Studies on spin polarization, spin fluctuations and multiband superconductivity using transport spectroscopic measurements.

A thesis

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by

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Dedicated to my parents
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Declaration

This thesis is a presentation of my original research work. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and acknowledgement of collaborative research and discussions.

This work was done under the guidance of Dr. Pratap Raychaudhuri at Tata Institute of Fundamental Research, Mumbai.

Sourin Mukhopadhyay

In my capacity as supervisor of the candidate’s thesis, I certify that the above statements are true to the best of my knowledge.

Dr. Pratap Raychaudhuri

Date:
Statement of joint work

The experiments reported in this thesis have been carried out under the guidance of Dr. Pratap Raychaudhuri in the department of Condensed Matter Physics and Material Science, Tata Institute of Fundamental Research, India. Most of the experiments have been conducted by me at TIFR. The results of the major portions of the work presented in this thesis have already been published in refereed journals. Some of the works presented in this thesis were performed in collaboration with other researchers. Parts of the PCAR experiments on the borocarbide superconductor were carried out jointly with Dr. Goutam sheet. The single crystals of superconducting borocarbide used in this thesis work were grown by Dr. H. Takeya, National Institute of Material Science, Japan. The structural characterizations of these samples using X-ray analysis were also done by him. The synthesis of NdNi₅ samples and their X-ray characterization were done by Dr. D. A. Joshi and Prof. C.V. Tomy at Indian Institute of Technology, Mumbai, India. The \( Ni_{3+x}Al_{4-x} \) samples were supplied by Prof. S. K. Dhar, TIFR, India.

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Synopsis

1. Introduction

Probing the interaction of electrons and their elementary excitations, close to the Fermi level, is of fundamental interest to understand electronic properties of metals. In this thesis, I will employ specific configurations of spectroscopic techniques, namely, point contact spectroscopy (PCS) and scanning tunneling spectroscopy (STS) to probe superconductivity and magnetism in various correlated electron systems. These fall in the broad class of transport spectroscopic measurements where the current–voltage (I-V) characteristics of a device or interface are used to extract spectroscopic information on the electrons close to Fermi level.

To set the foundation for understanding the physics encoded in the tunneling spectra, in chapter 1, I will introduce the electron tunneling between two metal electrodes separated by either an infinite or a finite barrier. The first one represents the operating principle behind the scanning tunneling microscopy (STM), tunnel junctions etc.; the second one is applicable to point contact spectroscopy and its variant point contact Andreev reflection (PCAR) spectroscopy. In chapter 2, I will describe the experimental set up, electronics and data acquisition involving PCAR spectroscopy in the temperature range 300 mK-300 K and in magnetic fields up to 9T and other experimental techniques, used in this thesis work. Chapter 3 will focus on the gap anisotropy and multiband superconductivity in YNi2B2C ($T_c$~16K) using PCAR as a momentum resolved probe. To get further insight into the evolution of multiband scenario, the changes in inter-band scattering due to non magnetic impurity (Pt) doping are investigated in YNi$_{2-x}$Pt$_x$B$_2$C ($x$=0-0.2). In chapter 4 of this thesis, we utilize PCAR spectroscopy as a spin resolved probe to investigate transport spin polarization and spin fluctuations present in different ferromagnets and nearly ferromagnetic metals. Finally, in chapter 5, I will describe the design, construction and operation of a variable temperature STM. I will also present some preliminary spectroscopic investigations on various systems, performed using our home build low temperature STM.

1.1. Tunneling spectroscopy and STM

Classically, for electrons to flow between two conductive materials, they must be in contact, at which point the Fermi energies ($E_F$) of the two materials balance at the
interface. In STM, this balancing process actually begins before the contact is made. The elastic tunneling between two metal electrodes is discussed based on work of Bardeen\(^1\), where the two electrodes are separated by large barrier with independent local density of states (DOS). When the two electrodes are brought within a few angstroms, the electronic wave functions begin to overlap significantly for the tunneling process to take place. With the application of a bias voltage (V), electrons tunnel from one electrode to the other, provided that there are available states in the counter electrode at the same energy. A detectable tunneling current \(I\) proportional to the local DOS \([N(E)]\) in each electrode flows across the barrier,

\[
I = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} |M_{ts}|^2 N_t(E - eV)N_s(E)[f(E) - f(E - eV)]dE
\]

Here, the Fermi function \(f(E) = \frac{1}{e^{(E-E_F)/k_BT} + 1}\), \(M_{ts}\) is the matrix element of the perturbation potential between the tip (t) and the sample (s). Tunneling studies involving superconductors are associated with energy scale \(~100\) meV at \(E_F\); within this limit, the \(N_t(E_F)\) can be taken as constant for most of the normal metal. In the limit \(T\rightarrow 0\), the Fermi function becomes a step function so that the integral becomes a definite integral between \(E_F\) and the applied bias voltage (eV). The expression for tunneling current simplifies to

\[
I \propto \int_{E_F}^{E_F+eV} N_s(E)dE
\]

The validity of these approximations provides a simple picture in which the tunneling current is the integral of the DOS between the Fermi energy and the applied voltage. Furthermore, it suggests that the differential conductance \((G=dI/dV)\) in a tunneling experiment can probe directly the local DOS on a sample surface.

### 1.2. Point contact spectroscopy

Point contact spectroscopy\(^2\) (PCS) represents the other regime of tunneling experiment, where unlike STM, the two metal electrodes physically touch each other with no intended tunneling barrier at the interface. Here, the electrical transport takes place through a narrow constriction formed at the interface between the two metal electrodes. The contact, so made, should be ballistic in nature \(i.e.,\) mean free path of the electrons in both the metals must be greater than the diameter of the point contact. For such a ballistic contact, with the application of a bias voltage, statistically, the electrons are accelerated
across the contact diameter without undergoing any scattering and therefore do not
dissipate energy. Outside a volume of radius of the point contact, the accelerated
electrons resonantly excite different elementary excitations (e.g., electron and hole like
quasiparticles in superconductors, phonons, magnons in metals etc.) present in a solid and
that leaves non-linearity in the I-V characteristic of the point contact spectra at energy
scales appropriate for different processes. This property of PCS is utilized to get energy
and momentum resolved information on different process at $E_F$. This is not achievable in
bulk transport, where the excitation of the elementary modes at definite energy is not
possible to regulate in such a controlled way.

1.3. Point contact Andreev reflection spectroscopy

In point contact experiments, when one of the normal metal (N) electrodes is replaced by
a superconductor (S), the ballistic transport takes place through the contact by the process
called Andreev reflection $^3$ (AR). In AR, an electron incident on the N-S interface gets
reflected back as a hole in the opposite spin band of the metal and a Cooper pair
propagates inside the superconductor. At zero temperature, for an N-S interface with no
barrier, the differential conductance ($G=\frac{dI}{dV}$) at low bias ($|V|<\frac{\Delta}{e}$) is enhanced by a
factor of 2 compared to its high bias [$G_n=G(|V|>>\frac{\Delta}{e})$] value. However, the experiments
are always performed at finite temperature and the barrier can never be completely
transparent due to Fermi velocity mismatch in the two electrodes and the presence of
oxide barrier at the interface. For such finite barriers, two peaks appear in the G-V
spectrum close to $\pm \frac{\Delta}{e}$. The AR process is modeled by Blonder, Tinkham, and Klapwijk
(BTK) theory $^4$ to calculate the current through the point contact using Bogoliubov–de
Gennes equation $^5$ (BdG) with a delta function potential of the form $V=V_0\delta(x)$ at the
interface. For convenience, the strength of the potential barrier is usually characterized by
a dimensionless parameter $Z = \frac{V_0}{\hbar v_F}$, which can vary from a fully transparent ($Z=0$) to
tunneling regime ($Z\rightarrow\infty$). The probability current of normal reflection $B(E)$ and that of
Andreev reflection $A(E)$ are derived by solving the BdG equation. The current ($I$) as a
function of voltage ($V$) is given by,

$$ I \propto N v_F \int_{-\infty}^{+\infty} \left[ f(E - eV, T) - f(E, T) \right] \left[ 1 + A(E) - B(E) \right] dE \quad (1.3) $$
It is clear from eqn. (1.3), that the ordinary reflection associated with $B(E)$ reduces the tunneling current; Andreev reflection associated with $A(E)$ enhances it by transmitting a Cooper pair over the interface for one incident electron. In the zero-temperature limit the differential conductance $\frac{dI}{dV} \propto [1 + A(E) - B(E)]$.

1.4. PCAR involving magnetic materials

In a non-magnetic metal the Andreev reflection process is always allowed, because every energy state in a normal metal has both spin-up and spin-down electrons. However, when the normal metal is replaced by a ferromagnetic metal (F), this is no longer true and Andreev reflection is limited by the minority spin population. The ferromagnetic metal electrode has unequal spin density of states in its spin-up $[N_{\uparrow}(E_F)]$ and spin-down $[N_{\downarrow}(E_F)]$ bands at the Fermi level. This inequality in spin density of states prevents some of the Andreev reflected hole to propagate back in the ferromagnet for energies less than the superconducting energy gap ($|eV| \leq \Delta$) and it decays at the interface as an evanescent wave. Therefore, the low bias ($|eV| \leq \Delta$) enhancement in the PCAR spectrum is suppressed. The value of transport spin polarization is estimated from the degree of this suppression according to modified BTK (mBTK) formalism$^6,7$. This enables PCAR also as a spin resolved probe.

1.5. The role of quasiparticle lifetime on the tunneling and PCAR spectra

For an ideal superconductor, the quasiparticles associated with elementary excitations over the Bardeen-Cooper-Schrieffer (BCS)$^5$ ground state (called the Bogoliubons) are infinitely lived (the superconducting quasiparticle lifetime $\tau \rightarrow \infty$). However, in a real superconductor, recombination of electron and hole like Bogoliubons through inelastic scattering$^8$ causes $\tau$ to have a finite value, which is reflected as the broadening of the superconducting DOS in tunneling spectroscopy. This effect is incorporated$^9$ in tunneling spectroscopy by an inelastic scattering parameter $\Gamma$, which has the dimension of energy and is inversely proportional to $\tau$ ($\Gamma=\hbar/\tau$). Conventionally $\Gamma$ is treated as a damping parameter associated with the decay of an eigen state due to external perturbation. The broadened BCS density of states is given by $N(E) = Re \left( \frac{E+i\Gamma}{\sqrt{(E+i\Gamma)^2-\Delta^2}} \right)$. For conventional s-wave superconductors $\Gamma$ is zero almost throughout the entire temperature range barring
very close to $T_c$, where it becomes finite but small ($\Gamma \sim 10^{-2}$ meV, $\tau \sim 10^{-13}$ s) due to intrinsic shortening of $\tau$ in the superconductor itself. I will show based on recent PCAR studies done on various magnetic systems, that the effect of $\Gamma$ can also become important even at $T \ll T_c$, when the superconductor is in close proximity to a spin fluctuating metal. The proximity effect leads $\Gamma$ to increase ($\Gamma \sim 1$ meV, $\tau \sim 10^{-15}$ s) drastically. We observe the smaller $\tau$ is, the smaller is $\Delta$ for the superconductor.

2. **Experimental Details**

The transport and PCAR studies are carried out in He-3/He-4 cryostat depending on the temperature range (300mK-300K) relevant and in magnetic fields up to 9 T. Critical field ($H_{c2}$) and critical temperature ($T_c$) of superconductors are measured using a planar coil a.c susceptometer. The design, fabrication, control electronics and data acquisition using Labview involved in these experimental set ups are done in house. While performing PCAR spectroscopy, care is taken to ensure the contact diameter is within the ballistic transport limit. Conventional a.c modulation technique is employed to measure differential conductance ($G = dI/dV$) of the contact. Complementary magnetization and heat capacity studies are used to characterize sample properties in a Quantum Design SQUID magnetometer and Physical Properties Measurement System (PPMS) respectively. I will describe the design, fabrication and development of the low temperature STM and related spectroscopic studies in section 5.

3. **Multiband superconductivity in YNi$_2$B$_2$C**

Superconductivity is a cooperative behavior of the conduction electrons in certain materials. In the BCS theory of superconductivity all electrons on the isotropic Fermi surface (FS) contribute equally to the superconducting pairing, giving a constant superconducting gap ($\Delta$). Different scenarios can arise, if the Fermi surface of a material is anisotropic and has multiple bands contributing to the superconductivity. These lead to anisotropic gap ($\Delta$) values in the superconductor. The difference of $\Delta$ on different sheets of the FS, or multi-band superconductivity was considered theoretically back in late 50s$^{10}$. Recently this has emerged as a possible explanation for the unusual physical properties observed in MgB$_2$,$^{11,12}$, YNi$_2$B$_2$C$^{13,14,15,16}$ etc. The simplest form of multiband
superconductivity arises when electrons on various Fermi sheets in a material have different electron-phonon coupling strengths leading to different superconducting energy gaps ($\Delta$).

In this section, I will focus on the properties of quaternary borocarbide superconductor YNi$_2$B$_2$C ($T_c \sim 16$K). First, using temperature and magnetic field variation of directional PCAR (DPCAR) spectroscopy we establish that the origin of superconductivity in this material is indeed multiband in nature. To investigate further, non magnetic impurity Pt is doped in this system to introduce scattering and evolution of multiband effects are studied.

### 3.1. Investigation of gap anisotropy in YNi$_2$B$_2$C using DPCAR spectroscopy

In DPCAR spectroscopy, the total current ($I$) constitutes of the net flux of electrons from a particular band $i$ on the FS and is given by\(^{17}\),

$$ I = \sum_i I_i \propto \int_{FS} N_{ik} (\hat{v}_{ik} \cdot \hat{n}) dS_F = \sum_i (N_{ik} v_{ik} \hat{n})_{FS} = \sum_i S_{ik} $$ \hspace{1cm} (1.4)

where $k$ is a wave-vector at the FS, $N_{ik}$ is the density of states, $(\hat{v}_{ik} \cdot \hat{n}) = v_{ik} \hat{n}$ is the component of the Fermi velocity along $\hat{n}$ and $dS_F$ is an elementary area on the Fermi surface. The total current is therefore proportional to the area of projection on the interface plane. Thus for an anisotropic FS, if $\Delta$ varies in different bands, different values of $\Delta$ along different directions is expected to arise from unequal contribution of the bands.

DPCAR spectroscopy is performed on YNi$_2$B$_2$C [Fig. 1(a-c)] along well defined facets [100] and [001] with Ag tip using ballistic transport. As both energy and momentum are conserved in the process, injecting current ($I$) along different crystallographic directions of the sample probes the DOS along different $k$-vectors in the momentum space of the FS. The spectra are fitted with the BTK model using $\Delta$, the barrier height $Z$ and the broadening term $\Gamma$ as fitting parameters. Temperature dependence of $\Delta$ along two different directions [Fig. 1(d)] clearly shows the existence of gap anisotropy ($\Delta_{||c}/\Delta_{||a} \sim 4$). The larger gap ($\Delta_{||c}$) follows BCS nature, the behavior of the smaller gap ($\Delta_{||a}$) shows BCS nature at lower temperatures and deviates towards the larger gap at higher temperatures. Also, $2\Delta_{||c}/k_B T_c \sim 3.6$ is close to the weak-coupling BCS value of 3.52 suggests that $T_c$ in YNi$_2$B$_2$C is governed by the large gap. These different
Figure 1. Temperature variation of PCAR spectra of YNi$_2$B$_2$C, (a) current (I) is injected along (001). (b-c) I is injected along (100) for T=300 mK-2K and 2.3-8K respectively. (d) Temperature dependence of the superconducting gap along I||c and I||a. Solid lines are BCS variation for the same.

The temperature variations of the two gaps along different directions are natural, if they originate from two different bands with weak but finite inter band scattering as predicted theoretically\textsuperscript{10,18} for a multiband superconductor.

To find out the effect of magnetic field ($H$) on the anisotropic superconducting energy gaps in YNi$_2$B$_2$C, DPCAR spectroscopy is performed\textsuperscript{19} in applied magnetic field for both the current directions [Fig. 2(a-b)]. The field variation of $\Delta_{||c}$ and $\Delta_{||a}$ are shown in Fig. 2(c). From the best fit parameters, the superconducting gaps in two directions are determined to be $\Delta_{||c} \approx 2.2 \pm 0.05$ meV and $\Delta_{||a} \approx 0.41 \pm 0.02$ meV respectively. This corresponds to a gap anisotropy of $\Delta_{||c}/\Delta_{||a} \approx 6$. Our key observations are the following: (i) For $I||a$, the small gap ($\Delta_{||a}$) decreases rapidly with $H$ and vanishes at $H \approx 3.25$T, which is much smaller than the $H_{c2}$ of the superconductor; (ii) the large gap $\Delta_{||c}$, on the other hand, decreases much more slowly with the magnetic field ($H$).

Figure 2. Magnetic field ($H$) variation of PCAR spectra of YNi$_2$B$_2$C, (a) current (I) is injected along (001). (b) I is injected along (100). (c) The variation of $\Delta$ with $H$, for $I||c$ and $I||a$. 
A comparison with band structure calculations\textsuperscript{20} indicates that in YNi$_2$B$_2$C there exist at least two groups of electrons on different Fermi sheets, with different Fermi velocities ($v_F$) that vary by a factor of $\sim 6$. The 1\textsuperscript{st} groups of electrons are on a “square-pancake” Fermi sheet, whereas the 2\textsuperscript{nd} groups of electrons are on a cylindrical Fermi sheet. The $H_{c2}$ is determined by the electrons on the “square-pancake” Fermi sheet\textsuperscript{19,21} since the superconductivity on the other Fermi sheet is rapidly suppressed under the application of a magnetic field. This behavior of the magnetic field variation of $\Delta_{\parallel a}$ and $\Delta_{\parallel c}$ strongly suggest like $T_c$, $H_{c2}$ is also governed by the larger gap.

### 3.2. Effect of doping non magnetic impurity in the multiband scenario

At this point, it is interesting to study the evolution of the superconducting properties when the system is driven towards the dirty limit by substituting with non-magnetic impurities, as the electrons in different bands with different $v_F$ are responsible for the anisotropic behavior of $\Delta$ in YNi$_2$B$_2$C. For this purpose, we study the evolution $T_c$ and $H_{c2}$ in a series of Pt doped single crystals of YNi$_{2-x}$Pt$_x$B$_2$C ($x=0.02-0.2$)\textsuperscript{22}. X-ray diffraction analysis reveals that pure YNi$_2$B$_2$C has tetragonal lattice structure with $a=b=3.52\text{Å}$ and $c=10.54\text{Å}$; and they [Fig. 3(a)] scales with each other with Pt doping. The increase in the volume of the unit cell in the range $x=0-0.2$ is $\sim 1.1\%$ indicates there is a continuous incorporation of Pt on Ni sites without significant change in atomic distances and structural anisotropy. Temperature and field variation of the real part of a.c susceptibility ($\chi'$) gives $T_c$ [Fig. 3(b)] and $H_{c2}$ in respective samples; it shows that both the $T_c$ and $H_{c2}$ in this series decreases with higher Pt concentration. This is very much unlike conventional s-wave superconductors, where the non-magnetic disorder results in an increase in the electronic scattering rate and decrease in the electronic mean free path ($l$). Consequently, the coherence length ($\xi$) decreases and an increase in $H_{c2}(\alpha \xi^2)$ is observed. The $T_c$ on the other hand is not affected by non-magnetic impurities\textsuperscript{23} unless the impurities result in a modification of the electronic or lattice properties, e.g. DOS at Fermi level [$N(E_F)$] or the Debye temperature ($\Theta_D$). On the other hand, here we find, with higher Pt concentrations both $H_{c2}$ and $T_c$ saturates to lower values [Fig. 3(c)]. The rapid decrease in $H_{c2}$ and $T_c$ in YNi$_2$B$_2$C upon substitution of Pt is clearly not consistent with the conventional scenario.

The reduction in $H_{c2}$ (and $T_c$) can also be due to the change in DOS with Pt doping,
but in this case, we do not expect any change in the DOS caused by Pt, as both Ni ([Ar].3d\(^9\).4s\(^1\)) and Pt ([Xe].4f\(^{14}\).5d\(^9\).6s\(^1\)) are elements from the same group in the periodic table and have the same outer shell electronic structures. To verify this, we have measured the specific heat \((C_p)\) on samples with \(x=0, 0.1\) and \(0.14\) at \(H=0\) and at \(H=9T\). Fitting the expression for the normal state specific heat \(24\ \gamma_n(T) = T + \beta T^3 + \alpha T^5\), where \(C_{\text{electronic}}=\gamma_n T\) and \(C_{\text{lattice}}(T) = \beta T^3 + \alpha T^5\) [the lattice contribution \(C_{\text{lattice}}(T)\) is evaluated. Since \(C_{\text{lattice}}(T)\) is independent of the magnetic field, the electronic specific heat \((C_\text{el})\) at \(H=0\) is determined by subtracting the phonon contribution from the measured \(C_p\) at \(H=0\). Fig. 3(d) shows the \(C_{\text{el}}/T\) vs. \(T\) for three samples. It is clear that \(C_{\text{el}}\) in the normal state does not change significantly showing that \(N(E_F)\) is not affected by Pt doping. The extracted value of \(\gamma_n\) and \(\Theta_D\) for the three samples varies \(\gamma_n=19\sim20.1\ (\pm\ 0.5)\) mJ/mol K\(^2\) and \(\Theta_D=507\sim523\ (\pm15)\) K. A comparison among them confirms that Pt doping in YNi\(_2\).\(_x\)Pt\(_x\)B\(_2\)C does not change the DOS at \(E_F\).

