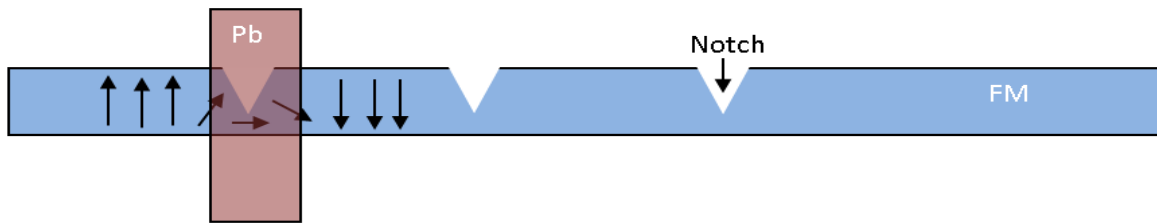


Figure 6.3: An FM wire (blue) has domain walls pinned at the notch and a Pb strip (red) would be placed over the region of the domain wall.

There are also spin mixing models that were mentioned in chapter 2 that would be interesting to test, such as the model of Löfwander et al. [7]. This models the zero bias conductance (Figure 2.14) of a half metal as a function of temperature and can be tested without PCARS. It can also be tested by a structure similar to that in Figure 6.1 but with the FM a half metal like CrO_2 and provides an additional way to identify if there are any correlations with the interface resistance. The model of Grein et al. [24] could also be investigated so that it is adapted to the current four-parameter fitting procedure to see if the spin mixing angle model provides a better understanding of the PCARS of Ho as a function of tip pressure. Also, the subgap structure seen in the theoretical conductance of Grein et al. [24] is something that wasn't seen in the spectra I measured, and may be a result of smearing at small but finite temperatures (i.e. 4.2K). Therefore, measuring at lower temperatures could show the subgap structure which may be more feasible using a fabricated planar SC/FM junction measured in a cryogen-free magnet system (CFM). However this idea may not work as there is a possibility of out-of-plane moments that can cause the SC to turn normal at the SC/FM interface.

Although there are some answers that this thesis cannot provide, concerning the spin-triplet pairing and its existence at a SC/FM interface, the results that are presented here can provide some understanding of the complexity of SC/FM interfaces in presence of a spin scattering interface and that the BTK model may not be sufficient in modelling the conductance across the interface.

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Evidence for spin mixing in holmium thin film and crystal samples

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In a number of recent experiments, holmium has been shown to promote spin-triplet pairing when in proximity to a spin-singlet superconductor. The condition for the support of spin-triplet pairing is that the ferromagnet should have an inhomogeneous magnetic state at the interface with the superconductor. Here we use Andreev reflection spectroscopy to study the properties of single ferromagnet/superconductor interfaces formed of holmium and niobium, as a function of the contact resistance of the junction between them. We find that both single-crystal and *c*-axis-oriented thin-film holmium show unusual behavior for low junction contact resistance, characteristic of spin-mixing-type properties, which are thought necessary to underpin spin-triplet formation. We also explore whether this signature is observed when the junction is formed of $\text{Ni}_{0.19}\text{Pd}_{0.81}$ and niobium.

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I. INTRODUCTION

At a superconductor/ferromagnet (*S/F*) junction conventional spin-singlet Cooper pairs penetrating into the ferromagnet will decay over a length of the order of $\xi_F = \sqrt{\frac{\hbar D_F}{E_{\text{ex}}}}$ due to destruction of the Cooper pair coherence as a result of the exchange field of the ferromagnet¹ (where D_F is the diffusion coefficient and E_{ex} is the exchange energy in the ferromagnet^{2,3}). In strong ferromagnets E_{ex} is large and ξ_F is of the order of ~ 1 nm at low temperature; however, theories have emerged recently suggesting the existence of a exotic proximity effect where spin-triplet pairing is generated at the *S/F* interface, resulting in a greatly extended decay length, $\xi_T \gg \xi_F$. This exotic proximity effect, named the “long-range spin-triplet proximity effect” (LRSTPE),^{4,5} only exists if either some form of inhomogeneous magnetization is present at the *S/F* interface or if there is a spin-active region (such as spin scattering in a strong spin-orbit coupled medium) between the *S* and *F* layers.^{4,5} Current thinking suggests that the inhomogeneous magnetic state could either be provided by a magnetic system that offers intrinsic inhomogeneity due to a noncollinear spin arrangement or could be artificially created in a number of ways, including the presence of domain walls (although domain-wall density may prove an issue), or through a thin-film multilayer arrangement using different types of ferromagnets.⁶ Either way, spin mixing

must occur close to the interface with the interrogating superconductor.