The variation of \(H_{c2}\) (and \(T_c\)) with Pt doping is consistent with the multiband nature
of superconductivity in YNi$_2$B$_2$C, where addition of impurities would result (i) in an increase in intraband scattering within each Fermi Sheet and (ii) an increase in interband scattering between the two Fermi sheets. The first effect will increase bulk $H_{c2}$ governed by the coherence length of the electrons on the “square pancake” Fermi sheet, whereas the latter would decrease $\Delta$ (and $H_{c2}$) on the “square pancake” due to the influence of the cylindrical Fermi sheet. The rapid decrease of $<H_{c2}>$ and the $H_{c2}$ anisotropy $\gamma_H (= H_{c2||a}/H_{c2||c})$ [inset Fig. 3(c)] with the increase in Pt doping suggest that the second effect dominates over the first one in the doping range of this study. Finally, I would like to note that the variation of $T_c$ with Pt doping can be understood from the same mechanism. With the increase in interband scattering, the $T_c$ will gradually decrease due to the influence of the 2$^{nd}$ group of electrons on the cylindrical Fermi sheet with lower $T_c$, and will go towards a limiting value given by the weighted average of the $T_c$ of the two bands. The rapid decrease in $T_c$ at small values of $x$ and the subsequent leveling off for $x>$0.14 supports this scenario. Thus, the changes in $H_{c2}$ and $T_c$ are solely due to impurity doping and influenced by inter-band scattering in this multiband superconductor YNi$_2$B$_2$C.

4. Studies on spin fluctuations in ferromagnets, nearly ferromagnetic metals and itinerant ferromagnetic systems:

In the field of spintronics, it is of interest to study the evolution of spin transport properties with temperature and correlate it to the bulk properties like magnetization in a magnetic metal. In recent times, it has been shown$^6$ that apart from Meservey-Tedrow$^{25}$ technique, PCAR spectroscopy can also be used to probe transport spin polarization in ferromagnets. Though it has a larger temperature range compared to Meservey-Tedrow technique (~1K), it is still limited by the critical temperature of the superconductor used as the counter electrode. This section describes studies aim to explore (i) the evolution of transport spin polarization ($P_t$) at $E_F$ and the spontaneous magnetization ($M_s$) with temperature and (ii) the effect of spin fluctuation on the superconducting quasiparticle lifetime ($\tau$), when a superconductor is kept in proximity to a magnetic metal with large spin fluctuation. For this purpose we choose NdNi$_5$$^{26}$, a ferromagnet with low Curie temperature ($T_{\text{Curie}}$~7.7K) and the superconductor Nb ($T_c$~9.2K) as the two electrodes in PCAR experiment. Our studies show, as $T \rightarrow T_{\text{Curie}}$, strong ferromagnetic spin fluctuation
take place and leave the signature by reducing $\tau$. The effect of spin fluctuation on $\tau$ is further confirmed by carrying out measurements on filled skutterudite compounds $\text{AFe}_3\text{Sb}_{12}$ ($\text{A}=\text{K, Ca, Yb}$)\textsuperscript{26} and on itinerant ferromagnet $\text{Ni}_{3+2x}\text{Al}_{1-x}$\textsuperscript{27}. The first group represents a family of isostructural-filled skutterudite, where the ground state can be transformed by changing “$\text{A}$” from an itinerant ferromagnet to a paramagnet with large spin fluctuations\textsuperscript{28} and in the later a small composition change ($x$) drives it from ferromagnetic to spin fluctuating\textsuperscript{29} ground state.

4.1. Studies on a low $T_{\text{Curie}}$ ferromagnet $\text{NdNi}_5$

Measurements are performed on arc melted polycrystalline samples of $\text{NdNi}_5$\textsuperscript{26}. Resistivity ($\rho$) [Inset Fig. 4(a)] and magnetization ($M$) studies [Fig. 4(a)] establish the sample characteristics. A clear ferromagnetic transition is seen around 7.7 K. Temperature variation of spontaneous magnetization $M_s(T)$ is extracted from isothermal $M$-$H$ curves [Fig. 4(b)]; close to $T_{\text{Curie}}$, $M_s$ is obtained from Arrot’s plot ($M^2$ vs. $H/M$). To compare $M_s(T)$ with $P_f(T)$, PCAR studies are done on $\text{NdNi}_5$ using a Nb tip [Fig. 5(a)] spanning across the $T_{\text{Curie}}$ of the ferromagnet. To analyze the PCAR data, we fix $\Delta$ of Nb within 5% of its BCS value, other free parameters are $P_n$, $Z$ and $\Gamma(=\hbar/\tau)$.

Fig. 5(b) shows the variation of $P_f(T)$ for a particular contact C1 along with $M_s(T)$. It is seen that the intuitive relation $P_f(T) \propto M_s(T)$ holds good. Inset of Fig. 5(b) shows that the absolute value of $P_f$ at 2.4K, decreases with increasing $Z$. It is seen that the of $P_f$ at 2.4K, decreases with increasing $Z$. This is due to the presence of a magnetic dead layer in the F-S interface, where spin flip scattering\textsuperscript{30} depolarise electrons and causes a reduction in the

![Figure 4. (a) Magnetization ($M$) vs. temperature ($T$) of $\text{NdNi}_5$ measured in 500 Oe. Inset shows the resistivity($\rho$) data. (b) Isothermal $M$-$H$ curves at various temperatures.](image-url)
Figure 5. (a) Normalized PCAR spectra of NdNi$_5$Nb. Solid lines are m-BTK fits to data. (b) Normalized temperature variation of $P_f$ for the contact [C1: $Z$ (2.4K) = 0.265] and $M_S$; inset shows variation of $P_f$ with $Z$. (c) Temperature dependence of $\Delta$, $Z$ and $\Gamma$. Solid line passing through $\Delta$ shows the theoretical temperature variation from BCS theory.

The most important observation [Fig. 5(c)] comes from the behavior of $\Gamma(T)$. We find for $T<<T_{Curie}$, $\Gamma=0$ ($\tau\rightarrow\infty$), it implies that the static perturbation due to the spontaneous moment being the largest at $T=0$, does not affect $\tau$. As $T$ increases, $\Gamma$ starts increasing and peaks close to $T_{Curie}$. We attribute this peak in $\Gamma$ as an effect caused by the critical spin fluctuation in the ferromagnet due to its proximity to the superconductor.

As a consistency check to the new results emerging from the previous studies involving spin fluctuations, PCAR studies are also carried out on Fe [Fig.6(a)]. In Fe, as $T_{Curie}$~1042K, we do not expect any effect of spin fluctuation on $\tau$ while investigating it through PCAR; we find both $P_f(T)$ [Fig. 6(b)] and $Z(T)$ [Fig. 6(c)] remain almost constant in the temperature range 2-9K. There is a small increase in $\Gamma$ [Fig. 6(c)] close to $T_c$ of the superconductor, due to intrinsic shortening of its quasiparticle lifetime. This small increase in $\Gamma$ is in qualitative agreement with the intrinsic decrease in $\tau$, as theoretically predicted$^{31}$ and experimentally observed in strong-coupling superconductors.$^8$

Figure 6 (a) Normalized PCAR spectra of Fe-Nb in the temperature range 2-9 K. (b) Variation of $P_f$ with $T$. (c) Temperature dependence of $\Delta$, $Z$, and $\Gamma$. 

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4.2. Studies on isostructural filled skutterudites

To confirm the role of spin fluctuation, further PCAR experiments are carried out on isostructural filled skutterudites. The skutterudites are represented by a general formula $\text{AT}_4\text{X}_{12}$, where T is a transition metal and X is pnictide. Changing the filler element “A”, magnetic properties of this system can be tuned; substitution of mono valent cation ($\text{K}^+$, $\text{Na}^+$) makes it ferromagnetic, while divalent filler ($\text{Ca}^{++}$, $\text{Yb}^{++}$) makes it nearly ferromagnetic\textsuperscript{109}. Accordingly, $\text{KFe}_4\text{Sb}_{12}$ is a ferromagnetic metal with $T_{\text{Curie}} \sim 80$ K, whereas $\text{CaFe}_4\text{Sb}_{12}$ and $\text{YbFe}_4\text{Sb}_{12}$ are nearly ferromagnetic metals for which large spin fluctuations are expected to be present even at the lowest temperature. PCAR spectroscopic studies [Fig. 7(a-c)] are performed on these set of crystals using a superconducting Nb tip. It reveals that for $\text{KFe}_4\text{Sb}_{12}$ at 3.5K, $P_I = 67.3\%$ for $Z = 0.08$, with no effect of $\Gamma$ being present, as it should be; whereas as for $\text{CaFe}_4\text{Sb}_{12}$ one gets $\Gamma = 0.35$ meV at 3.5K, a much higher value of $\Gamma = 0.9$ meV at 2.3 K is observed for $\text{YbFe}_4\text{Sb}_{12}$. This suggests that $\text{YbFe}_4\text{Sb}_{12}$ is more spin fluctuating compared to $\text{CaFe}_4\text{Sb}_{12}$, which is indeed true and verified by magnetization and heat capacity studies\textsuperscript{109}.

4.3. Spin fluctuation studies on itinerant ferromagnetic system $\text{Ni}_{3+\epsilon}\text{Al}_{1-x}$

Our claim that PCAR can detect spin fluctuation gets further support from the studies done on itinerant ferromagnetic system\textsuperscript{27} $\text{Ni}_{3+\epsilon}\text{Al}_{1-x}$. We have chosen three alloys namely (i) $\text{Ni}_{76}\text{Al}_{24}$, (ii) $\text{Ni}_{74}\text{Al}_{26}$ and (iii) $\text{Ni}_{73}\text{Al}_{27}$. Magnetization measurements [Fig. 8(a-c)] show both (i) and (ii) are ferromagnetic with $T_{\text{Curie}} \sim 72$K and 60 K respectively. In $\text{Ni}_{74}\text{Al}_{26}$ the moment is considerably smaller than $\text{Ni}_{76}\text{Al}_{24}$, also the magnetization does
Figure 8. (a-c) Temperature (T) variation of magnetization (M) for Ni76Al24, Ni74Al26 and Ni73Al27 respectively. Insets are the PCAR spectra with m-BTK fit (solid red line). (d) Variation of Δ, Γ and Pt with Al concentration.

not saturate down to the lowest temperature indicating the presence of spin fluctuations even below $T_{Curie}$. Ni73Al27 does not exhibit any ordering down to the lowest temperature. PCAR analysis [inset Fig. 8(a-c)] reveals (i) has $P_t \sim 51\%$ with $\Gamma=0$; for (ii) $P_t$ reduces to 39% and a small presence of $\Gamma=0.09$ meV is seen. In (iii) we find $P_t=0$ and $\Gamma$ increases to 0.44 meV, confirming the presence of inherent paramagnetic spin fluctuation. Fig. 8(d) shows the variation of $P_t$, $\Gamma$ and $\Delta$ with Al concentration. With increasing Al, $P_t$ decreases and as expected is zero for the paramagnetic Ni73Al27. $\Gamma$ is zero for the ferromagnetic Ni76Al24 and increases gradually with Al content. The superconducting energy gap (Δ) on the other hand decreases with increasing Al content as we go from the ferromagnetic to the spin fluctuating regime. To explore the effect of spin fluctuations on $\Gamma$, detailed PCAR studies are done on ferromagnetic Ni76Al24 and the spin fluctuating Ni73Al27. Different PCAR spectra are recorded by engaging the Nb tip several times on them at different places. These spectra correspond to the same sample-tip combinations but have statistically different values of Z. Fig. 9(a) shows the variation of $P_t$ with Z for Ni76Al24. Here also presence of magnetic dead layer at the F-S interface\textsuperscript{30} reduces the absolute
Figure 9. (a) Variation of $P_t$ with $Z$ at 2.4 K for different Ni$_{76}$Al$_{24}$-Nb contacts. (b) Variation of $\Gamma$ with $Z$ at 2.4 K for different Ni$_{73}$Al$_{27}$-Nb contacts. (c) Variation of $\Delta$ with $\Gamma$ for the same. Solid lines are a guide to eye.

value of $P_t$ with increasing barrier strength $Z$. Similar studies on Ni$_{73}$Al$_{27}$-Nb contacts [Fig. 9(b)] reveal a systematic variation between $Z$ and $\Gamma$, with increasing $Z$, $\Gamma$ decreases. This is expected since a larger barrier at the interface implies that the two electrodes are less strongly coupled to each other. Therefore, the influence of spin fluctuation would be less on the superconducting electrode. Consequently, there is also an inverse correlation between $\Delta$ and $\Gamma$ [Fig. 9(c)] for contacts with different $Z$, the smaller the lifetime of the quasiparticle ($\tau$), the smaller is $\Delta$ for the superconductor. This inverse correlation between $\Delta$ and $\Gamma$ provides a valuable consistency check of the intrinsic nature of proximity effect between a superconductor and a spin fluctuating metal.

5. **Fabrication of a variable temperature Scanning tunneling microscope (STM)**

5.1. **Principle of operation, design and instrumentation**

The last part of this thesis is on the design and fabrication of a variable temperature STM. This set up is intended to extend the spectroscopic measurements with spatial resolution. The STM described in this thesis is designed and fabricated in our lab. In this section, I will outline the related studies showing the energy and spatial resolution of our variable temperature STM. The essential components of a STM consists of a sharp probing tip, a piezoelectric scanning feedback unit, that controls the vertical and lateral movement of the tip; a coarse positioning unit, which brings the tip-sample separation to within the tunneling range (~5 Å); a vibration isolation stage and a set of control electronics. To initiate the tunneling process, the STM tip is brought to within several angstroms from the sample surface by the coarse approach using the piezo walker. Application of a bias
voltage between the sample and the tip gives rise to a quantum mechanical tunneling current that varies exponentially with distance as discussed in section 1.1. The tips used in these STM studies are prepared either by electrochemical etching of W wire in NaOH/KOH solution or by mechanically cutting Pt-Ir wire. Field emission on Cu/Au single crystals is used to clean the tip before the final experiment.

5.2. Topography

Our STM works in the constant current mode. The output voltages from the feedback loop to the z-electrode of the piezo tube are converted to deduce the vertical position of the tip as a function of its lateral position, z(x,y), giving topography of underlying surface. Figure 11 shows some of the images of Au thin film, which we have used to calibrate the STM.

![Topographic images of Au on glass at 300 K with V_{bias}=-25mV, I_{set}=40pA.](image)

Figure 11. Topographic images of Au on glass at 300 K with V_{bias}=-25mV, I_{set}=40pA.

5.3. Current vs. Tip-Sample Separation (I - Z) spectroscopy

The tunneling current (I) in an STM depends exponentially on the tip-sample separation.
(d) as $I \propto e^{kd}$. This exponential dependence of the tunneling current with $d$ is verified performing $I$ vs. $Z$ spectroscopy as shown in Figure 12(a). The linear curve [Fig. 12(b)] confirms the vacuum nature of the tunneling and a work function of 4.5 eV is deduced from its slope.

5.4. **Differential Conductance Spectroscopy**

In addition to measuring the work function and topography, the STM also has the ability to measure a much more scientifically interesting property of any conducting material – the electronic DOS. The ability to extract DOS information from the tunneling current can be easily seen from eqn. (1.2) as the differential tunneling conductance, $G(V)=dI/dV|_V$, is simply proportional to the local DOS of the sample at $E=eV$. Figure 13(a) shows topography of a cleaved Highly Oriented Pyrolytic Graphite (HOPG) sample with visible step edges. We have performed the $G(V)$-V measurements [Fig. 13(b)] on these armchair edges using a Pt-Ir tip at various temperatures. The bump like structure at positive bias in local DOS of HOPG is possibly due to a local electrostatic potential induced by the tip.

![Figure 13. (a) Topography and (b) dI/dV –V spectra on HOPG at various temperatures with Pt-Ir tip.](image)

5.5. **STM Studies on the superconductor NbN**

NbN is a conventional BCS superconductor with moderate high $T_c \sim 16K$. The short coherence length ($\xi<5$ nm) and large penetration depth ($\lambda\sim200$ nm) allows fabrication of few nanometer thick thin films. These films have good mechanical strength, chemically
stability in ambient atmosphere, and can be recycled from cryogenic temperatures to room temperature without any detectable degradation in their superconducting properties. These properties of NbN allow us to investigate its superconducting properties using our STM. The sample shows smooth grains with textured surface [Fig. 14(a)]. To study the
superconducting properties, STS experiments are performed [Fig. 14(b)-(e)] on it using a Pt-Ir tip. The tip is prepared by field emission on an Au single crystal (111) before the actual experiment to clean it from any impurities. The superconducting gap ($\Delta$) comes around 1.6 meV at 5.2 K. Further studies are going on to get a full understanding of the properties of the superconductor NbN.

6. Conclusion

DPCAR spectroscopic studies are performed on the anisotropic superconductor YNi$_2$B$_2$C to establish the multiband nature of superconductivity. Evolution of the multiband effects are investigated by doping non magnetic impurity (Pt) in YNi$_2$B$_2$C. Studies on YNi$_{2-x}$Pt$_x$B$_2$C reveal that the observed gap anisotropy in YNi$_2$B$_2$C disappears with Pt doping, as it introduces inter-band scattering, while specific heat studies confirms that the Pt doping has no effect on the DOS in YNi$_{2-x}$Pt$_x$B$_2$C ($x=0-0.2$). The scaling of $H_{c2}$ and $T_c$ due to Pt doping is in agreement with the multiband scenario. PCAR spectroscopic studies on ferromagnets (NdNi$_5$, Fe, KFe$_3$Sb$_{12}$), nearly ferromagnetic metals (CaFe$_4$Sb$_{12}$, YbFe$_4$Sb$_{12}$) and itinerant ferromagnetic ($Ni_{3+\pm x}Al_{1-\pm x}$) systems are done. In NdNi$_5$, temperature variation of spontaneous magnetization ($M_s$) follows closely the temperature variation of transport spin polarization ($P_s$). Our studies establish that PCAR spectroscopy can detect the signature of spin fluctuations through a decrease of superconducting quasiparticle lifetime ($\tau$) due to proximity effect, thus it can be used as a spin resolved probe to study spin fluctuation and transport spin polarization in magnetic systems. Apart from these, the design and operation of a home build variable temperature STM is presented and some preliminary results are shown.
List of publication


Chapter 1

Spectroscopic investigation of superconductivity and magnetism

1.1 Introduction

Probing the interaction of electrons and their elementary excitations, close to Fermi level \( E_F \), is of fundamental interest to understand electronic properties of metals. There are different spectroscopic techniques developed over the years to probe these electrons and the elementary excitations present in a solid, viz. tunneling spectroscopy, photoemission spectroscopy, and optical spectroscopy etc.. In this thesis, I will employ specific configurations of spectroscopic techniques, namely, point contact spectroscopy and scanning tunneling spectroscopy to probe superconductivity and magnetism in various correlated electron systems. These fall in the broad class of transport spectroscopic measurements where the current–voltage \( I-V \) characteristics of a device or interface are used to extract spectroscopic information on the electrons close to \( E_F \).

Electron tunneling spectroscopy in artificial solid-state tunneling structures was pioneered by the work of Esaki on semiconductor p-n junctions in 1958\textsuperscript{34}. Shortly after, Fisher and Giaever succeeded in fabricating thin-film metal-insulator-metal tunnel junctions\textsuperscript{35} in 1959. Furthermore, by cooling below the superconducting transition temperature of lead, in 1960 Giaever\textsuperscript{36} directly observed the superconducting energy gap in the differential tunneling conductance (dI/dV vs. V) of an aluminum-oxide-lead tunnel junction. Finally, Binnig and Rohrer invented the Scanning Tunneling Microscope (STM) in 1982\textsuperscript{37}. It is a unique experimental tool to analyze both structural and electronic properties of a surface on the atomic scale simultaneously. These discoveries demonstrated tunneling as a powerful spectroscopic tool to investigate the
electronic structures of conducting materials with high energy resolution.

This thesis primarily deals with the study of superconductors and probing various magnetic systems with superconductors using tunneling spectroscopy. Therefore, first I will give a background overview on superconductivity. Then, to set the foundation for understanding the physics encoded in the tunneling spectra, a review on the theory related to the vacuum tunneling process between two metal electrodes separated by an infinite barrier, as observed in tunneling spectroscopy and scanning tunneling microscopy (STM)\textsuperscript{38} is given. I will also describe the underlying principle of point contact Andreev reflection spectroscopy with finite barrier at the interface between a normal metal and a superconductor, based on Blonder, Tinkham, and Klapwijk (BTK) theory\textsuperscript{4}. Then I will show how PCAR spectroscopy can be used as a spin resolved probe to extract information about different magnetic systems based on modified BTK\textsuperscript{6,7} theory, when a magnetic electrode replaces the normal metal.

1.2 Introduction to superconductivity

Below a certain transition temperature ($T_c$), there are two observable properties which define a superconducting state, i.e. the zero resistivity and perfect diamagnetism. The first of which, the zero resistance state is the property that lead Kamerlingh Onnes\textsuperscript{39} in 1911 to the discovery of superconductivity in Hg by cooling it below the transition temperature ($T_c\sim$4K). It is the second defining property, i.e. the exclusion of magnetic field or perfect diamagnetism that distinguishes superconductivity from perfect conductivity (which is also a state of zero resistance). An ideal conductor expels an applied magnetic field only in the case when it is put in the zero resistance state before the application of the external magnetic field. However, superconductors act as a
perfect diamagnet regardless of whether the field is applied first or if cooling is applied first. Meissner and Ochsenfeld\textsuperscript{40} discovered this phenomenon in 1933 and it is known as Meissner effect. In 1935, F. London and H. London showed that the Meissner effect is a consequence of minimization of the electromagnetic free energy carried by superconducting current. In a magnetic field, screening currents are generated which flow on the surface of a superconductor and cancels the flux density within it. There is also a thermodynamic critical field, $H_c$, beyond which the flux can enter into the superconductor. $H_c$ is related thermodynamically to the difference in free energy of the normal and superconducting states in zero field. In early 1950, Ginzburg and Landau gave their phenomenological model\textsuperscript{41} that dealt mainly with the superconducting electrons and the spatial variation of the superconducting wave function. The Ginzburg-Landau theory is a macroscopic theory based on the general theory of the second order phase transitions, where a complex wave function $\Psi$, describing the superconducting electrons is introduced. Paired electrons occupy a single, macroscopic quantum state $\Psi(\vec{r}, t) = \psi(\vec{r}, t)e^{i\phi(\vec{r})}$, where $\phi$ is the phase. The paired electrons always maintain a fixed phase relation. $\Psi$ is assumed to be zero in the normal state, and attains a finite real value in the superconducting state. Finally, in 1957, Bardeen, Cooper and Schriefer (BCS) put forward their microscopic theory\textsuperscript{42} that provided a complete and satisfactory picture of the classical superconductors. In the context of BCS theory, zero resistivity and perfect diamagnetism are consequences of the macroscopic quantum state.

### 1.2.1 Overview of the Bardeen-Cooper-Schrieffer Theory

In 1957 John Bardeen, Leon Cooper, and Robert Schrieffer developed their theory of superconductivity in terms of electron pairing. In normal metals, the situation is well
described by free electron theory, where the electrons behave as free particles and the metallic ion is considered as a perturbation on the free electron wave function. BCS theory outlines how in the presence of an attractive interaction between electrons, the normal state of an otherwise free electron gas becomes unstable to the formation of a coherent many-body ground state. This can be visualized as follows: As an electron moves through a conductor, by virtue of the Coulomb attraction it will attract nearby positive charges in the lattice creating lattice deformation. This deformation of the lattice causes another electron, with opposite spin and momentum (i.e. \( k \uparrow \), \(-k \downarrow \)) to move into the region of higher positive charge density. It is then possible for these two electrons to experience a net attractive potential mediated by phonons, despite their like charge. When this attraction is larger than the screened Coulomb repulsion the two electrons form a bound state. However, the formation of a pair of electrons that are weakly bound by the lattice vibration is limited to low temperatures \( \sim 10K \). This bound pair of electrons with opposite spin and momentum is called the Cooper pair. The formation of the bound states creates instability in the ground state of the Fermi sea of electrons and a gap \( \Delta(T) \) opens up at the Fermi level between the BCS ground state and the first excited state. The gap corresponds to the minimum energy required to create a single-electron (hole) quasiparticle\(^1\) excitation from the superconducting ground state. Thus, the binding energy of a Cooper pair is two times the energy gap \( \Delta(T) \). These quasiparticle excitations above the BCS ground states are coherent superposition of the electron and hole quasiparticles and are in one-to one correspondence with excitations in the normal state. The key consequences of the BCS theory include a connection of

\(^1\) Quasiparticles are the elementary excitations of a superconductor, which are created when a Cooper pair breaks. They are also known as the Bogoliubons.
the gap parameter $\Delta$ to the transition temperature $T_c$,

$$2\Delta = 3.52k_BT_c$$ \hspace{0.5cm} (1.1)

and the Debye temperature ($\Theta_D$)

$$T_c = 1.14\Theta_D e^{N(0)V}$$ \hspace{0.5cm} (1.2)

where $N(0)$ is the density of states at the Fermi level, and $V$ is the attractive electron-phonon interaction potential. $T_c$ is in part determined by the Debye temperature, so that an observable shift in $\Theta_D$ should accompany an alteration of $T_c$. Such a change in $\Theta_D$ can be accomplished by replacing one element in the material with a different isotope of the same element. Indeed, measurements demonstrating such a shift in $T_c$, termed the isotope effect, provided convincing support for the BCS model of superconductivity.

For weak coupling superconductors\textsuperscript{II}, the reduced gap $\Delta(T)/\Delta(0)$ is a universal function of the reduced temperature $T/T_c$, near the critical temperature $T_c$,

$$\frac{\Delta(T)}{\Delta(0)} = 1.76 \left(1 - \frac{T}{T_c}\right)^{1/2}$$ \hspace{0.5cm} (1.3)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.pdf}
\caption{Variation of the reduced gap $\Delta(T)/\Delta(0)$ with the reduced temperature $T/T_c$ according to the BCS theory.}
\end{figure}

\textsuperscript{II} For weak coupling superconductors $N(0)V \ll 1$, correspondingly $2\Delta(0)/k_BT_c \approx 3.52$. 


so that the energy gap approaches zero continuously as $T \to T_c$ as shown in Figure 1. Superconductors, which obey eqn. (1.1) are considered to be weakly-coupled, in reference to the weak interaction energy between the two electrons in a Cooper pair. Furthermore, within BCS theory, the wave functions corresponding to electron pairs (Cooper pairs) are like an atomic $s$-orbital with angular momentum $L=0$. This implies that the spin part of the wave function is antisymmetric in accordance with Pauli’s exclusion principle. In particular, the electron pairs are in a spin-singlet state $S=0$ with antiparallel spins and the pairing symmetry in a conventional superconductor is $s$-wave spin-singlet. The energy gap of an $s$-wave superconductor is the same over the entire Fermi surface. In the PCAR studies contained in this work, we are interested in the amount of energy required to break a Cooper pair into two quasi-particles. Cooper pairs that contribute to the total energy reduction of the system lie within an energy $\pm \Delta$ of the Fermi level. Consequently, the density of states (DOS) for quasi-particles (Figure 2)

![Figure 2. BCS Density of states as a function of energy (E) relative to Fermi energy.](image-url)
which are excited out of the condensate, is given

\[ N(E) = N(0) \frac{|E|}{\sqrt{E^2 - \Delta^2}}, \quad |E| > \Delta \]
\[ = 0, \quad |E| < \Delta \]  \hspace{1cm} (1.4)

where, \(N(0)\) is the normal state DOS and \(E\) is the energy of the quasiparticle. Hence, any energy applied to the system is capable of destroying the superconducting state if applied in an amount equivalent to or greater than the superconducting gap magnitude, \(|E| \geq \Delta\); as we have already encountered the critical temperature \(T_c\), for which thermal energy destroys the superconducting state. If the energy is kinetic then it is the critical current \(J_c\) that is reached, and if the energy is magnetic then it is the critical field \(H_c\).

### 1.2.2 Multiband Superconductivity

Superconductivity is a cooperative behavior of the conduction electrons in certain materials. In the BCS theory of superconductivity all electrons on the isotropic Fermi surface (FS) contribute equally to the superconducting pairing, giving a constant superconducting gap \(\Delta\). Different scenario can arise, if the FS of a material is anisotropic and has multiple bands those contribute to the superconductivity; leading to anisotropic gap (\(\Delta\)) values in the superconductor. The difference of \(\Delta\) on different sheets of the FS, or multi-band superconductivity was considered theoretically back in the late 50s\(^{10}\). Recently this has emerged as a possible explanation for the unusual physical properties observed in MgB\(_2\)\(^{80}\), YNi\(_2\)B\(_2\)C\(_{13}\)\(^{43}\), namely, the large anisotropy in the superconducting order parameter\(^{15}\), a negative curvature\(^{44}\) in \(H_{c2}(T)\) close to \(T_c\) and transition form a hexagonal to a square flux line lattice\(^{45}\) at high magnetic fields etc.
The simplest form of multiband superconductivity arises when electrons on different Fermi sheets in the same material have different electron-phonon coupling strength leading to different superconducting energy gaps ($\Delta$). According to two-band model, the amount of interaction between the bands depends on their relative compatibility for pair exchange. In the event that pair exchange is small, the superconducting bands will behave independently and have separate critical temperatures. On the other hand, if pair exchange is large, the smaller band will be supported to the same $T_c$ as of the strong coupling band. This behavior is demonstrated in Figure 3, where an intermediate scenario has also been included. It turns out that quasiparticle exchange and scattering are also important in determining the critical field properties of two-band superconductors, in particular the $H_{c2}$. The signature of a second band is generally weak for bulk measurements such as resistive transition or even specific heat. For example, a resistive transition for the weaker of two superconducting bands would be masked by the fact that the resistance of the stronger coupling band is already zero. Therefore, a momentum resolved probe would be the most useful in investigating the two bands. Directional PCAR (DPCAR) spectroscopy then is particularly well suited to probe the multiple gaps due to its angle and high energy
resolution. This is the method that will be evoked in section 3.2, where we study the properties of quaternary borocarbide superconductor YNi$_2$B$_2$C ($T_c$~16K) using temperature and magnetic field variation of DPCAR spectroscopy.

1.3 Tunneling spectroscopy and STS as probes for density of states:

Classically, for electrons to flow between two conductive materials, they must be in contact, at which point the Fermi energies of the two materials balance at the interface. In STM, this balancing process actually begins before the contact is made. An energy barrier is defined by the nonconductive region between the two conductive materials in the form of vacuum. This prevents conduction when the materials are not in contact. As shown in Figure 4, the Fermi energies of the sample and tip, originally in coincidence when the systems are brought near contact. They get separated by an energy $eV$ due to the application of a sample bias voltage $V$. This allows electrons to tunnel through the vacuum barrier separating the two, leading to a detectable current. The magnitude of this current depends on the DOS of both tip and sample, on the distance between them, and on the amount of thermal broadening. In this section, a brief description on the elastic tunneling between two metal electrodes (tip and sample in STM) is discussed based on work of Bardeen$^1$, where the two electrodes are separated by large barrier with independent local density of states (LDOS). When the two electrodes are brought within a few angstroms, their electronic wave functions begin to overlap significantly. At this point, it is possible for electrons to tunnel from one electrode to the other provided that energy is conserved and there are available states in the counter-electrode. If these conditions are met, then a tunneling current proportional to the local density of states in each electrode flows across the barrier.
Figure 4. Energy level diagram of tip and sample. (a) Both the tip and sample are separated; (b) tip and sample are in thermal equilibrium, without any applied bias voltage; (c) positive sample bias; (d) negative sample bias.

According to Fermi’s golden rule, the transmission rate from the initial state $|i\rangle$ to a final state $|f\rangle$ is given by

$$ R_{i\rightarrow f} = \frac{2\pi}{\hbar} |M_{fi}|^2 \delta(E_i - E_f) $$

(1.5)

Here, $M_{fi}$ is the matrix element of the perturbation potential between the initial and the final states, the delta function ensures energy conservation. Following Fermi’s golden rule, the current flowing from the tip $(t)$ to the sample $(s)$ and correspondingly from sample to tip is given by

$$ I_{t\rightarrow s} \propto \int_{-\infty}^{\infty} |M_{ts}|^2 N_t(E - eV)f(E - eV)N_s(E)(1 - f(E))dE $$

(1.6)
where, the Fermi function 
\[ f(E) = \frac{1}{e^{(E-E_F)/k_B T+1}} \]
determines the distribution of electronic states at a given energy \((E)\), \(N(E)\) represents the LDOS in the tip or the sample at a given energy and \(I\) is the tunnel current flowing in the direction indicated by the subscripts. In the process, the occupied states \((N_t, f)\) can tunnel into unoccupied sample states \([N_s, (1-f)]\). The common energy scale is chosen to be that of the sample, and thus the tip energy scale is shifted by \(\Delta E = eV\). Then, the current measured by the STM is the net current described by the difference of these two expressions,

\[
I = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} |M_{ts}|^2 N_t(E-eV)N_s(E)[f(E)-f(E-eV)]dE \tag{1.8}
\]

where \(I\) is now the net tunnel current, \(e\) is the Coulomb constant, \(\hbar\) is Planck’s constant. A more intuitive physical description about the experimental realization of the tunneling process emerges from eqn.(1.8), when we make certain reasonable approximations. First, the tip is usually a simple metal with a relatively flat DOS near the Fermi energy \((E_F)\), also tunneling studies involving superconductors are associated with the energy scale \(\sim 100\) meV; within this limit, the \(N_t(E)\) can be taken as constant for most of the normal metal. Next, \(M_{ts}\) is the matrix element of the perturbation potential between the tip and the sample, at low bias voltage it can be approximated as a constant in energy, removing it from the integral. Furthermore, if the barrier height, defined by the average of the work functions \((\sim eV)\), is much larger than the difference between the work functions and the voltage applied \((\sim \text{meV})\), a WKB approximation can be applied to the tunneling matrix with a dependence only on the width of the barrier. This simplifies the problem into one in which a change in the barrier, i.e. an
increase or decrease the tip-sample distance, results in a proportional tunneling rate. The current is then proportional to the integral of the LDOS and Fermi distribution of the sample at a given barrier width, given by

$$ I \propto \int_{-\infty}^{\infty} N_g(E)[f(E) - f(E - eV)]dE $$  \hspace{1cm} (1.9)

The tunneling measurements presented in this thesis are performed at low temperatures ~4 K, permitting additional physical insight for $T \to 0$. At low temperatures, the Fermi function becomes a step function so that the integral becomes a definite integral between $E_F$ and the applied bias voltage

$$ I \propto \int_{E_F}^{eV+E_F} N_g(E)dE $$  \hspace{1cm} (1.10)

In reality, at finite temperatures, eqn. (1.10) will be modified by an apparent smearing of thermal energy features with width $\sim k_BT$. The validity of these approximations provides a simple picture in which the tunneling current is the integral of the density of state between the Fermi energy ($E_F$) and the applied voltage ($eV$). Furthermore, it suggests that the differential conductance ($G=dI/dV$) in a tunneling experiment can
probe directly the LDOS on a sample surface. Figure 5(a)-(b) show typical STM spectrum for Nb at 335 mK and a tunneling spectrum for Pb at 2.2K respectively.

In the next section, I will discuss point contact spectroscopy (PCAR) in connection with electron tunneling experiments. In PCAR spectroscopy the tip and the sample touches each other forming a micro-constriction with a finite barrier at the interface, unlike what we have seen in STS experiments. I will show following the BTK- theory how PCAR can be used as energy, momentum and spin resolved probe to extract information about various elementary excitations present in normal metals, ferromagnets and superconductors. I will also compare the limits and possibilities between these two measurements.

1.4 Point contact spectroscopy

Point contact spectroscopy\(^2\) (PCS) represents the other regime of tunneling experiment, where unlike STM, the two metal electrodes physically touch each other with no intended tunneling barrier at the interface. Here, the electrical transport takes place through a narrow constriction formed at the interface between two metallic electrodes. The contact, so made, should be ballistic in nature \(i.e.,\) mean free path of the electrons \((l)\) in both the materials must be greater than the diameter \((a)\) of the point contact as shown in Figure 6. For such a ballistic contact, with the application of a bias voltage, statistically, the electrons are accelerated across the contact diameter without undergoing any scattering and therefore do not dissipate energy. The accelerated electrons resonantly excite different elementary excitations (\(e.g.,\) electron and hole like quasiparticles in superconductors, phonons, magnons etc.) present in a solid and that leaves non-linearity in the I-V characteristic of the point contact spectra at the energy
scales appropriate for different processes. This property of point contact is used to get energy and momentum resolved spectroscopic information about electron-phonon interaction\textsuperscript{48} in metals, spin transport properties in ferromagnets\textsuperscript{7}, order parameter symmetry in superconductors\textsuperscript{16,49} etc. In PCS, one can precisely regulate the excitations of the elementary modes at definite energies in a controlled manner. This is not achievable in bulk transport, where it is impossible to impart a considerable energy to the electrons that is comparable to the energy of Debye phonons\textsuperscript{2}. It turns out that for the electron, energy acquired in the electric field to reach the characteristic phonon energies, the current density should exceed\textsuperscript{2} $10^9$ A/cm$^2$. Such high current densities in the bulk metal are unattainable because of the Joule heating arising from multiple scattering of electrons with lattice defects, impurities, phonons etc.

**Figure 6.** Ballistic transport in a point contact experiment.
1.4.1 Electron-Phonon interaction in normal metal

The vibrations of the atoms in a lattice can be represented in the form of excitation waves propagating in the crystal. The thermal vibrations of the lattice atoms are described in terms of quasiparticles — the phonons, thus the scattering of electrons by thermal vibrations of the lattice can be considered as the interaction of quasi-particles.

In this section, I will give a brief overview of this electron-phonon interaction in normal metal. Qualitatively the electron-phonon interaction process in a ballistic PCS experiment can be described as follows. At the increase of voltage by $\Delta V$, the change of resistance $\Delta R$ is proportional to the excitation probability $G(\varepsilon)$ of a phonon mode with energy $\varepsilon$ by the electrons in that contact zone, i.e. $\Delta R \propto G(\varepsilon) \Delta V$. Since $R \propto \Delta V/\Delta I$, the second derivative $d^2V/dI^2 \propto \Delta R/\Delta V \propto G(\varepsilon)$. Thus, the second derivative of the current-voltage characteristics of a PCS experiment reflects the probability of phonons emission $G(\varepsilon)$. The function $G(\varepsilon)$ is proportional to the phonon density of states $F(\varepsilon)$ multiplied by square of the electron-phonon interaction $\alpha^2(\varepsilon)$. Therefore, we can write

$$\frac{d^2V}{dI^2} \propto G(\varepsilon) = \alpha^2(\varepsilon)F(\varepsilon)$$

(1.11)

The $\alpha^2(\varepsilon)$ dependence in eqn.(1.11) is “smoother” function of energy (\varepsilon) compared to $F(\varepsilon)$, so the shape and peculiarities (maxima, minima) of $d^2V/dI^2$-V curves are to a greater extent dictated by the behavior of the phonon spectrum in a particular metal. To illustrate this, we have measured the phonon density of states in Ag at 2.4 K with

---

\[ \text{III} \quad \text{In experiments usually} \frac{d^2V}{dI^2} \text{ is measured and the theoretical calculations involving} \]
\[ \alpha^2(\varepsilon)F(\varepsilon) \text{ are done with} \frac{d^2I}{dV^2}. \text{These two are related as} \]
\[ \frac{d^2V}{dI^2} = R_D \frac{dR_D}{dV} = -R_D^3 \frac{d^2I}{dV^2}, \text{where} \]
\[ R_D = \frac{dV}{dI} \text{ is the differential resistance.} \]
Figure 7. (a) $dI/dV-V$ and (b) $d^2I/dV^2-V$ of the electron-phonon coupling spectra for Ag, measured with a Ag tip at $T=2.4$ K.

another Ag tip by point contact spectroscopy, which is shown in Figure 7(b). The associated phonon modes in Ag are the two transverse acoustic (TA) and one longitudinal acoustic (LA). The first two maxima are due to transverse vibrations of atoms in two perpendicular directions (polarizations) while the third maximum is due to more energized longitudinal vibrations since their excitation in a crystal causes the compression and extension waves. The phonon spectrum is an important characteristic of a solid. It enables determination of thermal characteristics of the lattice, the heat capacity and heat conductivity, plays a decisive role in kinetic phenomena stipulated by the electron-phonon interaction. The point-contact spectroscopy yields detailed information on the relative force of electrons binding with some groups of phonons, e.g. with those transversely or longitudinally polarized. Thus, it becomes clear which phonons play more important role in various processes. For normal metals, the study of PC spectra is the only experimental technique, which enables direct measurement of energy dependence of the spectral function of electron-phonon interaction.
1.4.2 Point contact Andreev reflection Spectroscopy

This is a variant of point contact spectroscopy based on the principle of Andreev reflection\(^3\), where one of the metal electrodes is replaced by a superconducting one. The theoretical formalism is also different from the vacuum tunneling process in the sense, that it contains much more physics apart from investigation of DOS, in terms of the elastic scattering that takes place at the interface of the two metal electrodes. This approach has the advantage of capturing an important process that the tunneling approach failed to, i.e., the Andreev reflection in the low-barrier N-S tunneling limit. In the process of Andreev reflection, an electron moving in a normal metal (N) with momentum \(\vec{k}\) hits an interface with a superconductor (S) and gets reflected back as a hole in the metal. The reflected particle (hole) has opposite charge and spin as the incident particle (electron). This is equivalent to two single electrons with opposite momentum and spin pairing up to form a Cooper pair, which travels inside the superconductor. The process is elastic\(^IV\) in nature and highly spin dependent, as the quasi-particle (excitation) energy is the same for the incident electron and the reflected hole. Because of its negative effective mass, the reflected hole has a velocity opposite to that of the incoming electron and carries charge current in the same direction. Thus, the reflected hole ensures current conservation. At zero temperature, for a N-S interface with no barrier, the differential conductance \((G=dI/dV)\) at low bias \((|V|<\Delta/e)\) is enhanced by a factor of 2 compared to its high bias \([G_n=G(V>>\Delta/e)]\) value. However, experiments are always performed at finite temperature and the barrier can never be completely transparent due to Fermi velocity mismatch in the two electrodes and presence of oxide barrier at the interface. For such non-transparent barriers, two peaks

\(^{IV}\) Energy and momentum are conserved in the process.
Figure 8. Andreev reflection at normal metal-superconductor (N-S) interface.

appear in the G-V spectrum close to $\pm \Delta/e$. Andreev reflection arises naturally from the Bogoliubov–de Gennes (BdG) equation with a spatially slowly varying order parameter $\Delta(x)$ and a vanishing barrier strength at the interface. The order parameter $\Delta(x)$ is approximately zero on the N side and is a constant on the S side. The Andreev reflection process has been taken into account by the BTK theory to calculate the current through the interface using the BdG equation. In the BTK formalism, the BdG equation is set up such that the interface between N and S is modeled as a delta function potential $V(x) = V_0 \delta(x)$. For convenience the strength of the potential barrier is usually characterized by a dimensionless parameter $Z = V_0 / \hbar v_F$, which can vary from a fully transparent ($Z=0$) to tunneling regime ($Z \to \infty$). It takes into account multiple effects: first, it takes into account the effect of any oxide barrier that may be
present at the interface and second, Z also accounts for an effective barrier arising from the Fermi velocity mismatch between the normal metal and the superconductor.

An electron in the normal metal with energy greater than the superconducting energy gap can get transmitted to the superconductor as an electron like quasiparticle. If the energy is less than the superconducting energy gap, the incident electron undergoes Andreev reflection. For finite barrier at the interface (Z ≠ 0), the electron has finite probability to undergo normal reflection as well. The incident and the reflected electron wave functions on the N-side of the electrode are given by

\[ ψ^N_{\text{incident}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{ikx}, \] (1.12)

\[ ψ^N_{\text{reflected}} = b \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-ikx} + a \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{-ikx}, \] (1.13)

and the transmitted wave function on the S-side of the electrode is

\[ ψ^S_{\text{trans}} = c \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} e^{ikx} + d \begin{pmatrix} v_0 \\ u_0 \end{pmatrix} e^{-iqx}. \] (1.14)

To calculate the total current across the N-S interface, we need to evaluate the Andreev reflection probability \[ A(E) = |a(E)|^2 \] and the normal reflection probability \[ B(E) = |b(E)|^2 \]. We use the following boundary conditions

(i) Continuity of the wave functions across the boundary

\[ \Psi_{\text{tot}}(x = 0) = \Psi_{\text{trans}}(x = 0) \]

(ii) The derivative of the wave functions satisfies

\[ \Psi'_{\text{trans}}(x = 0) - \Psi'_{\text{tot}}(x = 0) = \frac{2mV_0}{\hbar^2} \Psi_{\text{tot}}(x = 0), \]

appropriate for a delta function potential. The Andreev reflection and normal reflection probabilities in different scenario are listed below:
\[ A(E) = |a(E)|^2 = \frac{\Delta^2}{E^2 + (\Delta^2 - E^2)(1 + 2Z^2)} \]

\[ B(E)b = |b(E)|^2 = 1 - A(E) = \frac{(u_0^2 - v_0^2)^2 Z^2 (1 + Z^2)}{\gamma^2} \]

<table>
<thead>
<tr>
<th>Probability</th>
<th>(E&lt;\Delta)</th>
<th>(E&gt;\Delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A(E))</td>
<td>(u_0^2)</td>
<td>(u_0^2)</td>
</tr>
<tr>
<td>(B(E)b)</td>
<td>(v_0^2)</td>
<td>(v_0^2)</td>
</tr>
</tbody>
</table>

Table 1. Probabilities in the unpolarized scenario for the N-S interface from BTK theory (detailed calculations are shown in Appendix A).