It has been suggested that holmium (Ho) could provide the necessary magnetic inhomogeneity to induce the LRSTPE due to the intrinsically nonlinear cone structure of its ordered magnetic moments.⁷ Indeed, two recent experiments report evidence for triplet pairing promoted by Ho.^{8,9} Sosnin *et al.* used Andreev interferometry to measure phase-periodic conductance oscillations in Ho which formed the barrier of a Al/Ho/Al ring structure,⁸ while Robinson *et al.* measured the critical current behavior of Nb/Ho/Co/Ho/Nb junctions.⁹ Both experiments varied the thickness of the *F* layers (Ho and Co, respectively) and observed supercurrent signatures with thicknesses much greater than ξ_F .

Evidence for the LRSTPE has been observed also in other systems, including $\text{Pd}_{0.88}\text{Ni}_{0.12}$ and $\text{Pd}_{0.987}\text{Fe}_{0.013}$ coupled to Co in *S/F1/N/F2/N/F1/S*-type junctions,² Co nanowires with W superconducting leads,¹⁰ and CrO_2 , a half-metallic oxide coupled to NbTi or MoGe superconducting leads.^{11,12} In these systems the origin of LRSTPE is more likely to be related to artificially created inhomogeneity, either through the difference in spin scattering generated by the choice of thin films in the multilayer stack or through the particular arrangement that a polycrystalline random alignment of grains may present to the superconducting interface. Reviewing these experimental results shows that there is a great deal more to be

learned in this emerging field and, as predicted theoretically, the induced spin-triplet pairing is intimately linked to the properties of the interface. In view of the current status of the field it seems essential to examine the transport across S/F interfaces in more detail so that nature of the spin-singlet to spin-triplet conversion process can be better understood and possibly even controlled.

For any single S/F interface theory tells us that the conductance across the interface plays a pivotal role in determining whether the conventional even-frequency singlet¹³ proximity component or the odd-frequency triplet⁴ LRSTPE dominates.^{14,15} This balance between the singlet and triplet components is due to the competition between the effect of increasing spin mixing (which acts to destroy singlet pairing) and increasing junction transparency (which acts to provide a higher proportion of singlet Cooper pairs from the superconductor). Consequently, for constant, but sufficient, spin-mixing conditions, lower junction transparency (higher interface resistance) should promote the LRSTPE phase while for cleaner junctions (low interface resistance) singlet pairing will dominate. Point-contact Andreev reflection (PCAR) offers a potentially ideal probe as the conductance of the contact (and therefore the S/F interface resistance) can be controlled by varying the pressure on the tip-sample contact. In this paper we examine the properties of single S/F interfaces, primarily those formed between Nb and Ho, and use Andreev spectroscopy to extract details on how the properties of the interface change as the interface transparency is varied. We compare the Nb/Ho results to those obtained from junctions formed between Nb and copper foil and Nb and a $\text{Ni}_{0.19}\text{Pd}_{0.81}$ thin film.

II. EXPERIMENTAL

Holmium is a rare-earth metal with a complex magnetic phase diagram.^{16,17} As the temperature is reduced from room temperature, Ho first undergoes a transition to a spin-spiral antiferromagnetic (AFM) state with a Néel temperature of $T_N \sim 133$ K.¹⁶ In a previous study it was shown using polarized x-ray Bragg diffraction that there were domains of different chirality in the AFM state of a Ho single crystal.¹⁸ Below 19 K (the Curie temperature, T_C) there is a transition to a weak ferromagnetic alignment with a conelike structure where the cone axis lies along the crystallographic c axis in zero applied magnetic field [see the illustration in the inset of Fig. 1(b)].