The current \(I\) as a function of voltage \(V\) is given in terms of \(A(E)\) and \(B(E)\),

\[
I \propto Nv_F \int_{-\infty}^{+\infty} \left[ f(E - eV, T) - f(E, T) \right] [1 + A(E) - B(E)]dE \tag{1.15}
\]

It is clear from eqn.(1.15), that the ordinary reflection associated with \(B(E)\) reduces the current, Andreev reflection associated with \(A(E)\) enhances it by transmitting a Cooper pair over the interface for one incident electron. The zero-temperature differential tunneling conductance \(\frac{dI}{dv} \propto [1 + A(E) - B(E)]\) versus bias voltage \(V\) for a number of barrier heights \(Z\) are plotted in Figure 9. In the limit of zero-barrier \((Z \rightarrow 0)\), the conductance within the superconducting gap nearly doubles as most of the incident electrons are Andreev-reflected and the transmitted electron pairs across the interface carries double the amount of charge of the incident electrons. In the high-barrier limit \((Z \rightarrow \infty)\), the result given by the BTK formalism is essentially the same as that of the tunneling spectroscopy in STS.

This generalized semiconductor model takes account phenomenon relevant to a full range of junction resistances down to metallic limit. The theory describes tunneling for arbitrary barrier strengths by extending the semiconductor model to include state specific information using the Bogoliubov transformation\(^5\). Using the Bogoliubov
Figure 9. Variation of PCAR spectra with the interface barrier Z with $\Delta=1.5$ meV. (a) and (b) shows the transition from T=0 K to T=2 K. (e)-(f) are simulated by varying Z at fixed $T=2K$ and $\Delta=1.5$ meV.

equations for normal metal- superconductor junctions, with a junction impedance (Z) that can vary from metallic to tunneling regime, BTK have inserted information of the microscopic theory that is ordinarily lost by the semiconductor model.

1.5 PCAR as a spin resolved probe

Point contact spectroscopy$^2$ has been used for many years to investigate the static and dynamic spin dependent properties of magnetic systems at the Fermi level ($E_F$). Using the ballistic transport property of point contact, spectroscopic information about
different phenomenon in magnetic solids can also be probed, viz. electron-magnon interaction$^{52}$, Kondo scattering$^{53}$ etc. In recent years the other variant of this technique, namely, point contact Andreev reflection (PCAR)$^7$ spectroscopy has emerged as a popular technique to measure the spin polarization$^{6,7,17}$ in the transport current at the Fermi level in ferromagnetic metals. In the study of magnetic systems, this technique has a large technological impact since, a knowledge of the spin polarization at $E_F$ is essential for the better realization of spintronics$^{54}$ device applications. Conventionally two techniques, other than PCAR have widely been used for the determination of spin polarization in ferromagnetic materials. The first one, pioneered by Meservey and Tedrow$^{25}$, involves spin-dependent tunneling from a ferromagnet to a superconductor when the superconducting density of states is Zeeman split by the application of a magnetic field. This technique involves the tedious process of fabricating a tunnel junction and the need to apply a large perturbing magnetic field of several Tesla. The advantage of this technique is that it can distinguish the sign of the spin carriers and measure both the sign and magnitude of spin polarization at the $E_F$, which is not possible with the PCAR technique. The second one, spin-resolved photoemission$^{55}$, relies on the measurement of the spin of electrons that emerge from the surface of a ferromagnet close to the $E_F$. However, this technique is extremely surface sensitive as the electrons measured in photoemission experiments emerge from a depth of a few angstroms to a few tens of angstroms from the surface.

In order to give an overview of PCAR spectroscopy involving ferromagnets (F), in the subsequent sections I will introduce (i) the notion of transport spin polarization ($P_t$) and (ii) the modified BTK (mBTK) theory$^7$ used to analyze the PCAR spectroscopic data involving a ferromagnetic-superconductor interface.
1.5.1 Spin polarization in ferromagnets

Spin polarization of a ferromagnet is usually defined as

$$\begin{align*}
P &= \frac{N_U(E_F) - N_D(E_F)}{N_U(E_F) + N_D(E_F)}
\end{align*}$$

where $N_U(E_F)$ is the density of states (DOS) of the up (down) spin electrons at the Fermi level, as shown in Figure 10. Since the DOS of up-spin and down-spin electrons are equal in paramagnetic materials [$N_U(E_F) = N_D(E_F)$], $P=0$ for paramagnetic materials. On the other hand, since the density of state of up-spin and down-spins are different in ferromagnetic materials [$N_U(E_F) \neq N_D(E_F)$], $P$ is larger than 0, but smaller than 1 for ferromagnetic materials. The majority spin sub-band electrons dominate the spin transport in these materials. If a material has a band gap in the minority band (semiconducting) at the Fermi level and exhibits metallic behavior in the majority band, the density of state of the minority band is zero at the Fermi level. In this case, since only up-spin electrons are present at the Fermi level, $P=1$. This type of material (CrO$_2$) is called "half-metal" because it exhibits both metallic and semiconducting behaviors. However, for transport measurements, one has to consider the transport current ($I$) involving electronic spins, which depends on the spin polarization of the net flux of electrons crossing an interface and is given by the product of the density of states [$N(E_F)]$ and Fermi velocity ($v_F$). Transport spin polarization ($P_t$) of a ferromagnet is thus different from the spin polarization ($P$) and is defined as

$$P_t = \frac{(I_U - I_D)}{(I_U + I_D)}$$

where $I_U(D) = (N_U(D) v_{F_U(D)})_{FS}$ is the net flux averaged over the Fermi Surface$^{17}$. Here, $v_{F_U(D)}$ is the Fermi velocity of the spin up (down) electrons and $n$ gives the exponent.
Figure 10: The spin density of states \([N_{\uparrow \downarrow}(E_F)]\) at the Fermi level \((E_F)\).

appropriate for the concerned experimental regime (\(n=1\) for ballistic regime, \(n=2\) for diffusive regime). Only for an isotropic Fermi surface when the Fermi velocity of the spin up and spin down bands are equal we expect \(P_f=P\). The transport spin polarization measured using PCAR technique gives only the magnitude, it cannot discriminate the sign of the spin sub band that contributes to the spin polarization at the Fermi level.

1.5.2 Measurement of transport spin polarization using PCAR

In a non-magnetic metal the Andreev process is always allowed, because every energy state in a normal metal has both spin-up and spin-down electrons. However, in a magnetic metal, this is no longer true and the minority spin population limits Andreev reflection. The Andreev reflection process is highly spin dependent, if only one spin band is occupied by the conduction electrons in the metal electrode (i.e. it is fully spin polarized), Andreev reflection will be inhibited due to inability to form the Cooper pair in the superconductor and impossibility of single particle transmission. A ferromagnetic metal electrode has unequal spin density of states in its spin-up \((N_{\uparrow})\) and spin-down \((N_{\downarrow})\) bands at the Fermi level. These inequality in spin density of states prevents the
Andreev reflected hole to propagate back in the ferromagnet for energies less than the superconducting energy gap and it decays at the interface as an evanescent wave that carry no current. Andreev reflection is then forbidden, as there are no states for a hole to get reflected to, resulting in zero conductances across the interface below the gap. Therefore, the low bias enhancement in the PCAR spectrum is suppressed. The value of transport spin polarization ($P_t$) is estimated from the degree of this suppression according to the mBTK formalism. Here I will briefly outline the mBTK formalism to calculate the total current through an F-S point contact.

Likewise, for the N-S interface, here also the incident wave function for the electron with wave vector $k$ in the ferromagnetic electrode is given by

$$
\Psi_{\text{incident}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{ikx} \tag{1.18}
$$

The reflected wave function gets modified compared to the N-S case; it decays at the

---

**Figure 11.** Schematic of the Andreev reflection process for a half metal-superconductor interface, the half metal has 100% spin polarization at the Fermi level ($E_F$).
interface as an evanescent wave with the inverse of the decay length given by $\kappa$. The reflected wave function is given by

$$\Psi_{\text{reflected}} = b \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-ikx} + a \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{ikx}$$  \hspace{1cm} (1.19)$$

The transmitted wave function on the S-side of the electrode remains the same

$$\Psi_{\text{trans}} = c \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} e^{iqx} + d \begin{pmatrix} v_0 \\ u_0 \end{pmatrix} e^{-iqx}$$  \hspace{1cm} (1.20)$$

The total current across the F-S interface is calculated using the same boundary conditions as done for N-S interface. In the presence of a barrier potential ($Z = V_0/\hbar v_F$) at the interface, the total current is given by (detail calculations in appendix A)

$$I_{u,p} \propto N v_F \int_{-\infty}^{+\infty} [f(E - eV,T) - f(E,T)] \left[ 1 + A_{u,p}(E) - B_{u,p}(E) \right] dE \hspace{1cm} (1.21)$$

where $N$ is the density of states in normal metal and $f(E,T)$ is the Fermi function. $A_{u,p}(E)$ and $B_{u,p}(E)$ are probabilities for Andreev and normal reflection respectively for the unpolarized ($u$) and polarized ($p$) scenario, which are tabled below:

<table>
<thead>
<tr>
<th>Probability</th>
<th>E&lt;Δ</th>
<th>E&gt;Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_p(E)=</td>
<td>a(E)</td>
<td>^2$</td>
</tr>
<tr>
<td>$B_p(E)b=</td>
<td>b(E)</td>
<td>^2$</td>
</tr>
</tbody>
</table>

**Table 2.** Probabilities for spin polarized scenario from m-BTK theory, here $\epsilon = \frac{E^2-\Delta^2}{E^2}$.

In studying ferromagnet-superconductor interface, PCAR spectroscopy uses the correlation between the degree of suppression of Andreev reflection and the spin polarization of the material. For a ferromagnet with 100 % spin polarization at the $E_F$,
the Andreev reflection probability \( A_\phi(E) \) becomes zero. If a magnetic metal which is not 100% spin polarized, the total spin current \( I_{\text{tot}} \) through the interface can be decomposed as the sum of the spin polarized part \( I_p P_t \) and unpolarized part \( (1-P_t)I_u \), giving rise to a family of curves shown in Figure 12. The spin-polarized part of the current cannot Andreev-reflect and thus does not contribute to the overall conductance below the gap, whereas the unpolarized fraction of the current contributes \( 2(1-P_t)I \) to the overall conductance, as in the case of a normal metal. Hence, for any arbitrary \( P_t \), the total current can be written as

\[
I_{\text{tot}} = I_u (1 - P_t) + I_p P_t \tag{1.22}
\]

where \( I_u \) and \( I_p \) are the currents calculated for 0% and 100% spin polarization respectively using eqn. (1.21). The experimentally obtained PCAR spectrum between a ferromagnet and a superconductor is fitted by differentiating eqn.(1.22) with respect to the applied bias voltage \( V \). The parameters involved in the fitting procedure are the
transport spin polarization ($P_t$), the barrier ($Z$) at the interface and the superconducting energy gap ($\Delta$). Figure 12 shows the variation of transport spin polarization in PCAR spectra for a zero barrier at finite temperature. There is a continuous suppression of Andreev reflection with the increase in $P_t$, and for $P_t=1$, there is no Andreev reflection. Analysis of PCAR spectra requires that to get a proper fit to the data the fitting parameters ($\Delta$, $Z$ and $P_t$) must have no inter-correlation. Discussions on PCAR spectra in Figure 12 makes it clear that for a zero barrier at the interface, the introduction of $P_t$ reduces the Andreev reflection probability, and for a 100% spin polarized material, it becomes zero. I will discuss based on Figure 13, the evolution of the PCAR spectra when both $Z$ and $P_t$ are present. The red curve is the ideal PCAR spectra at $T=0$, $P_t=0$ and $Z=0$ with a double enhancement in its conductance [$G(V)$] value compared to its normal state value ($G_n$). The finite temperature effect broadens the PCAR spectra due

Figure 13. Variation of PCAR spectra with $P_t$ and $Z$ at a finite temperature ($T$).
to the Fermi function smearing, though conductance doubling is still being observed. The barrier at the interface introduces dips for voltages $|eV|\leq \Delta$ in the Andreev reflection spectra; the dips increases with $Z$, finally reaching the tunneling regime. The effect of $Z$ is to reduce the transparency of the barrier at the interface; but in no way it suppresses the Andreev reflection compared to the effect of $P_f$. Thus, these two effects are uncorrelated and can be distinguished independently from a PCAR spectrum.

1.6 The role of quasiparticle lifetime on the tunneling and PCAR spectra

The BTK model uses a generalized semiconductor scheme to match the wave functions at the N-S interface. Based on this scheme, BdG equations are solved to get the Andreev and normal reflection probabilities with the assumption that a delta function potential exists at the interface. It should be noted that the BTK model treats the problem as a one-dimensional case, and assumes that the superconducting energy gap ($\Delta$) varies in an asymptotic nature on a scale shorter than the coherence length ($\xi$) on both side of the interface in the micro-constriction. These assumptions are in good agreement with the theory and experiment, when we study conventional s-wave superconductors. For an ideal superconductor, the quasiparticles associated with elementary excitations over the Bardeen-Cooper-Schrieffer (BCS)\textsuperscript{5} ground state (called the Bogoliubons) are infinitely lived (the superconducting quasiparticle lifetime $\tau\rightarrow\infty$). However, in a real superconductor, inelastic scattering\textsuperscript{8} of the Bogoliubons cause $\tau$ to have a finite value, which is reflected as the broadening of the superconducting DOS in tunneling spectroscopy.

In order to incorporate this effect, a phenomenological inelastic scattering parameter $\Gamma$ is introduced\textsuperscript{9} in the Bogoliubov equations, which has the dimension of
energy and is inversely proportional to the superconducting quasiparticle lifetime ($\Gamma = \hbar/\tau$). Conventionally $\Gamma$ is treated as a damping parameter associated with the decay of an eigen state due to external perturbation. The modified BdG equations become

\[
\begin{align*}
\left[-\frac{\hbar^2}{2m} \nabla^2 - \mu(x) - i\Gamma + V(x)\right] u_k(x,t) + \Delta(x)v_k(x,t) &= i\hbar \frac{\partial u_k(x,t)}{\partial t} \\
\left[-\frac{\hbar^2}{2m} \nabla^2 - \mu(x) - i\Gamma + V(x)\right] v_k(x,t) + \Delta^*(x)u_k(x,t) &= i\hbar \frac{\partial v_k(x,t)}{\partial t}
\end{align*}
\] (1.23)

The trial wave functions with the decaying term $\Gamma$ can be written as

\[
u_k(x,t) = u_k e^{i(kx - \frac{E_k}{\hbar}) - \Gamma t/\hbar} \text{ and } v_k(x,t) = v_k e^{i(kx - \frac{E_k}{\hbar}) - \Gamma t/\hbar}.
\]

The Bogoliubov coherence factors $u_0$ and $v_0$ becomes

\[
1 - v_0^2 = u_0^2 = \frac{1}{2} \left[1 + \sqrt{\left(E + i\Gamma\right)^2 - \Delta^2} \right]
\] (1.24)

The broadened density of states is given by

\[
N(E, \Gamma) = Re \left(\frac{1}{u_0^2 - v_0^2}\right) = Re \left(\frac{E + i\Gamma}{\sqrt{(E + i\Gamma)^2 - \Delta^2}}\right)
\] (1.25)

**Figure 14:** Broadening of the BCS density of states $N(E)$ with increasing $\Gamma$. 

![Graph](image-url)
The modified probabilities for Andreev reflection and normal reflection, as calculated based on this are given by (details of the calculations follows from appendix A)

\[
A(E) = |a(E)|^2 = \frac{\sqrt{(\alpha^2 + \eta^2)(\beta^2 + \eta^2)}}{\gamma^2} \quad (1.26)
\]

\[
B(E) = |b(E)|^2 = Z^2 \frac{[(\alpha - \beta)Z - 2\eta^2] + [2\eta Z + (\alpha - \beta)]^2}{\gamma^2} \quad (1.27)
\]

where \(u_0^2 = \alpha + i\eta\) and \(v_0^2 = \beta - i\eta\).

This modification of the BTK theory leads to an excellent agreement with both the PCAR spectroscopy and tunneling experiments involving multiband superconductors\textsuperscript{19} and magnetic materials\textsuperscript{27}. In Figure 15 and Figure 16 we show some experimental results and their theoretical fits in various systems involving the broadening term \(\Gamma\).

\[\text{Figure 15. PCAR spectra for YNi2B2C using Ag tip at 305 mK.}\]

For conventional s-wave superconductors \(\Gamma\) is zero almost throughout the entire temperature range barring very close to \(T_c\), where it becomes finite but small (\(\Gamma \sim 10^{-2}\) meV, \(\tau \sim 10^{-13}\) s) due to intrinsic shortening of \(\tau\) in the superconductor itself. In chapter 3
**Figure 16.** PCAR spectra of Ni$_{73}$Al$_{27}$ using a superconducting Nb tip at 2.4 K. The red line is the mBTK fit to data with best fit parameters $P_T=0$, $\Gamma=0.44$ meV, $\Delta=1.18$ meV and $Z=0.72$. Green line is the simulated spectra for the same with $\Gamma=0$, $\Delta=1.28$ meV and $Z=0.32$ and $P_T\sim39\%$.

of this thesis, I will show based on recent PCAR studies done on various magnetic systems, that the effect of $\Gamma$ can also become important even at $T\ll T_c$, when the superconductor is in close proximity to a spin fluctuating metal. The proximity effect leads $\Gamma$ to increase ($\Gamma\sim1$ meV, $\tau\sim10^{-15}$s) drastically. We observe the smaller $\tau$ is, the smaller is $\Delta$ for the superconductor.

### 1.7 Point contact spectroscopy and STM: The momentum resolution

The basis of performing energy and momentum resolved spectroscopy using PCAR is controlled by the contact diameter ($a$) at the N/F-S interface. This can be achieved only if the electronic mean free path ($l$) in both the electrodes is greater than the contact diameter ($a$). Under the application of a bias voltage, in such a ballistic contact, statistically, the electron gets accelerates freely in the area of the contact volume without undergoing any scattering. The resistance of a ballistic contact between two
metals in their normal state is thus independent of the bulk resistivity (and purity) of the materials involved and is given by
$$R_S = \frac{2h}{e^2(ak_f)^2}$$, where $k_f$ is the Fermi momentum.

Hence, for a ballistic contact, both the energy and momentum information of the process are preserved.

The momentum resolved ballistic transport is a unique advantage in PCAR spectroscopy compared to the same in scanning tunneling microscope. We consider electrons in typical metals with mass ($m_e$) $\sim 10^{-27}$ gm and Fermi velocity ($v_F$) $\sim 10^8$ cm/s. Therefore, it carries a momentum ($p_F = m_e v_F$) $\sim 10^{-19}$ gm.cm/s. Now let us compare the momentum resolution in these two techniques based on the Heisenberg’s uncertainty principle $\Delta x \Delta p \geq \frac{\hbar}{2}$. In point contact spectroscopy, typical contact diameter is $\sim 50$ Å, hence the uncertainty in momentum $\Delta p \sim 10^{-21}$ gm.cm/s; the momentum resolution becomes $\frac{\Delta p}{p} \sim 10^{-2}$. Thus, the momentum information at the Fermi surface is preserved in a point contact experiment involving the ballistic transport. On the other hand, in an STM experiment, the typical spatial resolution ($\Delta x$) is $\sim 1$ Å with the uncertainty in momentum is given by $\Delta p \sim 10^{-19}$ gm.cm/s. This limits the momentum resolution to $\frac{\Delta p}{p} \sim 1$, i.e., the uncertainty in momentum is itself of the order of Fermi momentum and consequently all the momentum information is lost. At the end, I would like to mention that recent developments in the Fourier transformed scanning tunneling spectroscopy (FS-STS) imaging can reveal momentum-space structure of elastic scattering processes as it has been shown in high-$T_c$ Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$.

In summary I have discussed different regimes of electron tunneling with scanning tunneling microscopy/spectroscopy and point contact Andreev reflection spectroscopy. I have also shown how spectroscopic information can be extracted using
these techniques. Most of the importance naturally lies on the point contact spectroscopy involving normal metals, ferromagnets and superconductors, which constitute a major part in this thesis.

The thesis is organized as follows. In chapter 2, I will describe the experimental set up, electronics and data acquisition involving PCAR spectroscopy with temperature range 300 mK-300 K and in magnetic fields up to 9T. Chapter 3 will focus on the gap anisotropy in the superconductor YNi$_2$B$_2$C. Using PCAR as a momentum resolved probe, we show that the origin of superconductivity in YNi$_2$B$_2$C is multiband in nature. To investigate further, non-magnetic impurity (Pt) is doped in the system and the evolution of multiband superconductivity is investigated. In chapter 4, I will present the work done on ferromagnets, itinerant ferromagnets and on nearly ferromagnetic metals using PCAR as a spin resolved probe. Finally, in chapter 5, I will present the construction and operations of a variable temperature STM. I will also present some spectroscopic investigations on various systems, performed using our home made STM.
Appendix

I. Blonder-Tinkham-Klapwijk Formalism

The Bogoliubov–de Gennes (BdG)\textsuperscript{37} equations generalize the BCS formalism to treat superconductors with spatially varying pairing strength $\Delta(x)$, chemical potential $\mu(x)$, and Hartree potential $V(x)$. The elementary excitations in a superconductor described by the Bogoliubov-Valatin operators as

$$
\gamma^+_{\vec{k} \uparrow} = u_{\vec{k}} \hat{c}_{\vec{k} \uparrow}^\dagger - v_{\vec{k}} \hat{c}_{-\vec{k} \downarrow},
$$

(A.1)

$$
\gamma^-_{-\vec{k} \downarrow} = u_{\vec{k}} \hat{c}_{-\vec{k} \downarrow} + v_{\vec{k}} \hat{c}_{\vec{k} \uparrow}^\dagger;
$$

(A.2)

$|v_{\vec{k}}|^2$ gives the probability of the pair ($|\vec{k} \uparrow\rangle, |-\vec{k} \downarrow\rangle$) being occupied and $|u_{\vec{k}}|^2$ gives the probability of the pair being unoccupied, with the normalization condition $|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1$. The operator $\gamma^+_{\vec{k} \uparrow}$ ($\gamma^-_{-\vec{k} \downarrow}$) creates a quasiparticle excitation $|\vec{k} \uparrow\rangle$ ($|-\vec{k} \downarrow\rangle$) from the BCS ground state. Since the ground state contains no quasiparticle excitations, we have $\gamma |\Psi_{BCS}\rangle = 0$, on the other hand an excited state with one quasiparticle is represented as, $\gamma^+ |\Psi_{BCS}\rangle = |\vec{k}\rangle$.

In real space, the operator $\gamma^+_{\vec{k} \uparrow}$ can be represented as a two-element column vector

$$
\psi_{\vec{k}} = \begin{bmatrix} u_{\vec{k}}(x,t) \\ v_{\vec{k}}(x,t) \end{bmatrix},
$$

(A.3)

where $u_{\vec{k}}$ and $v_{\vec{k}}$ satisfies the equations

$$
\begin{cases}
-\frac{\hbar^2}{2m} \nabla^2 + V(x) - \mu(x) u_{\vec{k}}(x,t) + \Delta(x)v_{\vec{k}}(x,t) = i\hbar \frac{\partial u_{\vec{k}}(x,t)}{\partial t} \\
-\frac{\hbar^2}{2m} \nabla^2 + V(x) - \mu(x) v_{\vec{k}}(x,t) + \Delta^*(x)u_{\vec{k}}(x,t) = i\hbar \frac{\partial v_{\vec{k}}(x,t)}{\partial t}
\end{cases}
$$

(A.4)
Deep in the superconducting electrode where $\Delta(x)$, $\mu(x)$, and $V(x)$ are constants, the solutions to (A.4) are time-independent plane waves.

Let $u_k(x, t) = u_k \, e^{i(kx-Et/h)}$ and $v_k(x, t) = v_k \, e^{i(kx-Et/h)}$

For $V(x)=0$, eqn. (A.4) becomes

$$Eu_k = \left[ \frac{h^2 k^2}{2m} - \mu \right] u_k + \Delta v_k$$

$$Ev_k = -\left[ \frac{h^2 k^2}{2m} - \mu \right] v_k + \Delta u_k$$

Solving eqn.(A.5) and eqn.(A.6), we get

$$E = \pm \sqrt{\left[ \frac{h^2 k^2}{2m} - \mu \right]^2 + \Delta^2}$$

here $k_+$ represents electron-like quasiparticle and $k_-$ represents hole-like quasiparticles.

The normalization condition gives

$$1 - v_k^2 = u_k^2 = \frac{1}{2} \left[ 1 \pm \sqrt{\frac{E^2 - \Delta^2}{E}} \right]$$

In the superconducting side, the corresponding wave functions become

$$\psi_{k}^S = \begin{bmatrix} u_{k_+}(x)e^{iEt/h} \\ v_{k_+}(x)e^{iEt/h} \end{bmatrix} = e^{ik_+x} \begin{bmatrix} \frac{1}{2} (1 \pm \sqrt{\frac{E^2 - \Delta^2}{E_k}}) \\ \sqrt{\frac{1}{2} (1 \pm \sqrt{\frac{E^2 - \Delta^2}{E}})} \end{bmatrix} e^{-iEt/h}$$

Similarly, in the normal metal side of the electrode far away from the interface, we have $V(x)=\Delta(x)=0$ with $\frac{h^2 k^2}{2m} = \mu \pm E$.

The corresponding wave functions in the normal metal side are
Where,

\[ E = \begin{cases} 
\frac{\hbar^2 k_+^2}{2m} - \mu, & (|k_+| > k_F) \\
\mu - \frac{\hbar^2 k_+^2}{2m}, & (|k_+| > k_F)
\end{cases} \quad (A.12) \]

To model the N-S interface, BTK represents the interface with a repulsive delta-function potential \( V(x) = V_\delta \delta(x) \). Considering only the elastic tunneling process, only four different processes can take place in the N-S interface. Given an incident electron from the normal electrode, it can be Andreev-reflected as a hole, normal reflected as an electron, transmitted as an electron-like quasiparticle, or transmitted as a hole-like quasiparticle. Therefore, for electrons traveling from N to S, the wave functions of the normal and superconducting electrodes consist of

\[ \psi^N_{\text{incident}} = \left( \begin{array}{c} 1 \\ 0 \end{array} \right) e^{ik_+x}, \quad \frac{\hbar^2 q_+^2}{2m} = \mu \pm E \quad (A.13) \]

\[ \psi^N_{\text{reflected}} = b \left( \begin{array}{c} 1 \\ 0 \end{array} \right) e^{-i q_+ x} + a \left( \begin{array}{c} 0 \\ 1 \end{array} \right) e^{-i q_- x}, \quad (A.14) \]

\[ \psi^S_{\text{trans}} = c \left( \begin{array}{c} u_k \\ v_k \end{array} \right) e^{ik_+ x} + d \left( \begin{array}{c} v_k \\ u_k \end{array} \right) e^{-ik_- x}. \quad (A.15) \]

Since, we are dealing with the excitations above the ground state, one must have \( E_k \geq 0 \), and then the normalization condition in (A.8) becomes
\[ 1 - v_0^2 = u_0^2 = \frac{1}{2} \left( 1 + \frac{\sqrt{E^2 - \Delta^2}}{E} \right) \]  
(A.16)

The coefficients \( a, b, c, \) and \( d \) are calculated using the following boundary conditions

1. The wave function values are continuous at the interface \( x=0 \)
   \[ \Psi_{tot}(x = 0) = \Psi_{trans}(x = 0) \]  
   (A.17)

2. The derivatives of the wave functions satisfies
   \[ \Psi'_{trans}(x = 0) - \Psi'_{tot}(x = 0) = \frac{2mV_0}{\hbar^2} \Psi_{tot}(x = 0) \]  
   (A.18)

Applying the boundary conditions and letting \( k_i = k = k_f = k \), we get

\[ a = \frac{u_0 v_0}{\gamma} \]  
(A.19)

\[ b = -\frac{(u_0^2 - v_0^2)(Z^2 + iZ)}{\gamma} \]  
(A.20)

\[ c = \frac{u_0(1 - iZ)}{\gamma} \]  
(A.21)

\[ d = \frac{i v_0 Z}{\gamma} \]  
(A.22)

where

\[ Z = \frac{mV_0}{\hbar^2 k_F} = \frac{V_0}{\hbar v_F} \]  
(A.23)

and

\[ \gamma = u_0^2 + (u_0^2 - v_0^2)Z^2 \]  
(A.24)

Finally the probability current for Andreev reflection \( A(E) \) and that for normal reflection \( B(E) \) are given by
\[
\begin{array}{|c|c|c|}
\hline
\text{Probability} & \text{E<}\Delta & \text{E>}\Delta \\
\hline
A(E)=|a(E)|^2 & \frac{\Delta^2}{E^2 + (\Delta^2 - E^2)(1 + 2Z^2)} & \frac{u_0^2 v_0^2}{\gamma^2} \\
\hline
B(E)b = |b(E)|^2 & 1-A(E) & \frac{(u_0^2 - v_0^2)^2 Z^2 (1 + Z^2)}{\gamma^2} \\
\hline
\end{array}
\]

Consequently, when a bias voltage is applied, the total current flowing from the normal to the superconducting electrode is

\[
l \propto N v_F \int_{-\infty}^{+\infty} [f(E - eV, T) - f(E, T)] [1 + A(E) - B(E)] dE \quad \text{(A.25)}
\]

Equation (A.25) shows that Andreev reflection increases the current transmission while the normal reflection reduces tunneling current.

**II. Modified Blonder-Tinkham-Klapwijk Formalism**

Modified BTK formalism\(^7\) is applied to investigate the current-voltage characteristic of the ferromagnet-superconductor point contacts. In this scenario, ferromagnetic electrode has unequal number of spin up and spin down states at the Fermi level, hence the Andreev reflected hole cannot propagate back inside the ferromagnet and decays at the interface as an evanescent wave. The incident and reflected wave functions of the electron at the interface (x=0) with wave vector \(k\) are given by

\[
\Psi_{\text{incident}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{i q x} \quad \text{(A.26)}
\]

\[
\Psi_{\text{reflected}} = b \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-i q x} + a \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{i k x} \quad \text{(A.27)}
\]
where $\kappa$ is inverse of the length over which the evanescent wave decays at the interface, $a$ and $b$ are the coefficients for Andreev reflection and normal reflection respectively. Thus using eq. (A.26) and (A.27), the total wave function in the normal metal becomes

$$\Psi_{tot} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{iqx} + b \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-iqx} + a \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{i\kappa x}$$  \hfill (A.28)

The transmitted component of the wave function on the S side of the electrode is

$$\Psi_{trans} = c \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} e^{ikx} + d \begin{pmatrix} v_0 \\ u_0 \end{pmatrix} e^{-ikx}$$  \hfill (A.29)

Here $u_0$ and $v_0$ are obtained from the solution of the BdG equation in the superconductor with the normalization condition $u_0^2 = 1 - v_0^2 = \frac{1}{2}[1 + ((E^2 - \Delta^2)/E^2)^{1/2}]$, we also assume $k=q=k_F$ for the incoming and transmitted wave. The coefficients $a$, $b$, $c$, and $d$ are calculated using the boundary conditions

$$\Psi_{tot}(x = 0) = \Psi_{trans}(x = 0)$$  \hfill (A.30)

and

$$\Psi'_{trans}(x = 0) - \Psi'_{tot}(x = 0) = \frac{2mV_0}{\hbar^2} \Psi_{tot}(x = 0)$$  \hfill (A.31)

Using eqn.(A.30) and (A.31) we get

$$cu_0 + dv_0 = 1 + b,$$ \hfill (A.32)

$$cv_0 + du_0 = a,$$ \hfill (A.33)

$$cu_0 - dv_0 - 1 + b = -2iZ(1 + b),$$ \hfill (A.34)

$$cv_0 - du_0 - i\kappa \frac{a}{k} = -2iZa.$$ \hfill (A.35)
Since the actual value of $\kappa$ matters in a relatively narrow region of voltages above the gap, the use of the approximation $\frac{\kappa}{q} \rightarrow \infty$ is justified. Finally, solving the above set of linear equations using this approximation we get

$$a = 0; \quad b = \frac{Z(u_0^2 - v_0^2) - iv_0^2}{Z(u_0^2 - v_0^2) - iu_0^2}$$

(A.36)

Thus in the 100% spin polarized scenario, the Andreev reflection probability becomes

$$A(E) = |a(E)|^2 = 0$$

(A.37)

and the normal reflection probability is given by

$$B_p(E) = |b(E)|^2 = \frac{(\varepsilon^{1/2} - 1)^2 + 4z^2\varepsilon}{(\varepsilon^{1/2} + 1)^2 + 4z^2\varepsilon}$$

(A.38)

where $\varepsilon = (E^2 - \Delta^2)/E^2$. 


Chapter 2
Experimental techniques

2.1 Introduction

In this chapter, I will present details of the instrumentation, data acquisition and experimental techniques related to point contact spectroscopy (PCS), dc transport and magnetization measurements. These instruments are designed and fabricated at TIFR, I was actively involved in all of these projects. As the major part of this thesis deals with PCS and its variant point contact Andreev reflection (PCAR) spectroscopy, first I will introduce the concepts of contact size limitations in PCS. This is essential, because most of the time the contact diameter plays a detrimental role deciding the nature of PCS/PCAR spectrum. Then I will describe in details about the experimental realization of PCS along with the other experimental techniques.

2.2 Contact size limitations in PCS

In point contact spectroscopy\(^2\), we are concerned with the fundamentals of microscopic transport of electric current through a narrow metallic constriction. The PCS would be impossible if the characteristics to be measured were critically dependent on the constriction geometry. Ideally, in a conventional PCAR experiment two symmetric peaks appear in the G(V)-V spectrum at bias voltages $eV=\pm\Delta$, which corresponds to the energy gap of the superconductor. Beyond the superconducting gap voltage, no structure apart from the smooth decay of the density of states is expected. However, at times, large zero bias conductance peak or anomalous dip structures appear at bias voltages beyond the superconducting energy gap in the PCAR spectra. To understand
the origin of these anomalous features in a PCAR spectrum, we need to look at a microscopic level, where the contact geometry becomes important and play a dominant role\textsuperscript{58} in determining the shape of the spectra. To get proper and clean data as shown in Figure 15, the size of the contact must be within the ballistic limit. This is determined by two properties of the sample (tip) and one property of the contact: $l_{el}$, $l_{in}$, and $a$. Here $l_{el}$ is the elastic mean free path\textsuperscript{V} and $l_{in}$ is the inelastic mean free path\textsuperscript{VI} of the electron in a sample (tip), and $a$ is the characteristic size of the point contact. Depending on contact size, different regimes of transport in PCS can be defined as follows:

1. **Ballistic regime**: In the ballistic limit (also known as the Sharvin limit\textsuperscript{59}) the elastic mean free ($l_{el}$) path of the electron is much greater than the contact diameter ($a$), i.e. $l_{el} \gg a$. Here the electrons can pass through the contact, statistically without undergoing any elastic or inelastic scattering events at the interface. If there is an inelastic collision, the additional energy absorbed by the electron (due to the applied bias voltage) may be sufficient to excite the quasi-particles states resonantly. The resistance of a ballistic contact between two metals in their normal state is independent of the bulk resistivity of the material and the Sharvin resistance is given by

$$R_S = \frac{2h}{e^2 (ak_F)^2} \quad (2.1)$$

where $k_F$ is the Fermi momentum. When the contact diameter ($a$) becomes comparable to the Fermi wavelength ($\lambda_F \sim 2\text{Å}$) of the electrons, the quantum ballistic regime is entered. In this external ballistic regime, the wave like nature of the electron becomes prominent and conductance quantization\textsuperscript{60} is observed in units of $(2e^2)/h$.

\textsuperscript{V} The momentum of the electron alters but the energy remains the same.

\textsuperscript{VI} Both the momentum and the energy of the electron get modified.
2. Thermal regime: The thermal limit is the other extreme of ballistic regime. Here the point contact diameter is larger than both the elastic and inelastic mean free path of the electrons in a sample, i.e. $\sqrt{l_{el} l_{in}} \ll a$. The contact resistance in this limit is given by Maxwell resistance\(^6\) as

$$R_M = \frac{\rho(T_{eff})}{2a} \tag{2.2}$$

where, $\rho$ is the bulk resistivity of the sample and $T_{eff}$ is the effective temperature of the contact. The contact area being too large results in multiple scattering events and excessive heat (Joule heating) is generated within the contact volume. This excessive heat increases the local temperature of the contact by a large amount with the voltage rise. This can be significant if there are any critical points in the resistivity near the temperature at which the experiment is being carried out. Hence, all the transport spectroscopic information is lost when the contact is in the thermal regime.

An intermediate scenario, known as the diffusive regime, can be also be defined when the contact diameter is in between the the ballistic and the thermal limit. In this case the size of the point contact is defined as $l_{el} \ll a \ll l_{in}$. The contact resistance in this intermediate scenario is given by the Wexler formula\(^6\) as

$$R_D = R_S + \frac{1}{\alpha} R_M \tag{2.3}$$

where $F\left(\frac{1}{\alpha}\right)$ is a slowly varying function or the order of unity. In eqn.(2.3), $R_S$ varies as $\frac{1}{a^2}$ and $R_M$ varies as $\frac{1}{a}$. For low resistivity materials (clean samples, large mean free path) and small contacts eqn.(2.3) is dominated by $R_S$, vice versa for dirty samples (very small mean free path) and large area contacts $R_M$ dominates the same expression. In the intermediate scenario, contribution from both $R_M$ and $R_S$ becomes important. In
Figure 17. Evolution of the dip structures with contact resistance (size) in the spin triplet superconductor Sr$_2$RuO$_4$ measured with a normal metal Ag tip at 300mK. The blue curve corresponds to the conventional spectrum. The dips are marked by arrows.

In the study of superconductor-normal metal contacts using PCAR spectroscopy, the contact resistance is dramatically affected when the superconducting transition takes place and $\rho(T_{\text{eff}})$ becomes zero. In the I-V characteristic, this transition causes a sharp change in the slope at the voltage corresponding to the critical current of the superconductor. Consequently, dip structures appear in the normalized differential conductance versus voltage (PCAR) spectrum as shown in Figure 17. These dips can appear anywhere in the voltage scale depending on the contact geometry and how the critical current is reached. With the reduction of the contact size (increase in the contact resistance) ballistic limit is reached from the intermediate one. It is also important to note that, for a large area contact (large contribution from $R_M$) when the current reaches its critical value, the superconductor suddenly becomes normal in that contact region its resistance becomes finite. As a result, there is a large zero bias enhancements in the $G(V)$-V spectrum. The origin of all these anomalous features depends on the contact geometry, hence extreme care should be taken while analyzing the PC/PCAR spectra.
2.3 PCAR experimental details

2.3.1 The cryostats

We have three different cryostats in our lab. The first one is a continuous flow cryostat. It is the smallest one, does not require liquid N\textsubscript{2} to precool it before transferring liquid 4He. The cryostat is connected directly to the liquid He container by a syphon. Liquid He is pumped into the cryostat through the syphon using a diaphram pump. In the continuous flow method, starting from room temperature it takes only 30 minutes to reach the base temperature of 2.8 K. In the single shot method the temperature goes down to 1.8K, and stays there maximum upto 30 minutes. We have an electromagnet of 1.5 T, within which the cryostat is placed as shown in Figure 18.

The second one is a 4He cryostat, with an 11T superconducting magnet. It has a capacity of 20 lt. of liquid He, needs pre-cooling with liquid N\textsubscript{2} before the He transfer.

![Continuous flow cryostat setup](image)

**Figure 18.** Continuous flow cryostat setup.
Figure 19. The 4He and 3He cryostats and the experimental set ups.

The base temperature that we can reach, pumping over 4He is around 1.6K. The helium retention of this cryostat is very good and lasts for around 36 hours with a single liquid helium transfer (90% of the full capacity).

The third one is the 3He cryostat with a 7 T superconducting magnet attached to it, the operating temperature ranges from 300 mK to 300 K. The 3He gas is stored into a self-contained dump vessel so that it does not get mixed with 4He. The cool down process from 300K to 300 mK is as follows. First, we pre-cool the system with liquid N$_2$ to reach 77K. Next, the variable temperature insert (VTI) is cooled to approximately 4.2 K with liquid 4He. To facilitate the 3He transfer, the 1 K pot in the VTI is pumped and the needle valve is opened slightly to allow liquid helium (4He) to flow into the pot, cooling it below 1.5 K. During this process, the sorb (contains activated charcoal to absorb gas) is kept at 45 K so that it does not absorb 3He gas. At this point, we open
the 3He dump vessel slowly by monitoring its pressure on the dump vessel. The 3He gas enters the lower part of the VTI through the feed capillary and it condenses on the 1 K pot assembly and runs down to cool the 3He pot and sample. It takes around 20 minutes for most the gas to get condensed. The 1 K pot needle valve is closed completely so that it cools to the lowest possible temperature for optimum condensation. At this stage, the 3He pot is nearly full with liquid 3He at approximately 1.2 K. The sorb heater is now switched off, it allows the sorb to cool to ~8K. With this, the vapour pressure above the liquid 3He reduces and the sample temperature drops. The minimum temperature that can be achieved in this type of cryostat is approximately 270 mK with no experimental heat load. The temperature control in the range 300mK-2K is done by controlling the sorb temperature up to a maximum of 45K. When the sorb temperature is above 45 K, it will not pump, and the 3He temperature will be largely dependent upon the temperature of the 1 K pot. In the high temperature range (beyond 2K), the sample temperature is controlled by balancing the heat supplied to the heater on the 3He pot along with the heater in the sample holder. During the experiment, the sample is cooled by conduction through, and convection of the 3He gas in the central access of the insert. The temperature of the sorb is not critical but ideally it should be kept within the temperature range from 30 K to 50 K, so that it is ready to come into operation when the sample is to be cooled again. The hold time at base temperature (300 mK) in our system is around 6 hours. After that, again we have to repeat the cooling procedure by filling the 1K pot with liquid 4He and condensing liquid 3He. Extreme care must be taken to prevent the mixing between 4He and 3He due to presence of leaks in the system. We ensure this before the experiment using a mass spectrometer leak detector.
2.3.2 The Insert and head design

Depending on the experimental requirements, we have designed and fabricated several PCS inserts in our lab. The materials used to make these inserts are non-magnetic (SS, Cu). All of them have almost the same design (Figure 20), the PCS head with a differential screw arrangement and a stepper motor at the top of the insert. The stepper motor from outside the cryostat controls the tip motion using the differential screw. In this type of arrangement, the rotational motion of the differential screw is translated into the linear motion. The differential screw has 100 threads per inch, hence a rotation

Figure 20. Different point contact inserts used in 4He and 3He cryostats.
by 1° corresponds to a linear motion of 0.7 μm. The tip is mounted at the end of a differential screw in a copper tip holder, which enables the tip to move closer/away from the sample [Figure 21(a)-(b)]. At times, we also use an additional piezo tube attached to the end of the differential screw to fine tune the contact. We have used Cernox temperature sensor for the thermometry. Electrical connections on the inserts
are done using twisted pairs of copper wires. For the insert used in 3He cryostat, constantan wire is used to minimize the heat loss due to its low thermal conductivity. A 50Ω heater coil (twisted pair of manganin wire) is attached to the lower end of the PCS head, using this we control the sample temperature.