The Ho single crystal studied here was $(2.44 \times 1.82 \times 0.9)$ mm in size and was grown at the Ames Laboratory using strain annealing.¹⁹ The 300-nm-thick Ho thin film was prepared in a UHV system by dc magnetron sputtering onto a 200-nm-thick Nb buffer on $\sim(5 \times 5)$ mm area heated (~ 873 K) c -plane sapphire. The Ho target was presputtered for 15 min prior to film growth and the system's base pressure was better than 10^{-8} Pa. The films are epitaxial and c -axis oriented as determined by x-ray diffraction. The total Ho thin-film thickness was determined by low-angle x-ray diffraction and by fitting the period of the Kiessig fringes using simulation software. The films were capped with a 10-nm protective layer of gold to prevent surface oxidation. A number of polycrystalline $\text{Ni}_{0.19}\text{Pd}_{0.81}$ thin films (108 nm) were also prepared for comparative measurements. These films were grown by sputter deposition in a UHV chamber on a Si substrate, as described

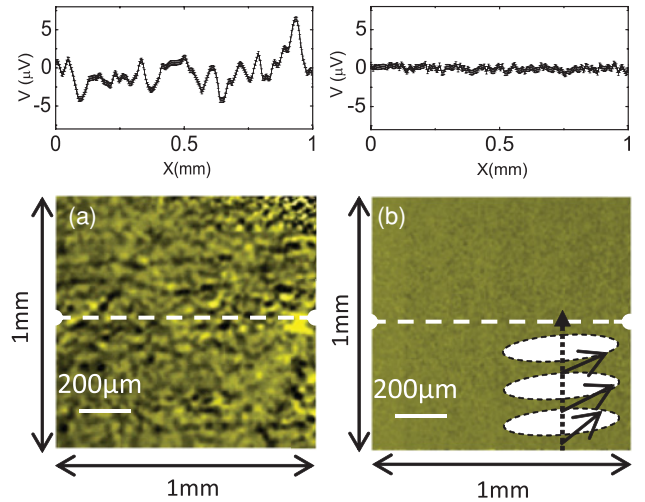


FIG. 1. (Color online) Hall images of (a) single-crystal and (b) thin-film Ho at zero field and 6 K. Black regions represent negative induction and bright regions represent positive induction. Line scans across the center of the images (white dashed lines) are shown in the top panels. Inset to (b) shows a schematic of the cone structure in Ho for $T < 19$ K; the dashed arrow corresponds to the direction of the c axis and solid arrows represent the ferromagnetic vectors locked out of plane.

previously.²⁰ The $\text{Ni}_{0.19}\text{Pd}_{0.81}$ films have a Curie temperature of 230 K, determined from magnetometry measurements and an easy axis out of the plane. The slightly higher Curie temperature in comparison to the earlier report²⁰ is probably due to a small change in the surface composition of the target. A copper film prepared by sputtering was used as a benchmark to show how the extracted parameters vary with tip pressure for a nonmagnetic film.

PCAR measurements were taken at 4.2 K using superconducting tips that were mechanically cut from 0.25-mm-diam Nb wire.²¹ Spectra were also taken using platinum tips to identify nonsuperconductivity-related components to the “background” conductance spectra.²² All measurements were performed with the tip aligned parallel to the c axis of the Ho crystal or Ho thin film, which is the ideal crystallographic direction as it lies along the spin cone axis [see the inset of Fig. 1(b)]. The tip-sample distance was controlled by a stepper motor connected to a differential screw such that systematic measurements could be made as a function of contact pressure. In addition to PCAR measurements, the surfaces of the Ho single crystal and thin film were scanned using a Hall probe²³ to identify any variation in the magnetic properties between the crystal and the thin film.