2.3.3 Tip making

Depending on the interest of our study, we normally use normal metals like Ag, Au, Cu, Pt, Pt-Ir or superconductors such as Nb, Ta, Sn wires of 99.99% purity from Alfa Aesar. The tip is prepared either by electrochemical etching or by mechanically cutting a wire. The starting diameter of the wire is usually 250 microns. After processing, the tip diameter is reduced to a few tens of nanometer. However, the pressure on the tip and presence of the dielectric layer at the interface controls the final contact diameter. The details of the procedure are given in chapter 5 in the context of STM tip preparation.

2.4 How to make a ballistic point contact

Different methods are employed to establish a point contact between two conducting metal electrodes viz. needle-anvil technique, shear method, lithographic method, break junctions etc. We follow the needle-anvil method in our PCS experiment. In this method, a fine metallic tip is brought in contact with the sample of interest by a precision control using a differential screw arrangement. Since the interface at the point contact plays a major role in PCS experiments, one has to pay extra attention while preparing the tip and sample surfaces. To avoid any surface degradation, the tip is prepared and loaded on the PCS head just before the experiment; also, the sample is polished and cleaned with fine emery paper and ethanol, acetone respectively.
However, with time a thin surface oxide layer develops on both the tip and the sample surface. After establishing the contact, we need to ensure that the contact lies in the ballistic limit, which is done as follows. First, by controlling the pressure on the tip, we puncture the dielectric layer at the interface and small cracks in the insulating dielectric layer opens up. These small channels allow the current to flow. Thereafter, the ballistic contact is achieved by slightly withdrawing the tip, thereby decreasing the contact area (increasing the contact resistance, $R_d$). At times, application of high voltage electrical pulses at the interface also helps to modify the contact, causing a local breakdown of the dielectric layer. For each contact, a spectrum is recorded and from its nature, we identify the ballistic contact. Typical contact resistance of a ballistic contact lies in the range $\sim 1$-$100\, \Omega$.

### 2.5 Measurement of the differential conductance

The conductance-voltage $[G(V)-V]$ measurement in a PCAR spectroscopy is done by the standard ac modulation technique with phase sensitive detection. The measurement is done in the four probe geometry, the schematic of the experimental set-up is given in Figure 22(a). In this technique, a dc voltage ($V_{dc}$) is modulated by a small ac voltage [$V_{ac} \cos(\omega t)$]. The voltage to current converter [shown in Figure 19(b)] converts the voltage to current $[(I+i \cos(\omega t))]$, which is then passed through the tip-sample junction. The output of the contact voltage can be presented by a Taylor series as

\[
V(I+i \cos(\omega t)) = V(I) + \frac{dV}{dl} i \cos(\omega t) + \frac{1}{2} \frac{d^2V}{dI^2} i^2 \cos^2(\omega t) + \cdots \tag{2.4}
\]

\[
= V(I) + \frac{dV}{dl} i \cos(\omega t) + \frac{1}{4} \frac{d^2V}{dI^2} i^2 (1 + \cos(2\omega t)) + \cdots
\]

If the current $i$ is sufficiently small, the higher order terms in $i$ terms eqn. (2.4) can be
Figure 22 (a). Schematic of the experimental set up for Point contact spectroscopy, (b) Electronic circuit of the voltage (V)-current (I) converter.
neglected. It can be seen from the same equation, that the signal measured with the lock-in at the frequency $\omega$ is proportional to the first derivative $dV/dI$ of the current voltage characteristics, while that measured at the frequency $2\omega$ is proportional to the second derivative $d^2V/dI^2$. The data acquisition programs are developed in house using the Labview-7 software. The dc output voltage ($V$) across the point contact is measured by a digital multimeter and a lock-in amplifier measures the ac output voltage ($dV$). To measure the ac part of the current, it is passed through a standard 10$\Omega$ resistor connected in series with the point contact and the current ($dI$) is measured using a second lock-in. In above mentioned modulation measurement, we keep the frequency $\omega$ =373Hz to avoid any coupling to the line frequency of 50 Hz. The excitation voltage is kept around 1-10% of the voltage scale of interest. In PCAR spectroscopy, since we are dealing with various superconductors with energy gaps ~meV, the excitation voltage varies on the ~10$\mu$V scale. Finally, the differential conductance $G(V) = \frac{dV}{dI}$ of the junction is recorded as a function of bias voltage ($V$). The PCAR spectra is generally depicted by the normalized conductance $VII \frac{G(V)}{G_N}$ vs. the bias voltage ($V$).

2.6 High Frequency ac susceptibility measurement

The high frequency ac susceptibility measurement, as an experimental technique, is very useful in characterizing superconductors. It utilizes the property, perfect diamagnetism, exhibited by superconductors to estimate the transition temperature ($T_c$) and critical field ($H_c$) of the same. The measurement relies on the change of the mutual inductance of a set of two planar coils (100 turns each) when a sample is sandwiched

\(^{VII}\) Normalized at a high bias voltage $|eV|\gg \Delta$. 

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Figure 23. Schematic of AC susceptibility set-up

between them. Schematic of the planar coil geometry is shown in Figure 23. A sinusoidal voltage of high frequency (15kHz) is applied to the primary coil. Due to this, a voltage proportional to the frequency is induced in the secondary coil. The in-phase and out-of-phase components (w.r.t. the driving current of the primary coil) of the voltage are proportional to the real $\chi'$ (diamagnetic response) and imaginary $\chi''$ (power loss) components of the susceptibility respectively. A lock-in amplifier detects the response of the secondary coil. When the sample becomes superconducting at $T_c$, it shields the magnetic flux of the primary coil. Hence, there is a sharp drop in the voltage of the secondary coil (signal) corresponding to the critical temperature ($T_c$) of the superconductor. This gives the superconducting transition temperature ($T_c$) of the sample. When the signal from the secondary coil is recorded while sweeping the magnetic field ($H$), a sudden increase in signal at a particular field denotes the critical field ($H_c$) of the sample, the field at which the sample becomes normal.

It is important to note that though this method does not give the absolute value of the magnetization. However, it is an extremely sensitive technique to measure the superconducting transition, especially for thin films due to its geometry. In conventional susceptometers (SQUID, VSM), the signal is proportional to the volume
of the sample and is not very efficient for the measurement of thin film where the volume is very low. In this geometry, the signal is proportional to the area of the sample making it ideal for the measurement of thin films, samples with larger surface area and small volume. I have used this technique extensively while characterizing the superconducting properties of YNi$_2$B$_2$C (chapter 3).

2.7 Four probe resistivity

When a simple measurement of the electrical resistance of a sample is performed by attaching two wires to it, one inadvertently also measures the resistance of the contact point of the wires to the sample. Typically, the resistance of the point of contact (called contact resistance) is far smaller than the resistance of the sample, and thus can be ignored. However, when one is measuring a very small sample resistance, especially under variable temperature conditions, the contact resistance can dominate and completely obscure changes in the resistance of the sample itself. The effects of contact resistance can be eliminated with the use of a four point probe. A schematic of a four point probe is shown in Figure 24. Four electrical contacts on the sample are made with 100-micron thin gold wires using silver epoxy. A constant current is made to flow

![Figure 24. Schematic of the four probe method.](image-url)
along the length of the sample through probes labeled “1” and “4” in the figure using a current source. The voltage drop between probes “2” and “3” is measured by a digital voltmeter. The four-probe method isolates the current and voltage contacts. As long as the sample and contact resistance is less than the resistance of the voltmeter, the contact resistances does not affect the resistance of the sample as the voltage leads do not draw any appreciable current.

2.8 Noise and energy resolution in transport spectroscopic measurements

Noises present an important problem in every experimental technique. In this section, I will discuss about different sources of noise that affect the energy resolution of transport spectroscopic measurements. In addition, I will discuss the origin of contact heating in a PCS experiment, when the point contact lies in the thermal regime.

2.8.1 Energy resolution

The energy resolution of a transport spectroscopic measurement (by modulation technique) is defined by the thermal smearing and lock-in modulation broadening associated with it. The thermal smearing is estimated by the fact that the derivative of the Fermi function can be fairly well approximated by a Gaussian of width 3.5\(k_bT\). Thus, the thermal energy resolution becomes 1.08 meV at 4.2K and 77 \(\mu\text{eV}\) at 300 mK. The energy broadening due to modulation comes from the amplitude of the bias oscillation that the lock-in uses to measure \(\frac{dl}{dv}\). For a modulation of \(dV_{\text{mod}}\), the resultant energy broadening is given by the peak-peak variation in the bias - 2\(\sqrt{2}dV_{\text{mod}}^2\). Thus, the total energy resolution is given by

\[\text{Energy resolution} = \sqrt{\text{Thermal smearing}^2 + \text{Modulation broadening}^2}\]
\[ \pm \Delta E \approx \sqrt{(3k_B T)^2 + (2.5 e d V_{mod})^2} \]  

(2.5)

Therefore, to get the highest resolved spectral information, measurements should be carried out at temperatures considerably lower than the characteristic temperature (Debye temperature) of excitations being under investigation and with smaller modulation voltages.

2.8.2 Contact heating in PCS

In section 2.2, I have introduced different regimes of transport in PCS experiment, where we encountered the thermal regime for \( a \gg l_{el} l_{in} \). In this regime, all the spectroscopic information is lost due to contact heating. In metals, the conduction electrons principally take part in the heat removal from the hot region to the bulk of the sample. The heat removal from such large contacts with small electronic mean free path is less efficient than in the ballistic regime. It is shown\(^2\) that when the Wiedemann-Franz law holds, the voltage drop (eV) and the temperature at the contact (\( T_{PC} \)) are related as

\[ (k_B T_{PC})^2 = (k_B T_0)^2 + \frac{(eV)^2}{4L} \]  

(2.6)

where \( T_0 \) is the measurement temperature, \( L \) is the Lorentz number. If measurements are performed at low temperatures, i.e. \( T\rightarrow0 \), the contact temperature is linearly dependent on its voltage as \( k_B T_{PC} = \frac{eV}{2\sqrt{L}} \). Substituting the value of \( L = 2.45 \times 10^{-8} \text{ V}^2\text{K}^{-2} \), we get that \( T_{PC} \approx 3.2 \text{ K/mV} \), i.e. a voltage of 1 mV raises the temperature at the contact center by 3.2 degrees. This means that when the sample is at liquid helium temperature, and if we apply a voltage of only 100 mV to the contact (in the thermal regime), the
temperature of the contact becomes higher than the room temperature. This has been verified experimentally in ferromagnetic metals using PCS. In ferromagnetic metals, above the Curie temperature \( T_{\text{Curie}} \), transition from a ferromagnetic to a paramagnetic state occurs. As a result, a kink appears in the electrical resistivity curve. The contact resistance in the thermal regime is expressed by the Maxwell formula \( R_M = \frac{\rho(T)}{2a} \), therefore reaching the \( T_{\text{Curie}} \) in the contact, its resistance curve will have features similar to that of \( \rho(T) \). Such features of the point-contact spectrum for ferromagnetic metals are observed\(^6\) at the voltage corresponding to the \( T_{\text{Curie}} \) of a ferromagnet, which show up in the \( \frac{d^2V}{dt^2} - V \) spectrum in a PCS experiment.

### 2.9 Summary

In summary, in this chapter I have described in details, experimental techniques like PCS and PCAR spectroscopy, resistivity measurement and high frequency ac susceptibility. All these experimental set ups are designed and fabricated in our lab. These techniques along with other the standard measurements like SQUID magnetometer, vibrating sample magnetometer (VSM) and physical properties measurement system (PPMS) are used to characterize different magnetic and superconducting samples studied in this thesis. I have also introduced different regimes of PCS, which plays a major role deciding the nature of PCS/PCAR spectrum. The noise and energy resolution involved in transport spectroscopic measurements are also discussed.
Chapter 3

Studies on the multiband superconductivity in YNi$_2$B$_2$C

3.1 Introduction

The quaternary borocarbide superconductors RNi$_2$B$_2$C (R= Dy, Ho, Er, Tm, Lu, and Y) has received renewed interest in the last couple of years due to their unusual superconducting and magnetic properties. They show departure, in many ways, from the conventional BCS superconductors. Particular attention has been given at determining symmetry of the superconducting order parameter, which is essential in establishing a microscopic model of superconductivity in this group of materials. In this chapter, I will focus on the order parameter symmetry and the evolution of the superconducting properties in YNi$_2$B$_2$C$^{13}$, one of the members of this group. This material has a tetragonal lattice structure with alternating layers of Y-C and Ni$_2$B$_2$. It is a type II superconductor with a transition temperature $T_c \sim 16$K and upper critical field $H_{c2} \sim 10$T. At an early stage, the order parameter in YNi$_2$B$_2$C was considered to be a conventional isotropic s-wave pairing mediated by electron phonon interactions; which is verified by isotope effect$^{68}$. However, recent experiments like field angle dependence of thermal conductivity$^{14,69}$, specific heat$^{15}$, tunneling$^{70}$, point-contact spectroscopy$^{16}$, and ultrasonic attenuation$^{71}$ etc. indicate existence of large anisotropy in the superconducting order parameter. A positive curvature$^{72}$ in $H_{c2}(T)$ near $T_c$ observed in this group of materials shows departure from the conventional s-wave scenario. Evidences against the conventional s-wave order parameter symmetry also comes from the neutron scattering experiment$^{73}$, where occurrence of square vortex flux line lattice at magnetic fields higher than 0.1T is observed. In the conventional s-wave scenario,
the vortex lattice is expected to be hexagonal. The existence of square vortex flux line lattice indicates towards a four-fold symmetry of the order parameter. This is similar to the four-fold $d$-wave order parameter symmetry seen in high $T_c$ cuprates. Following, a $d$-wave order parameter symmetry was suggested\textsuperscript{72} for YNi$_2$B$_2$C. However, experiments like field angle dependence of thermal conductivity\textsuperscript{14,69}, specific heat\textsuperscript{15} also seem to provide strong evidence of sharp minima in the gap function along certain $k$ directions with possible point nodes along [100] and [001]. Based on the shape of the gap function, an order parameter symmetry with mixed angular momentum—namely, $s+g$ symmetry\textsuperscript{74}—has been proposed for this compound. Though, $s+g$ symmetry seems to be consistent with experimental observations of the gap anisotropy at low temperatures, the origin of this symmetry still remains debatable. Moreover, in the $s+g$ descriptions so far proposed, a roughly spherical Fermi surface (FS) is implicitly assumed, where the multiband nature of the complex Fermi surface\textsuperscript{75,76,77,78} in YNi$_2$B$_2$C remains largely ignored. An alternative scenario has also been explored in YNi$_2$B$_2$C where the gap anisotropy could originate from different bands on the Fermi surface having different gap values due to the difference in their electron-phonon coupling strengths. Band structure calculations as well as de Haas–van Alphen (dHvA) studies reveal that YNi$_2$B$_2$C has a multiply connected FS extending over three bands\textsuperscript{78}. From an analysis of the temperature dependence of $H_{c2}$ in YNi$_2$B$_2$C, it has been proposed\textsuperscript{44} that both strongly coupled slow electrons as well as weakly coupled fast electrons coexist on the FS. The existence of weakly coupled Fermi-surface pockets with small or zero gaps is further corroborated from quantum oscillation measurements\textsuperscript{79}, where one of the oscillation frequencies arising from one particular extremal orbit persists deep in the superconducting state whereas the others damp out below 0.8$H_{c2}$.\textsuperscript{44}
Therefore, the possible role of the multiband nature of the FS on the observed gap anisotropy in this material needs to be explored more carefully.

In measurements such as thermal and electrical conductivity, tunneling, optical spectroscopy and point-contact spectroscopy, the contribution from a particular band in a particular \( k \) direction depends on the weighted average of the Fermi velocity \( v_F(k) \) and the density of states \( N_\delta(E_F) \). Therefore, for a nonspherical Fermi surface the contribution of different bands could be different in different \( k \) directions. Recent point-contact spectroscopy studies have shown that such a situation indeed exists in the known two-band superconductor MgB\(_2\)\(^{11,12,80}\). In this case, the relative contribution of \( \pi \) and \( \sigma \) bands in the point-contact current is different when the current is injected along the \( a \) direction from the scenario when it is injected along the \( c \) direction.

In this chapter, first I will introduce the technique — directional point contact Andreev reflection (DPCAR) spectroscopy, where the point contact spectrum is recorded by injecting current along different crystal directions. This is a powerful tool to investigate the gap anisotropy in unconventional superconductors. In contrast to measurements like angular variation of thermal conductivity or specific heat in applied magnetic field, this technique allows a direct measurement of the superconducting energy gap in different \( k \)-direction over a wide temperature and magnetic field range. To investigate further, non magnetic impurity Pt is doped in this system to introduce scattering and evolution of multiband effects are studied in YNi\(_{2.3}\)Pt\(_x\)B\(_2\)C.
3.2 Directional PCAR spectroscopy

In DPCAR spectroscopy\(^{17}\), the total current \((I)\) constitutes of the net flux of electrons from a particular band \(i\) on the FS and is given by,

\[
I = \sum_i I_i \propto \int_{FS} N_{ik}(\vec{v}_{ik} \cdot \hat{n}) \, dS_F = \sum_i \langle N_{ik} \vec{v}_{ik} \hat{n} \rangle_{FS} = \sum_i S_{ik} \tag{3.1}
\]

where \(k\) is an wave-vector at the FS, \(N_{ik}(E_F) = \frac{1}{4\pi^2|\hat{v}_k|E(k)|}\) is the density of states, \((\vec{v}_{ik} \cdot \hat{n}) = v_{ik\hat{n}} \left( v_k = \frac{1}{\hbar} \{\nabla_k [E(k)]\} \right)\) is the component of the Fermi velocity along \(\hat{n}\) and \(dS_F\) is an elementary area on the FS. The total current\(^{81}\) is therefore proportional to the area of projection on the interface plane. The underlying correspondence between the momentum space and the real space can be visualized from Figure 25. In the most simplistic situation, let us consider an ellipsoidal gap function over a spherical FS with maxima along \(\vec{k}_{F_x}\) and minima along \(\vec{k}_{F_x} \left( \vec{k}_{F_y} \right)\). When we probe the crystal along the \(c-\)

\[\langle \Delta \rangle_{I\parallel c} \sim \int_{FS} \Delta_k \, dS_{sk}\]

\[\langle \Delta \rangle_{I\parallel a} \sim \int_{FS} \Delta_k \, dS_{sk}\]

\[\text{Figure 25. Diagrammatic representation of DPCAR spectroscopic technique.}\]
direction using DPCAR spectroscopy, we will mainly encounter the larger gap, as \( \langle \Delta \rangle_{||c} \sim \int_{FS} \Delta_k \; dS_{zk} \). Similarly injecting current along \( \alpha \)-direction, we will probe the superconductivity at the FS, the total current \( I \) is given by the sum over all bands, namely, \( I = \sum_i I_i \), where the contribution from each band is proportional to its area of projection on the interface plane. In general, for a non-spherical FS, the area of projection of a given band will be different along different directions. If the FS extends over several Brillouin zones, the contribution of different Fermi surface sheets to the current will be different in different directions. In a point contact Andreev reflection experiment, where the observed spectrum contains contribution from different bands in proportion to their projection area on a plane perpendicular to the current flow, the average value of \( \Delta \) for \( I||\hat{n} \) is given by a weighted average of the form

\[
\frac{\sum \langle \Delta_a N_a v_{ai} \rangle_{FS}}{\sum \langle N_a v_{ai} \rangle_{FS}}.
\]

Thus for an anisotropic FS, if the superconducting energy gap varies in different bands, different values of \( \Delta \) in different crystallographic directions is expected to arise from the unequal contribution of different bands \(^{82}\). Hence in superconductors like MgB\(_2\), YNi\(_2\)B\(_2\)C, where the FS is extremely anisotropic and different bands on the FS contributes to superconductivity, a significant difference in the relative contribution of different bands can be expected when measured using DPCAR spectroscopy along the crystallographic directions.
3.3 Investigation of gap anisotropy in YNi$_2$B$_2$C using DPCAR spectroscopy

3.3.1 Temperature variation of the energy gap

High quality singly crystals of YNi$_2$B$_2$C are grown by traveling solvent floating zone method. The measurements are carried out on relatively large crystals (0.5mm×0.5mm×2mm) with well-defined facets along [100] and [001]. For DPCAR measurements, a mechanically cut fine silver tip is brought in contact with [100] or dependence of $\Delta$ along two different directions also shows the existence of anisotropy ($\Delta_{||c}/\Delta_{||a} \sim 4$) in the amplitude of the superconducting order parameter. The value $2\Delta_{||c}/k_BT_c \sim 3.6$, which is close to the weak-coupling BCS value $\sim 3.52$, suggests that $T_c$ in YNi$_2$B$_2$C is governed by the larger gap.

These results cannot be explained using a single band anisotropic gap model, where the two gaps would scale by a proportionality factor $\Delta(\vec{k}) = \Delta_0 f(\vec{k})$ or by mixed angular momentum symmetry scenario, such as $s+g$ previously suggested$^{74}$ for this material. However in the $s+g$ model, this variation of the energy gap with temperature can be realized if we assume (i) at the lowest temperature $\Delta_s \neq \Delta_g$ and (ii) both $\Delta_s$ and $\Delta_g$ have different temperature dependence. To verify this scenario, Yuan and Thalmeier$^{83}$ have performed calculations on the temperature variation of amplitudes $\Delta_s$ and $\Delta_g$ for the $s+g$ wave order parameter. According to their results the ratio of $\Delta_s$ and $\Delta_g$ does not change appreciably up to the critical temperature within the BCS formalism. Therefore the difference in temperature dependence of the amplitudes (i.e. $\Delta_s$ and $\Delta_g$) is not rationalized within the BCS theory and needs further investigation. The different temperature variations of the two gaps along different directions are natural, if they originate from two different bands with weak but finite
Figure 26. Temperature variation of PCAR spectra of YNi$_2$B$_2$C. (a) current (I) is injected along (001). (b-c) I is injected along (100) for T=300 mK-2K and 2.3-8K respectively. (d) Temperature dependence of the superconducting gap along I||c and I||a. Orange circles denote the mK data. Solid lines are BCS variation for the same.
inter band scattering as predicted theoretically\textsuperscript{10,18} for a multiband superconductor. For a weakly interacting two-band scenario the temperature dependence of the two-band will be different if the coupling strengths on the two bands are different. Therefore, the difference in temperature dependence of $\Delta_{I||a}$ and $\Delta_{I||c}$ finds a natural explanation in the two-band scenario if the observed gaps in the two directions arise from two different bands.