The Andreev spectra were fitted as described previously,²¹ using the Blonder-Tinkham-Klapwijk (BTK) equations modified for spin polarization by Mazin *et al.*^{24,25} Spectra were fitted for the polarization P , the dimensionless parameter Z , which incorporates the interface scattering, and a smearing parameter ω , which accounts for both thermal and inelastic broadening effects. As any effect of the LRSTPE on the conductance spectra is expected to be subtle, the spectra were fitted using a fixed value for the gap voltage of $\Delta = 1.5$ meV, i.e., the Nb gap value at low temperature.²⁶ Restricting the fitting routine to a

three-parameter fit ensured that the fitting was robust and that any error introduced by the fitting procedure was systematic across the series. It is usual to define the contact resistance of a junction at zero bias, R_{C0} . However, as the interface properties change drastically with tip pressure, we have extracted the 30-mV resistance at each junction (R_{CB}), and use this value to define the contact resistance.

III. RESULTS

Figure 1 shows the scanning Hall probe images of the out-of-plane magnetic moment in the single crystal oriented in the c axis and in zero applied magnetic field. The noise floor of the 5- μm Hall probe used was $\sim 0.3 \mu\text{V}$ with a 7.7 mV/T sensitivity. While the crystal shows a considerable moment directed along the c axis [Fig. 1(a)], the signal from the film (which has approximately three orders of magnitude smaller volume) is below the noise floor of the Hall probe sensor [Fig. 1(b)]. We show the results on the film for completeness. The line scans taken across the center of both samples are shown in the top frames in Figs. 1(a) and 1(b). Although it is not possible to determine the chiral sense of the domains with the scanning Hall probe, the size and distribution of the domains indicated in Fig. 1(a) are consistent with (and remarkably similar to) the chiral domain structures in the AFM state observed using circularly polarized x-rays by Lang *et al.*¹⁸

The evolution of the PCAR spectra with contact resistance (R_{CB}) for the Ho single crystal and Ho thin film are shown in Figs. 2(a) and 2(d), respectively. The data for the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ film are shown in Fig. 2(f). The high bias dips on the spectra have been associated with the critical current being exceeded in the contact region.²⁷ In order to fit the data, the spectra for the single crystal were normalized to the conductance spectra obtained using a nonsuperconducting Pt tip, as shown in Fig. 2(b). For the crystal, the background conductance was typically V shaped using either the Pt or Nb tip, and because of the similarity of this feature, we were able to normalize the spectra taken with the Nb tip using the Pt tip spectra as shown in Fig. 2(c). Compared to the crystal, the background spectra obtained on the film were consistently featureless and flat, which meant that the spectra could be normalized directly by the high bias conductance value [Fig. 2(e)]. The fitted spectra generated using the Mazin model are shown in Figs. 2(c) and 2(e) for the crystal and film, respectively, and Fig. 2(g) for the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ film.

Fitting to the spectra shown in Fig. 2 allows the extraction of the polarization P and (dimensionless) interface parameter Z and the relationship between P and Z for the crystal and film are shown in Figs. 3(a) and 3(b), respectively. The P - Z relationship of a S/F interface always takes a similar form in that high P is associated with low Z and vice versa, and the origin of this dependence has been widely discussed in the literature.^{28–32} The “intrinsic” polarization is usually obtained by extrapolating a P - Z plot to low Z —although not usually to $Z = 0$ (Ref. 29) because Z also includes the effect of Fermi velocity mismatch between the S/F materials.³³ The trends we find for the P - Z relationship are not unusual in this respect. However, when we show the explicit relationship of P and Z

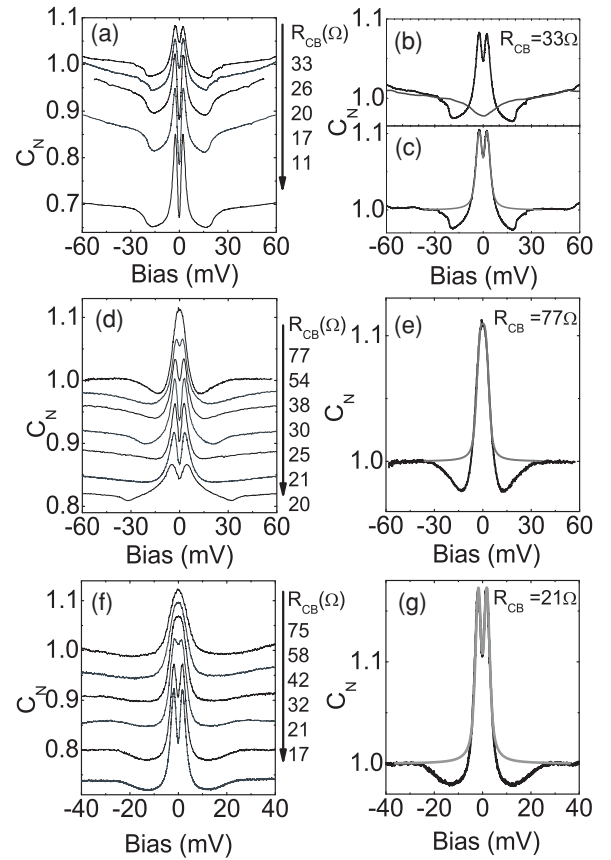


FIG. 2. Point-contact Andreev reflection data at 4.2 K; C_N is the normalized conductance. (a) Normalized conductance spectra as a function of R_{CB} for the Ho crystal. (b) High R_{CB} spectrum taken with a Nb tip (black line) and with a Pt tip (gray line) for the Ho crystal. (c) Same spectrum as (b), but after normalization and fitting (with fitted parameters $\Delta = 1.5$ meV, $\omega = 1.24$ meV, $P = 19.5\%$, $Z = 0.63$). (d) Normalized conductance spectra as a function of R_{CB} for the Ho film. (e) Spectrum taken with a Nb tip shows a flatter background than in the crystal case, so can be fitted using the high bias conductance as shown (fitted parameters $\Delta = 1.5$ meV, $\omega = 1.18$ meV, $P = 35.5\%$, $Z = 0.32$). (f) C_N as a function of R_{CB} for a $\text{Ni}_{0.19}\text{Pd}_{0.81}$ film. (g) Normalized spectrum and fit from the data set in (f) (with fitted parameters $\Delta = 1.5$ meV, $\omega = 0.72$ meV, $P = 27.5\%$, $Z = 0.41$). The arrows in (a), (d), and (f) indicate decreasing contact resistance. All curves have been offset in the vertical scale for clarity.

with the contact resistance, R_{CB} , of the junction, it becomes clear that the P - Z plot masks a much less obvious relationship.

Figures 4(a) and 4(b) show the behavior of three separate contacts made to the single crystal and Figs. 4(c) and 4(d) show the equivalent for two separate contacts made to the thin film. Both sets of spectra change in an unusual way with increased tip pressure. In both types of samples, as tip pressure is increased (decreasing R_{CB}), Z increases anomalously and sharply, and P shows a corresponding precipitous drop. By direct examination of the spectra shown in Fig. 2, it is clear that the sharpening of spectral features as R_{CB} drops indicates that the effective interface barrier is increasing. This is most clear in Fig. 2(a), the series of spectra taken on the Ho crystal. We are confident that these changes to the Z and P parameters are real (i.e., not an artifact of the fitting process). Furthermore,