3.3.2 Magnetic field variation of the energy gap

To find out the effect of magnetic field ($H$) on the anisotropic superconducting energy gaps in YNi$_2$B$_2$C, DPCAR spectroscopy is performed\textsuperscript{19} along both the crystallographic directions [Figure 27(a-b)] with the magnetic field ($H$) applied parallel to the current. In zero field, the best-fit parameters for $I||c$ and $I||a$ are $\Delta_{I||c} \sim 2.2 \pm 0.05$ meV, $Z=0.585$, $\Gamma_{I||c}=0.2$, and $\Delta_{I||a} \sim 0.41 \pm 0.02$ meV, $Z=0.63$, $\Gamma_{I||a}=0.145$ respectively. The large value of $\Delta_{I||c}$ compared to $\Delta_{I||a}$ is consistent with our earlier observations of the temperature variation of the two gaps, however here the gap anisotropy is somewhat larger ($\Delta_{I||c}/\Delta_{I||a} \sim 6$) than earlier. This difference is possibly due to our inability to precisely control the direction of the current due to surface roughness. Consistent with our earlier observation the relative broadening ($\Delta/\Gamma$) in zero field is also different for the two directions\textsuperscript{84}, ($\Gamma_{I||c}/\Delta_{I||c}$)$\sim 0.09$ and ($\Gamma_{I||a}/\Delta_{I||a}$)$\sim 0.392$. The field variation of $\Delta_{I||c}$, $\Delta_{I||a}$ and $\Gamma_{I||c}$, $\Gamma_{I||a}$ are shown in Figure 27(c) and (d) respectively. Our key observations are the following: (i) For $I||a$, the small gap $\Delta_{I||a}$ decreases rapidly with $H$ and vanishes at $H \sim 3.25$T, which is much smaller than the $H_{c2}$ of the superconductor; (ii) the large gap $\Delta_{I||c}$, on the other hand, decreases much more slowly with the magnetic field ($H$). Since
at present we do not have a theoretical model, which accounts for the multiband nature of superconductivity in YNi$_2$B$_2$C, we qualitatively compare our data with the predictions of the vortex state of a two-band superconductor with weak interband scattering$^{18,85}$ proposed in the context of MgB$_2$. The faster decrease of the small gap ($\Delta_{||a}$) with magnetic field compared to large gap ($\Delta_{||c}$) is consistent with the prediction of a two band model, where the diffusion constant (defined as $D_i = 2\pi T \xi_i^2$ where $\xi_i$ is the coherence length of the $i^{th}$ band) of the band with small gap is 20% of that of the large gap. For the same parameters it was theoretically predicted that the zero energy
Figure 28. The variation of the zero-bias density of states \([N_{0}(0)]\) after subtracting the zero-field contribution for \(I\parallel a\) and \(I\parallel c\) as a function of the reduced magnetic field \((h=H/H_{c2})\). Inset: the total zero-bias density of states \([N(0)]\) as a function of magnetic field extracted from the point-contact spectra for \(I\parallel a\) and \(I\parallel c\).

DOS \([N(0)]\) for the small gap will reach its normal state value for fields much smaller than \(H_{c2}\). To compare this prediction with our experimental results we calculate the zero energy DOS as a function of magnetic field from eqn. (1.25). The field variation of \(N(0)\) extracted for the two current directions is shown in the inset of Figure 28. For \(I\parallel a\) a significant zero bias DOS, presumably arising from gapless regions of the FS is seen even for zero field. To look at the field variation we separate \(N(0)\) into an intrinsic part \([N_{i}(0)]\) and a field dependent part \(N_{n}(0)=N(0)-N_{i}(0)\), where \(N_{i}(0)\) is the zero energy DOS in zero field. Figure 28 shows the variation of \(N_{n}(0)\) for \(I\parallel a\) and \(I\parallel c\) normalized to their respective values at the highest field, as a function of the reduced magnetic field, \(h(=H/H_{c2})\). The striking similarity of the experimental data with the two-band prediction strongly suggests that the observed spectra for \(I\parallel a\) and \(I\parallel c\) originate from two different bands on the Fermi surface with different coupling strength along the two directions. In this context, therefore, it is interesting to look at the band structure of \(YNi_{2}B_{2}C\).
3.4 Band structure of YNi$_2$B$_2$C

We can now try to speculate on the FS sheets that are likely to be responsible for the observed large and small energy gaps along two different directions. Band structure calculations\textsuperscript{77,20} for non-magnetic borocarbides (Y/Lu)Ni$_2$B$_2$C show (Figure 29), there are three bands crossing the FS produce five Fermi surface sheets: Two ellipsoids

![Figure 29. (a) The calculated large FS with the distribution of Fermi velocities in atomic units (see the colour ridge, blue=slow, red=fast) for the superconducting YNi$_2$B$_2$C. (b) The pillow-ridge square FS for the same. Velocities are in units of 1.14x10$^6$ cm/s. Figures are taken from ref. 20.](image-url)
centered at the $\Gamma$ points, with their long axes parallel to $c$-axis, two square FS centered at $P$ with sides parallel to [100] and [010], and a cylindrical FS constricted along [100] and [010] planes near to $k_z = \pi/c$. The broad structures of these calculations have been verified from different experiments, such as dHvA oscillations and two-dimensional angular correlation of electron–positron annihilation radiation (2D-ACAR) technique. In dHvA measurements, the frequency arising from the extremal orbit enclosing the ellipsoid sheet persists down to 3T suggesting that this sheet possibly remains gapless. However, this Fermi sheet encloses only ~0.3% of the first Brillouin zone and plays a relatively minor role in point contact experiments. On the remaining two kinds of FS sheets, band structure calculations reveal that the Fermi velocity ($v_F$) varies by a factor of 6; where the 1$^{st}$ groups of electrons are on a “square-pancake” Fermi sheet and the 2$^{nd}$ groups of electrons are on a cylindrical Fermi sheet. From an analysis of the temperature variation of $H_{c2}$, it has been suggested that slow electrons are strongly coupled to the lattice and contribute primarily to superconductivity. Since, for the cylindrical FS the Fermi velocity is predominantly in the $k_x$-$k_y$ plane ($v_F \approx 0$), it can be seen from equation (3.1) that this band will primarily contribute in the current for $I||a$ (The contribution of this band for $I||c$ will arise only from the deviation from ideal cylindrical nature.). This surface primarily comprises of fast electrons with only small pockets of slow electrons and is likely to contribute to the small gap observed for $I||a$. For $I||c$, on the other hand the predominant contribution is likely to arise from the square FS centered at $P$, for which on most points on the Fermi surface, $\vec{v}_F$ has a large component along $\hat{z}$. On this FS, regions in the vicinity of $k_{Fz}$ primarily consist of slow electrons which are likely to be responsible for the large gap observed for $I||c$. The electrons on the “square-pancake” Fermi sheet determine the $H_{c2}$, since the
superconductivity on the other Fermi sheet is rapidly suppressed under the application of a magnetic field. This behavior of the magnetic field variation of $\Delta_{||a}$ and $\Delta_{||c}$ strongly suggest like $T_c$, $H_{c2}$ is also governed by the larger gap.

In summary, I have presented a detailed study of temperature dependence and the magnetic field variation of the anisotropic superconducting energy gap in YNi$_2$B$_2$C using directional point contact spectroscopy. The results cannot be explained from single band anisotropic model $\Delta(\vec{k}) = \Delta_0 f(\vec{k})$ or by mixed angular momentum symmetry scenario, such as $s+g$ previously suggested$^{74}$ for this material. The difference in the temperature dependence of the superconducting energy gap in different directions along with the field dependence of $\Delta$ as well $N(0)$ are in good agreement with theoretical predictions for a two-band superconductor, suggesting that the unusual gap anisotropy possibly originates from a multiband scenario, where different bands on the FS have different coupling strengths.

At this point, it is interesting to study the evolution of the superconducting properties when the system is driven towards the dirty limit by substituting with non-magnetic impurities, as the electrons in different bands with different $v_F$ are responsible for the anisotropic behavior of the superconducting energy gaps in YNi$_2$B$_2$C. For this purpose, in the next section, I will focus the evolution $T_c$ and $H_{c2}$ in a series of Pt doped single crystals YNi$_{2-x}$Pt$_x$B$_2$C ($x=0.02-0.2$).
3.5 Effect of doping non magnetic impurity in the multiband scenario

In a conventional s-wave superconductor, non-magnetic disorder results in an increase in electronic scattering rate and decrease in the electronic mean free path ($l$). This results in a decrease in the coherence length ($\xi_0$) and consequently an increase in the upper critical field ($H_{c2}$) is observed. The $T_c$, on the other hand, is not affected by non-magnetic impurities unless the impurities result in a modification of the electronic or lattice properties, e.g. density of states at Fermi level [$N(E_F)$] or the Debye temperature ($\Theta_D$). In contrast, the situation in multiband superconductors is more complicated. For multiband superconductors in the clean limit, the band with strongest electron phonon coupling governs the bulk superconducting properties such as $T_c$ and $H_{c2}$. Substitution of non-magnetic impurities results in intraband scattering of electrons on individual Fermi sheets as well as interband scattering of electrons between different Fermi sheets. The former has an effect similar to conventional superconductor for individual bands, whereas the latter causes the bulk properties to be governed in the dirty limit by an average property of all the electrons instead of being governed by those with strongest electron-phonon coupling strength. Therefore, the evolution of $T_c$ and $H_{c2}$ in a multiband superconductor with substitution of non-magnetic impurities is governed by a complex interplay of interband and intraband scattering. In particular, $H_{c2}$ need not necessarily increase with increase in electronic scattering. The evolution of $H_{c2}$ in a multiband superconductor with impurity doping is therefore a matter of considerable interest. In the following section, I will focus on the evolution of the superconducting properties of in YNi$_2$B$_2$C with non-magnetic impurity (Pt) doping.
3.5.1 Structural characterization of the samples

Single crystals of YNi$_{2-x}$Pt$_x$B$_2$C ($x=0.02$, 0.06, 0.1, 0.14 and 0.2) are grown by the traveling-solvent floating-zone method using an image furnace. X-ray powder

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**Figure 30.** The observed and calculated X-ray diffraction pattern of YNi$_{2-x}$Pt$_x$B$_2$C along with their difference. The vertical bars indicate Bragg reflections.
diffraction using the crushed YNi\textsubscript{2-x}Pt\textsubscript{x}B\textsubscript{2}C single crystals are performed to determine the lattice parameters. X-ray profiles are analyzed (Figure 30) through Rietveld refinement using the FULLPROF program. X-ray diffraction analysis (Figure 31) reveals that pure YNi\textsubscript{2}B\textsubscript{2}C has tetragonal lattice structure with lattice parameters $a$ = 3.52Å and $c$ = 10.54Å. With Pt doping the lattice parameters along both $a$ and $c$ axes increase monotonically and for $x$=0.2 the lattice constants along [100] and [001] become 3.54 Å and 10.62 Å respectively. The increase in the volume of the unit cell in the range $x$=0-0.2 is ~1.1%. Thus, there is a continuous incorporation of Pt on Ni sites without significant change in the atomic distances and the structural anisotropy.

**3.5.2 Evolution of $H_{c2}$ and $T_c$ and the multiband effects**

A homemade high frequency (15KHz) planar coil a.c susceptibility setup is used to determine the critical temperatures ($T_c$) of these samples. Figure 32(a) shows the
Figure 32. (a) Normalized real part of a.c susceptibility ($\chi'$) as a function of temperature (T) in $\text{YNi}_{2-x}\text{Pt}_x\text{B}_2\text{C}$, for $x=0-0.2$. (b) Variation of $T_c$ with the same Pt doping. Solid lines are a guide to eye.

normalized real part of ac susceptibility ($\chi'$) as a function of temperature for all the samples. The $T_c$ values are determined from the onset of superconducting transition, defined as 5% of the full signal change of the real part of a.c susceptibility [$\chi'(T)$]. For the undoped $\text{YNi}_2\text{B}_2\text{C}$, the superconducting transition temperature is $T_c \sim 15.85$ K. With increased incorporation of Pt, $T_c$ decreases monotonically: $T_c$ falls sharply from 15.85K ($x=0$) to 13.6 K ($x=0.06$) and then decreases gradually to 13K in the range $x=0.06-0.2$. 
Figure 33. Variation of $H_{c2}$ with temperature along $H||a$ and $H||c$ for YNi$_{2-x}$Pt$_x$B$_2$C, with $x=0-0.2$. Solid lines are a guide to eye. The insets show variation of $\chi'(H)$ with magnetic field ($H$) at 2.2K for the same. All crystals show a pronounced “peak effect” close to $H_{c2}$. 
as shown in Figure 32(b). The critical fields ($H_{c2}$) along two crystallographic directions “a” and “c” are determined using the same a.c susceptibility set up down to 2.2K and magnetic fields up to 8.5T. Figure 33 shows $H_{c2}\parallel a$ and $H_{c2}\parallel c$ extracted from the field variation of $\chi'(H)$ for all the six samples as a function of temperature ($T$). The variation of $\chi'(H)$ with magnetic field at 2.2K is shown in the insets for both $H\parallel a$ and $H\parallel c$. Almost all the $\chi'(H)-H$ graph shows a pronounced “peak effect” [dip in $\chi'(H)$] just before $H_{c2}$ arising from the order disorder transition of the vortex lattice. The $H_{c2}$ values at different temperatures are determined form the $\chi(T)-H$ data [inset Figure 33(a-f)] using the same criterion as fixed to extract the $T_c$ values. For the undoped YNi$_2$B$_2$C sample the $H_{c2}$ for $H\parallel a$ is larger than the maximum magnetic field for our a.c susceptibility cryostat. This value is therefore obtained form a separate measurement (Figure 34) of the isothermal magnetization versus field ($M-H$) loop at 2.2K upto 12T using an Oxford Instrument vibrating sample magnetometer.

**Figure 34.** Isothermal M-H loop for YNi$_2$B$_2$C sample at 2.2K. The inset shows an expanded view of the curve close to $H_{c2}$. $H_{c2}$ is determined from the field at which the M-H curve deviates from the high field linear behavior. The negative slope at high field is due to the diamagnetic contribution of the sample holder.
Figure 35. (a) Isothermal $M$-$H$ loop for YNi$_{1.8}$Pt$_{0.2}$B$_2$C measured in a VSM. (b) Variation of $H_{c2}$ with temperature ($T$) for the same, measured with a.c susceptibility for both $H||c$ (black) and $H||a$ (blue). Red circles show the same from isothermal $M$-$H$ measurements for $H||c$. Solid lines are a guide to the eye.

To check the consistency of this procedure of extracting $H_{c2}(T)$, we have also compared the $H_{c2}(T)$ determined from isothermal $M$-$H$ measurements for the sample with $x=0.2$ in a vibrating sample magnetometer (VSM). The raw data is shown in Figure 35. $H_{c2}$ values are determined by fitting a straight line to the high field $M$-$H$ data and determining the point at which the experimental curve departs from this linear behavior. This method is necessary since in clean Type II superconductor since the critical current (and therefore the irreversibility in the M-H loop) disappears at fields below $H_{c2}$ due to flux flow and thermally activated flux creep. The two curves are identical within the error bar of our measurement. In the analysis of $H_{c2}$ for all these samples, there is a large anisotropy in the undoped YNi$_2$B$_2$C single crystal, with $\gamma_H = H_{c2||a}/H_{c2||c} \approx 1.8$. In pure YNi$_2$B$_2$C at 2.2K, $H_{c2||c} \approx 8.25$ T and $H_{c2||a} \approx 9.77$ T. With increase in Pt, $H_{c2}(T)$ decreases in both the directions. The variation of $T_c$, $H_{c2||a}$ and $H_{c2||c}$ (at 2.2K) as a function of $x$ is shown in Figure 36. The anisotropy ratio decreases from $\gamma_H \approx 1.18$ for the undoped sample to $\gamma_H \approx 1$ for the sample with $x=0.2$ (inset Figure 36).
The rapid decrease in $H_{c2}$ in YNi$_2$B$_2$C upon substitution of Pt impurities is clearly not consistent with a conventional scenario. However, since the Fermi surface of YNi$_2$B$_2$C is very anisotropic, I will first compare the results with that of a single band superconductor with anisotropic Fermi surface. For a single band superconductor with anisotropic Fermi surface in the clean limit,

$$H_{c2}||c = \frac{\Phi_0}{2\pi (\xi_{0ab})^2} = \frac{\Phi_0 \pi \Delta^2}{2\hbar^2 (v_{Fab})^2}$$  \hspace{1cm} (3.2)$$

$$H_{c2}||a = \frac{\Phi_0}{2\pi \xi_{0a} \xi_{0c}} = \frac{\Phi_0 \pi \Delta^2}{2\hbar^2 v_{F_{Fa}} v_{F_{Fc}}}$$  \hspace{1cm} (3.3)$$

where $\Phi_0$ is the flux quantum and $v_{F_{Fa}}$ and $v_{F_{Fc}}$ are the Fermi velocities in the two directions (We assume $v_a=v_b=v_{ab}$ and $\xi_a=\xi_b=\xi_{ab}$ consistent with the tetragonal symmetry of the system). The anisotropy for such a superconductor given by $\gamma_H = v_{F_{Fa}}/v_{F_{Fc}}$ would gradually decrease with increase intraband scattering. However, the
average value of the critical fields, $H_{c2}||a$ and $H_{c2}||c$ ($<H_{c2}>$) would show an increase due to reduction of electronic mean free path. In contrast, in YNi$_2$B$_2$C, in addition to the decrease in the individual values of $H_{c2}||a$ and $H_{c2}||c$, $<H_{c2}>$ decreases with increase in Pt doping to almost half its value in the clean limit.

The reduction in $H_{c2}$ (and $T_c$) can also be due to the change in DOS with Pt doping, but in this case, we do not expect any change in the DOS caused by Pt, as both Ni ([Ar].3d$^8$.4s$^1$) and Pt ([Xe].4f$^{14}$.5d$^9$.6s$^1$) are elements from the same group in the periodic table and have the same outer shell electronic structures. To verify whether this evolution of $H_{c2}$ results from a change in $N(E_F)$ or $\Theta_D$ upon substitution of Pt at the Ni site, specific heat ($C_p$) measurements are done on the samples with $x$=0, 0.1 and 0.14. For all three samples measurements are carried out at $H$=0 and at $H$=9T, where the superconductivity is suppressed. The expression for the normal state specific heat ($C_n$) is given by,

$$C_n(T) = \gamma_n T + \beta T^3 + \alpha T^5$$  \hspace{1cm} (3.4)

where

$$C_{\text{electronic}}(T) = \gamma_n T$$ \hspace{1cm} (3.5)

and

$$C_{\text{lattice}}(T) = \beta T^3 + \alpha T^5$$ \hspace{1cm} (3.6)

The electronic term $\gamma_n$ is related to the normal state density of states [$N(E_F)$] as

$$\gamma_n T = \frac{\pi^2}{3} N(E_F) k_B^2$$ \hspace{1cm} (3.7)

From the value of $\beta$ we get an estimate of the Debye temperature ($\Theta_D$) of the system as

$$\beta = \frac{1944.94Z}{\Theta_D^2}$$ \hspace{1cm} (3.8)
where $Z$ is the number of atoms per formula unit, $\alpha$ is a higher order correction to lattice specific heat due to the phonon contribution. By fitting this expression [(3.4)] for the normal state specific heat with the $C_p$ measured at 9T, the lattice contribution $C_{\text{lattice}}(T)$ is evaluated. Since $C_{\text{lattice}}(T)$ is independent of magnetic field, the electronic specific heat ($C_e$) at $H=0$ is determined by subtracting the phonon contribution from the measured $C_p$ at $H=0$, i.e. $C_{\text{el}}(T) = C_n(T) - C_{\text{lattice}}(T)$. Figure 37 shows the $C_{\text{el}}/T$ vs. $T$ for three samples. It is clear that $C_e$ in the normal state does not change significantly showing that $N(E_F)$ is not affected by Pt doping. The extracted value of $\gamma_n$ and $\Theta_D$ are listed below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\gamma_n$ (mJ/mol K$^2$)</th>
<th>$\beta$ (mJ/mol K$^4$)</th>
<th>$\Theta_D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YNi$_2$B$_2$C</td>
<td>19±0.5</td>
<td>0.089 ±0.02</td>
<td>507.7±15</td>
</tr>
<tr>
<td>YNi$<em>{1.9}$Pt$</em>{0.1}$B$_2$C</td>
<td>20.1±0.5</td>
<td>0.0819 ±0.005</td>
<td>522.2±10</td>
</tr>
<tr>
<td>YNi$<em>{1.86}$Pt$</em>{0.14}$B$_2$C</td>
<td>19.2±0.5</td>
<td>0.0812 ±0.005</td>
<td>523.7±10</td>
</tr>
</tbody>
</table>

The specific heat of the other composition could not be measured due to the small mass of the crystals; within the error bars of our measurements, both $\gamma_n$ and $\Theta_D$ remain constant with Pt doping showing that the unusual variation of $H_{c2}$ does not result from modification of $N(E_F)$ and $\Theta_D$. Therefore, the variation, $H_{c2}$ in YNi$_2$$_x$Pt$_x$B$_2$C has to be analyzed beyond single band scenario.