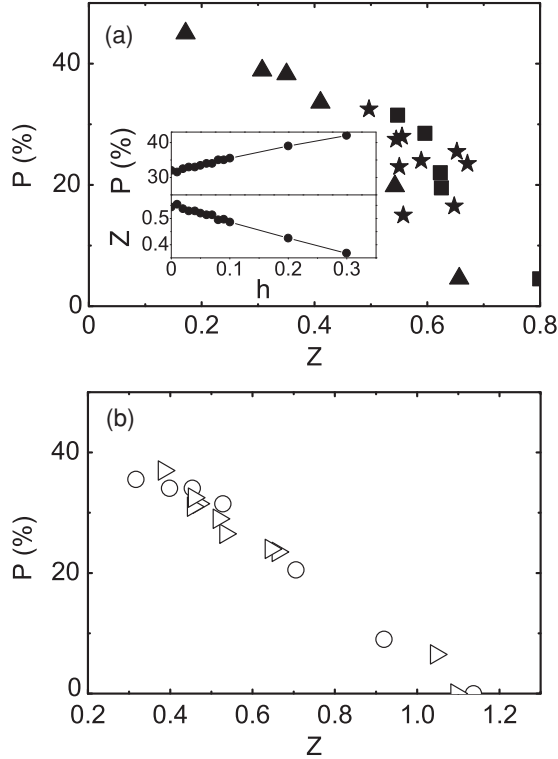


FIG. 3. $P(Z)$ relation on the Ho crystal (a) and Ho thin film (b). Symbols represent different contacts. The inset to (a) is a simulation of the effects of increasing the normalized field $h = H/H_{C2}$ (where H_{C2} is the upper critical field of Nb) using the datum point associated with $R_{CB \text{ peak}}$ shown in Fig. 4(a).

in case of the crystal, the data for $P(R_{CB})$ and $Z(R_{CB})$ show a domelike and a diplike nonmonotonic dependence. We make this more clear in Figs. 4(a) and 4(b) by plotting P, Z as function of $R_{CB}/R_{CB \text{ peak}}$, where $R_{CB \text{ peak}}$ is the value of R_{CB} at the peak in the polarization. For the film, the peak in polarization or dip in Z value is not observed [Fig. 4(c)]. Instead, at higher R_{CB} , the polarization is constant, then starts to decrease with decreasing R_{CB} . The differences between the Ho film and crystal are subtle—what they have in common is that both show the anomalous rise in Z and drop in P at a high tip pressure.

In order to show how anomalous this behavior is, we show the equivalent P and Z behavior when a Nb tip is pressed into a copper foil, or for a Nb tip on a $\text{Ni}_{0.19}\text{Pd}_{0.81}$ film, plotted in Figs. 4(c) and 4(d). In the case of Cu, Z decreases slightly as R_{CB} is reduced, owing to the increasing transparency of the tip-sample interface²¹ (for Cu, $P = 0\%$). In the case of $\text{Ni}_{0.19}\text{Pd}_{0.81}$, hardly a change in P or Z is found. Note that the difference in behavior of Z in the Ho cannot be explained purely by an increase in the smearing parameter with decreasing contact resistance, as both the Ho crystal and the Cu sample show the same trend of decreased smearing as the contact resistance is reduced.²⁸

Before drawing any definitive conclusion, it is also important to try to eliminate any artificial trend in P and Z in the case of the Nb/Ho contact due to the effects of stray magnetic fields on tip properties.³¹ In order to examine this in more detail, we have taken the spectrum at the onset to the anomalous rise in Z (and precipitous drop in P) and modeled the effect on this

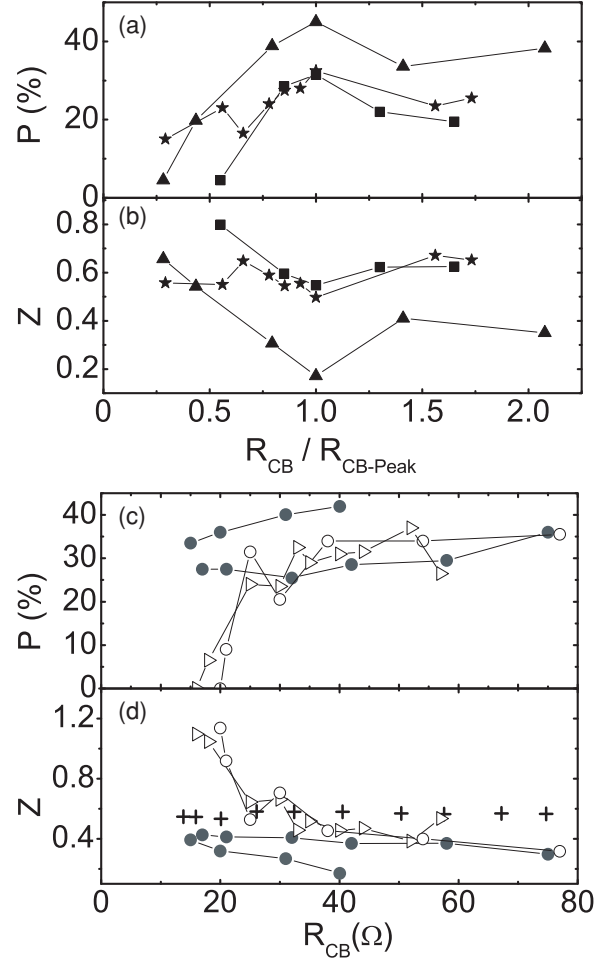


FIG. 4. Dependence of (a) P and (b) Z of the Ho crystal as function of $R_{CB}/R_{CB \text{ peak}}$, where $R_{CB \text{ peak}}$ is the value of R_{CB} at the peak in the polarization with $R_{CB \text{ peak}} = 20, 39$, and 41Ω for the squares, triangles, and stars in (a) and (b), respectively. The dependence of (c) P and (d) Z on R_{CB} for the spectra taken on the Ho thin film (unfilled symbols), the $\text{Ni}_{0.19}\text{Pd}_{0.81}$ thin film (filled circles), and copper foil (cross symbols).

spectrum of the presence of an external magnetic field. We do this by using a model we developed previously called “the two-channel model,” which we have shown simulates the effect of a magnetic field on the tip properties up to a field of $\sim 80\%$ of the upper critical field H_{C2} of the Nb tip (i.e., $h = H/H_{C2} = 0.8$). The results of this simulation are shown in the inset to Fig. 3(a) up to $h = 0.3$. The plots show that if the effect of increasing tip pressure was simply to experience an increasing magnetic field, P would increase and Z would decrease. This is opposite to the observations that we have made in the main plots of Fig. 4 and therefore we can rule out any possible effects from stray fields. The apparent increase in the Z parameter as the contact resistance drops indeed appears to be a real and anomalous effect. We suggest that it is indicative of a unique form of spin scattering which also results in a reduced P .

IV. DISCUSSION

Theoretical calculations of the expected Andreev conductance spectra in the presence of the LRSTPE^{34–37} indicate

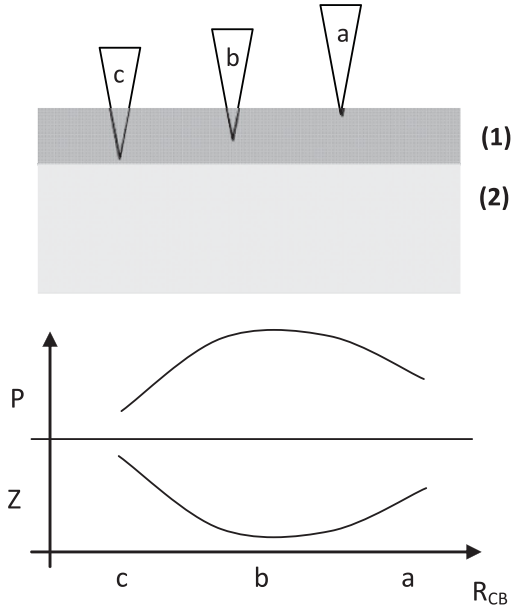


FIG. 5. Schematic illustrating the behavior of P and Z as a function of tip pressure for a system with a surface scattering layer. Layer (1) is a thin surface oxide and layer (2) represents bulk Ho.

that spin mixing at the S/F interface leads to an enhancement of the subgap conductance, either via a direct increase in the conductance³⁴ or via the formation of Andreev bound states.³⁶ A number of experimental reports have shown possible signatures of the LRSTPE,^{38–40} although it remains to be determined what the “signature” of the LRSTPE is in the Andreev reflection spectra. It is clear, however, from both theoretical and experimental works that if the LRSTPE can be reliably turned “on” and “off,” changes should be observed in the parameters used to fit the spectra that indicate the subgap conductance, i.e., P and Z . Although we see clear changes in P and Z with R_{CB} , we do not see any evidence of a subgap structure in the spectra (Fig. 2). However, the magnitude of the subgap conductance expected as a result of spin mixing or the LRSTPE may be below the resolution of the spectra shown.^{41–43} The changes in P and Z suggest that the scattering mechanism probed by the PCAR at low R_{CB} is an indication of spin mixing that is the precursor to the LRSTPE (i.e., P is reduced as the scattering increases).

The dependence of $P, Z(R_{CB})$ can be understood qualitatively using a simple schematic, as shown in Fig. 5. The behavior of Z at high R_{CB} in the Ho crystal implies the existence of a surface layer, probably an oxide, as proposed for other systems.⁴⁴ For the crystal, as the Nb tip first approaches the Ho [Fig. 5(a)], the surface layer acts as a spin-scattering layer, resulting in a low P (and high Z) in the conventional way. As the tip is pushed further into the crystal surface [Fig. 5(b)],

the Andreev reflection probes the spin alignment of the Ho with a Z parameter that is indicative of a clean interface and the observed P is maximal. Finally, as the tip goes through this surface layer completely [Fig. 5(c)], the spin mixing of the Ho becomes dominant (Z increases) and so P is once again reduced. In the case of the film, the thin Au capping layer prevents the oxide from forming, and so as the tip first approaches the capped film surface, the intrinsic P of the Ho is preserved through the thin metallic capping layer and P is approximately constant with R_{CB} . Once the tip punctures the capping layer, the intrinsic spin mixing of the Ho results in the same high Z value and low P behavior, as observed in the Ho crystal. The results indicate that, at low R_C in both the crystal and the film, spin mixing occurs. Note that, in PCAR, R_{CB} can decrease either due to a cleaner interface or due to an increase in the physical size of the contact.^{30,44} This may explain why the effects observed here vary in magnitude between different contacts [for example, the square and star datasets in Fig. 4(a)].

Figures 4(c) and 4(d) also shows our first results on a 108-nm-thick $\text{Ni}_{0.19}\text{Pd}_{0.81}$ film. The spectra and fit to a spectrum are shown in Figs. 2(f) and 2(g). Interestingly, although reports that thin films (<4 nm) of $\text{Pd}_{0.88}\text{Ni}_{0.12}$ promote triplet behavior,² here we see no significant anomalous upturn in Z as compared with Ho. However, this result is consistent with the view that, whereas in Ho the spin-triplet state is promoted by the intrinsic inhomogeneity of the spin state of the material, in the multilayer stack, the inhomogeneous magnetization has been created artificially and that a $\text{Ni}_{0.19}\text{Pd}_{0.81}$ film would not necessarily be expected to support proximity-induced spin-triplet behavior in isolation. Our inference concerning NiPd agrees with the recent publication from the Birge group.⁴⁵

In conclusion, we have shown an anomalous dependence of the polarization P and the interface scattering parameter Z on contact resistance R_{CB} in the magnetically inhomogeneous system Ho, using point-contact Andreev reflection spectroscopy. Similarities in the PCAR spectra taken on both single-crystal and thin-film Ho suggest a common scattering mechanism. This scattering results in reduced polarization and strongly suggests increased spin mixing, a fundamental precursor to the LRSTPE effect. We do not see this effect when we perform the same experiments using copper foil or $\text{Ni}_{0.19}\text{Pd}_{0.81}$ thin films.

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Erratum: Evidence for spin mixing in holmium thin film and crystal samples
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We wish to correct two errors in the paper. The removal of these errors does not affect the results and conclusions of this paper.

(1) Page 3, 2nd paragraph in Results section should read as follows: “In order to fit the data, the spectra for the single crystal were normalized to the conductance spectra obtained either using a nonsuperconducting Pt tip, as shown in Fig. 2(b), or from a Nb tip, where the spectra were taken at temperatures above and close to the superconducting critical temperature (11.7 K).

(2) To withdraw one set of data [triangles shown in Figs. 3(a), 4(a), and 4(b)], because the P and Z trends as a function of contact resistance were found to be dependent on normalization procedure and therefore are not robust.