To understand the variation of $H_{c2}$ with Pt doping, we have to take into account the multiband nature of superconductivity in YNi$_2$B$_2$C. Spectroscopic measurements using DPCAR on YNi$_2$B$_2$C single crystals in the clean limit (section 3.3) revealed$^{10,89}$ that the presence of at least two groups of electrons on two different Fermi sheets, for which the superconducting energy gap and $T_c$ vary by a factor of 5-6. Since the “square
The "square pancake" Fermi sheet is very anisotropic, for the clean system without significant interband scattering the $H_{c2}(0)$ will be given by equations (3.2) and (3.3) where $\Delta$ and $v_{Fab}$ and $v_{Fc}$ have to be replaced by the ones corresponding to the "square pancake" Fermi sheet. The anisotropy, $\gamma_H$ in the undoped compound thus reflects the anisotropy of the square pancake Fermi sheet for which $v_{Fab} >> v_{Fc}$. This value is however much smaller than the ratio $v_{Fab}/v_{Fc} > 5$ estimated for this Fermi sheet from electronic structure calculations. This indicates that even in the undoped system individual bands are already in the dirty limit with significant intraband scattering, which decreases the $H_{c2}$ anisotropy expected in a clean system. In such a system, addition of impurities would result (i) in an increase in intraband scattering within each Fermi Sheet and (ii) an increase in interband scattering between the two Fermi sheets. The first effect will increase the bulk $H_{c2}$ governed by the coherence length of the electrons on the "square pancake" Fermi sheet, whereas the latter would decrease the superconducting energy gap (and $H_{c2}$) on the "square pancake" due to the influence of
the cylindrical Fermi sheet. The rapid decrease of $<H_{c2}>$ with increase in Pt doping suggests that that the second effect dominates over the first one in the doping range of this study. This is expected since both the “square pancake” Fermi sheet and the cylindrical Fermi sheet have large contribution from the Ni 3$d$ band. Pt doping at the Ni site is likely to increases the interband scattering between these two Fermi sheets. At the same time $\gamma_H$ decrease with increasing $x$ due to the decrease in anisotropy of individual bands. Finally, I would like to note that the variation of $T_c$ with Pt doping can be understood from the same mechanism. With increase in interband scattering the $T_c$ will gradually decrease due to the influence of the 2$^{\text{nd}}$ group of electrons\textsuperscript{10} with lower $T_c$, and will go towards a limiting value given by the weighted average of the $T_c$ of the two bands. The rapid decrease in $T_c$ at small values of $x$ and the subsequent leveling off for $x > 0.14$ supports this scenario.

In summary, I have investigated the effect of impurities on $H_{c2}$ by studying a series of YNi$_{2-x}$Pt$_x$B$_2$C single crystals. We show that both $H_{c2}||a$ and $H_{c2}||c$ and the $T_c$ decreases with increasing $x$. These results can be understood within a multiband scenario where the dominant contribution comes from the increase in interband scattering arising from Pt impurities. The changes in $H_{c2}$ and $T_c$ are solely due to impurity the increase in scattering and influenced by inter-band scattering in this multiband superconductor YNi$_2$B$_2$C; the relative insensitivity of $H_{c2}$ and $T_c$ for $x>0.14$ suggests that at large doping YNi$_{2-x}$Pt$_x$B$_2$C behaves as an effective single band superconductor due to large interband scattering. This study elucidates the role of interband scattering on the upper critical field in a multiband superconductor and reinforces the multiband nature of superconductivity in this material.
3.6 Summary

DPCAR spectroscopic studies are performed on the anisotropic superconductor YNi$_2$B$_2$C along the crystallographic directions $a$ (100) and $c$ (001) using a normal metal Ag tip. From the temperature and magnetic field variations of the superconducting energy gaps along the two crystallographic directions a clear elucidation of the multiband nature of superconductivity in this material is shown. Band structure calculations also suggest that there exist mainly two types of electrons with anisotropic Fermi velocities that vary by a factor of 6. Further, the evolution of the multiband effects on the upper critical field $H_{c2}$ and the critical transition temperature $T_c$ are investigated by doping non magnetic impurity (Pt) in YNi$_2$B$_2$C. Studies on YNi$_{2-x}$Pt$_x$B$_2$C reveal that the observed anisotropy in $H_{c2}$ and $T_c$ disappears with Pt doping, as it introduces inter-band scattering. Specific heat studies confirms that the Pt doping has no effect on the density of states in YNi$_{2-x}$Pt$_x$B$_2$C ($x$=0-0.2). The scaling of $H_{c2}$ and $T_c$ due to Pt doping is in agreement with the multiband scenario.
Chapter 4
Studies on spin polarizations and spin fluctuations

4.1 Introduction

In the field of spintronics\textsuperscript{94}, it is of interest to study the evolution of spin transport properties with temperature and correlate it to the bulk properties like magnetization in a magnetic metal. In recent times, it has been shown\textsuperscript{6} that apart from Meservey-Tedrow\textsuperscript{25} technique, PCAR spectroscopy can also be used to probe transport spin polarization ($P_t$) in ferromagnets. However, no studies are reported on the effect of spin fluctuation on Andreev reflection close to ferromagnetic transition temperature ($T_{Curie}$). This is due to the obvious limitation of the PCAR technique as the temperature range of measurement is limited by the superconducting transition temperature ($T_c$) of the superconducting tip. The determination of spin polarization ($P$) of ferromagnets is typically carried out at temperatures two orders of magnitude lower than the $T_{Curie}$ of most ferromagnets. Since much of the practical interest is in the value of spin polarization close to room temperature, the bulk spin polarization at elevated temperature is often estimated based on the assumption $P(T) \propto M_s(T)$, i.e., that the spin polarization of the electrons close to the Fermi level is proportional to the spontaneous magnetization $M_s(T)$ of the ferromagnet\textsuperscript{95,96,97,98}. Though the spin polarization as a function of temperature has been measured using spin-polarized photoemission for a few ferromagnets\textsuperscript{99,100}, this simple relation has so far remained experimentally unverified even for relatively simple ferromagnets\textsuperscript{101}. The experimental verification of this relation is important for two reasons. First, $M_s$ is a bulk property, which depends on the total number difference of the up- and downspin electrons, whereas $P$ is only
sensitive to the electrons close to Fermi level. This intuitive relation is thus based on a simplistic picture, which is strictly valid for free electron like parabolic bands only. Second, both PCAR and the Meservey-Tedrow technique measure the spin polarization in the transport current\(^{17}\) \((P_t)\) rather than the spin polarization in the density of states, and \(P_t\) depends on a weighted average of the density of states and Fermi velocity of the two spin bands. It is not obvious that the temperature dependence of the spin polarization extracted from these techniques should follow \(M_s\). However, since this relation forms the basis of much of the experimental studies related to spin transport in a variety of spintronic materials, it is important to investigate if it holds good in a typical ferromagnet.

In this chapter, I investigate different classes of magnetic materials and their physical properties using transport, magnetization and PCAR spectroscopic studies. These studies aim to explore (i) the evolution of transport spin polarization \((P_t)\) at \(E_F\) and the spontaneous magnetization \((M_s)\) with temperature and (ii) the effect of spin fluctuation on the superconducting quasiparticle lifetime \((\tau)\), when a superconductor is kept in proximity to a magnetic metal with large spin fluctuation. For this purpose, we choose \(\text{NdNi}_5\), a ferromagnet with low Curie temperature \((T_{\text{Curie}} \approx 7.7\text{K})\) and the superconductor \(\text{Nb}\) \((T_c \approx 9.2\text{K})\) as the two electrodes in the PCAR experiment. As \(T \to T_{\text{Curies}}\), strong ferromagnetic spin fluctuations take place and leave the signature by reducing \(\tau\). Our studies show, in addition to transport spin polarization, PCAR can also be used to detect spin fluctuations in systems that are close to a magnetic instability\(^{26}\). The effect of spin fluctuation on \(\tau\) is further confirmed by carrying out measurements on filled skutterudite compounds \(\text{AFe}_4\text{Sb}_{12}\) \((\text{A} = \text{K, Ca, Yb})\) and on itinerant ferromagnet \(\text{Ni}_{3\pm x}\text{Al}_{1-x}\). The first group represents a family of isostructural-filled
skutterudite, where the ground state can be transformed by changing “A” from an itinerant ferromagnet to a paramagnet with large spin fluctuations. In the latter, a small composition change (x) drives it from ferromagnetic to spin fluctuating ground state.

4.2 Sample characterization

In this section, I will describe the characterization of the NdNi₅ samples on which PCAR measurements are performed. For the sake of completeness, I will also briefly describe the sample preparation. The polycrystalline samples are prepared by repeated arc melting of the stoichiometric amounts of the constituent elements on water-cooled copper hearth in a purified argon atmosphere. The button was flipped and remelted several times to ensure the homogeneity. A titanium button is used as an oxygen getter. The total weight loss during the arc melting was less than 0.5% and hence the alloy compositions are assumed to remain unchanged from the original stoichiometric ratios. A room-temperature powder X-ray diffraction pattern of the sample is obtained using a

![Figure 38](image_url)

**Figure 38:** The observed and calculated X-ray diffraction pattern of NdNi₅ along with their difference. The vertical bars indicate Bragg reflections.
panalytical X-ray diffractometer equipped with Cu $K\alpha$ radiation. In order to obtain the lattice parameters of the compound and confirm its homogeneity to the accuracy of the X-ray pattern, a Rietveld refinement using the FULLPROF program of the obtained X-ray diffraction pattern is done. shows the Rietveld refinement of the X-ray pattern of NdNi$_5$, which forms in a CaCu$_5$-type hexagonal structure with a space group $P6/mmm$. The excellent agreement with the experimental diffraction pattern confirms that the material is single phase. The obtained lattice parameters $a=4.953$ Å and $c=3.967$ Å are in agreement with the published reports$^{102}$.

![Figure 39](image)

**Figure 39:** Magnetization ($M$) vs temperature ($T$) of NdNi$_5$ measured in 500 G. The inset shows the resistivity as a function of temperature.

The resistivity ($\rho$) and magnetization ($M$) of the sample are measured in the temperature range 3–300 K using a homemade resistivity setup and Quantum Design SQUID magnetometer respectively. The magnetization versus temperature of the NdNi$_5$ sample (shown in Figure 39) measured at 500 G reveals a sharp ferromagnetic transition with $T_c\sim 7.7$ K. The resistivity (inset Figure 39) also shows a pronounced anomaly at the same temperature. Figure 40(a)-(b) shows the isothermal $M$-$H$ curves
recorded at various temperatures. The $M$-$H$ curve does not saturate up to 2.5 T due to the large magneto-crystalline anisotropy in this material. At low temperatures, $M_s$ is estimated by linearly extrapolating the high-field slope of the $M$-$H$ curve. Like most $R$Ni$_5$ ($R$ = rare earth) compounds, the moment primarily resides on the Nd sites inducing a small moment on the Ni sites. The value of $M_s$ at 2 K ($\sim 1.68 \mu_B$/f.u.) is much lower than the expected saturation moment of $3.28 \mu_B$ for the free Nd$^{3+}$ ion. This is due to crystal-field splitting of the 4$f$ energy levels in Nd, as has been shown in numerous previous studies$^{103,104}$.

**Figure 40:** (a) Isothermal $M$-$H$ curves at various temperatures. (b) Arott plots ($M^2$ vs $H/M$) at four temperatures close to $T_c$. 
Above 6.4K the high-field $M$-$H$ curve is no longer linear. In this temperature range, $M_s$ is estimated from Arott plots ($M^2$ vs. $H/M$) as shown in Figure 40(b).

### 4.3 PCAR spectroscopy on NdNi$_5$

The low Curie temperature of NdNi$_5$ enables us to extract the transport spin polarization $P_r(T)$ all the way up to $T_{Curie}$ using a superconducting Nb tip with superconducting transition temperature $T_c \sim 9.2$ K. PCAR measurements are performed in the temperature range 2.4 to 9 K in a continuous-flow/normal 4-He cryostat. The sample is polished to a mirror finish and loaded immediately for experiment to avoid surface degradation. A mechanically cut sharp Nb tip is brought in contact with the sample at low temperatures using the differential screw arrangement. The conductance $[G(V)]$ versus voltage (V) characteristics of the contact is measured using a four-probe current modulation technique. Typical contact resistance in these measurements ranged between 10 and 20 $\Omega$.

In Figure 41, we show the PCAR G(V)-V spectra (normalized with respect to the conductance values at large bias, $G_n$) for three different NdNi$_5$-Nb contacts recorded at various temperatures. The normalized conductance spectra are fitted with the m-BTK theory$^7$. The fitting parameters are the barrier ($Z$) at the interface, transport spin polarization $P_r$, the superconducting energy gap ($\Delta$) and the broadening parameter $\Gamma$. In order to reduce the number of free parameters, $\Delta$ is restricted to within 5% of its BCS value for Nb at all temperatures.

The extracted values of $P_r$ of NdNi$_5$ as a function of temperature for three different contacts (C1, C2, C3) are shown in Figure 42. While in the absence of a detailed estimate of the elastic and inelastic mean-free paths, we cannot ascertain
Figure 41: (a-c) Temperature variation of normalized PCAR spectra for three different contacts (C1: $Z(2.4\text{K}) = 0.265$; C2: $Z(2.4\text{K}) = 0.275$; C3: $Z(2.4\text{K}) = 0.35$) NdNi$_5$-Nb contacts. The solid lines show the fits to the spectra using the m-BTK model.
whether the contacts are in the ballistic or diffusive limit, the latter is more likely since our sample has a relatively small residual resistivity ratio given by $\rho(300\text{K})/\rho(3\text{K})=3.59$. In the same graph, we also show the temperature variation of $M_s$. It is easily seen that the temperature variation of the two quantities is similar for all the three contacts. To further illustrate this point, in the inset we plot $P_t$ as a function of $M_s$. Barring temperatures very close to $T_c$ there is a small deviation, however most of the points fall on a straight line with zero intercept showing that the transport spin polarization $P_t(T) \propto M_s(T)$.

For all the NdNi$_5$-Nb contacts that we have explored (Figure 43), we find that the absolute values of transport spin polarization ($P_t$) changes with different contacts. With increasing barrier strength ($Z$), there is a reduction in the absolute value of $P_t$. This gives a strong indication that the effect of large $Z$ contacts is to depolarize a fraction of the current through the contact, since an increase in the parameter $Z$ effectively indicates an increase in the scattering strength of the barrier. This is because of the fact

Figure 42: Temperature variation of $P_t/P_t(0)$ for 3 different contacts: C1 : $Z(2.4\text{K}) = 0.265$; C2 : $Z(2.4\text{K}) = 0.275$; C3 : $Z(2.4\text{K}) = 0.35$ and $M_s/M_s(0)$ (solid line). The inset shows the linear variation of $M_s$ as a function of $P_t$ for contact C1.
that, for a ferromagnet-superconductor interface, this barrier often contains a magnetic dead layer, where spin flip scattering depolarizes the electron\textsuperscript{30}, as it passes through the interface. Therefore, the interface with larger \( Z \) becomes magnetically more disordered and its negative effect is reflected as a reduction in the measured value of \( P_t \). The intrinsic spin polarization of the current can be extracted in the limit \( Z \to 0 \). This behavior has been verified on several metal oxides \( \text{CrO}_2 \textsuperscript{105}, \text{SrRuO}_3 \textsuperscript{106} \) and on ferromagnetic metals like Ni, Co, Fe\textsuperscript{105,30}. Extrapolating the variation of \( P_t \) with \( Z \) up to \( Z=0 \) we get the intrinsic transport spin polarization of NdNi\textsubscript{5}, defined as \( P_t (Z \to 0) \), to have a value of 49.58%.

For a detail description, I explore temperature dependence of PCAR spectra for three different contacts labeled as C1, C2 and C3 respectively. I will focus on the temperature dependence of the other quantities, namely, \( \Delta \), \( \Gamma \), and \( Z \). The temperature variations of these three quantities are extracted from the fits in Figure 43 and are shown in Figure 44. I would like to mention that all the spectra could be fitted very
Figure 44: Temperature dependence of the barrier parameter Z and the broadening parameter \( \Gamma \). (Same symbols and colors as used in Figure 5).

well with the constraint on \( \Delta \) stated earlier, with \( \Delta(T=0)=1.45 \) meV. Figure 44 shows the temperature variations of \( \Delta \), \( \Gamma \), and \( Z \) for all the three contacts C1, C2, C3. The variations of these three parameters with temperature show similar trends. For the purpose of description, I will consider the contact C1. In the temperature range 2.4–4 K, the spectra can be fitted without incorporating any broadening parameter \( (\Gamma=0) \) for all three contacts. Above 4 K, \( \Gamma \) gradually increases and reaches a maximum value of \( \Gamma=0.65 \) meV at 8 K for the contact C1, which coincides with the \( T_{\text{Curie}} \) of NdNi5. Above 8 K, \( \Gamma \) decreases with temperature and finally becomes \( \Gamma=0.16 \) meV at 9 K. The barrier parameter \( Z \), on the other hand, remains constant in the range 2.4–4 K for all three contacts, for C1 it is being \( Z=0.27 \). Above 4K, \( Z \) increases monotonically up to 8 K and tends to saturate to a value of \( Z=0.635 \).

Before discussing the implications of these results, I would first like to comment on the reliability of the fits of the PCAR spectra, particularly at elevated temperatures.
Figure 45. Comparison of the fits of PCAR spectra for Nb-NdNi₅ contact at 8.5 K with two sets of fitting parameters shown in solid (blue) and dashed (Red) lines. The fit parameters for the two fits are shown in the figure. $\Delta$ and $\Gamma$ are in meV. The inset is an enlarged view for the low-bias region.

With increasing temperature, gradually PCAR spectra get thermally smeared. At temperatures greater than 8 K the most dominant feature of the spectra, namely, the two peaks in the conductance spectra associated with the superconducting energy gap, gets smeared into one broad peak. Since the saturation in the value of $Z$ happens in this temperature range, the fit of the spectra for $T$>8 K needs careful attention. To crosscheck the reliability of the fits, in Figure 45 two fits of the same spectra taken at 8.5 K are shown: The best fit curve is shown in Figure 45 (solid blue line), in the second one (dashed red line) $Z$ is deliberately reduced and $\Gamma$ is adjusted to obtain the best possible fit. However, the parameters can be adjusted to reproduce the peak value in the normalized $G(V)$ vs. $V$ curves in both cases, the latter does not reproduce the width of the curve close to zero bias (inset of Figure 45). Nevertheless, above 7.5K the uncertainty in the value of $Z$ and $\Gamma$ significantly increases as shown in Figure 44.
Now I will discuss the significance of the temperature variation of $\Gamma$ and $Z$. First, I will focus on the temperature dependence of $\Gamma$. The increase in $\Gamma$, which peaks close to the critical temperature ($T_{Curie}$) of the ferromagnet, signifies a corresponding decrease in quasiparticle lifetime at the same temperature. It is known that ferromagnetic spin fluctuation in an s-wave superconductor increases the singlet-state repulsion\(^{107}\). Since ferromagnetic spin fluctuation in NdNi\textsubscript{5} is the maximum at temperatures close to $T_{Curie}$, it would be natural to attribute this decrease in the superconducting quasiparticle lifetime to the proximity of the superconductor to strong ferromagnetic spin fluctuation. In addition, at temperatures close to the superconducting transition temperature ($T_c$), additional broadening is likely to arise from the intrinsic decrease in the quasiparticle lifetime of the superconductor. Therefore, for temperatures $T \geq 8$ K, $\Gamma$ can also have a contribution from intrinsic origin. This effect may change the temperature variation of the $\Gamma$ arising from the ferromagnetic spin fluctuation to a smaller extent, however the basic feature would remain unchanged.

The temperature variation of $Z$, on the other hand, is more complex to understand. It has been pointed out by several authors that in the analysis of a ferromagnet/superconductor interface, $Z$ implicitly incorporates much more physics than a simple potential barrier at the interface. For a nonmagnetic metal-superconductor interface, the effective barrier $Z$ is given by\(^{108}\)

$$Z = Z_b + \left(\frac{r - 1}{4r}\right)^2 = Z_b + Z_i$$

(4.1)

where $r = \frac{k_{FS}}{k_{FN}}$ is the ratio of the Fermi wave vectors ($k_F$) in the normal metal (N) and the superconductor (S), note that $Z$ remains invariant under $r \rightarrow \frac{1}{r}$. The first term $Z_b$ comes
from the physical barrier arising from imperfect interface and oxide barrier, and the second term $Z_i$ incorporates the effect of Fermi velocity mismatch between the normal metal and the superconductor. In the case where the normal metal is a ferromagnet with different Fermi velocity of the up- and down-spin bands, the derivation of the second term is not straightforward. In this case, it is expected that $Z_i$ would be governed by a weighted average of two contributions: (i) The mismatch between the spin-up-band Fermi velocity ($v_{F\uparrow}$) and the Fermi velocity in the superconductor and (ii) the mismatch between the spin-down-band ($v_{F\downarrow}$) Fermi velocity and the Fermi velocity in the superconductor. The dominant contribution will, however, come from the mismatch between the Fermi velocity of the majority spin sub band and the superconductor. At temperature $T<\ll T_{Curie}$, where the exchange splitting is roughly temperature independent, $Z_i$ will be constant as a function of temperature. Again, at temperatures $T>\gg T_{Curie}$, the exchange splitting disappears and $Z_i$ is solely determined by the Fermi velocity in the paramagnetic state. At intermediate temperatures the $Z$ will either increase or decrease depending on the relative values of the mismatch between the Fermi velocities of the majority spin sub band and the superconductor in the ferromagnetic state, and the mismatch between the Fermi velocities in the paramagnetic state and the superconductor. As the temperature of the ferromagnet is raised towards the ferromagnetic transition, the Fermi velocities of the spin up ($v_{F\uparrow}$) and spin down ($v_{F\downarrow}$) bands gradually change due to the reduction in exchange splitting and eventually become equal at $T_{Curie}$. The gradual change in $Z$ from 4 to 8 K and the leveling off to a constant value above 8 K suggests that this evolution in $v_{F\uparrow}$ and $v_{F\downarrow}$ is reflected in the temperature dependence of $Z$. 


Figure 46: (a) Normalized PCAR spectra of Fe-Nb point contact at different temperatures. The solid lines show the fits to the spectra using the modified BTK model. (b) Temperature variation of the transport spin polarization ($P_t$) in the temperature range 2.3–9 K. The solid line is a guide to the eye. (c) Temperature dependence of the superconducting energy gap ($\Delta$), the barrier parameter ($Z$), and the broadening parameter ($\Gamma$). The solid line passing through $\Delta$ shows the expected temperature variation from BCS theory. The solid lines passing through $Z$ and $\Gamma$ are guides to the eye.
As a consistency check to the new results emerging from the previous studies involving spin fluctuations, PCAR studies are also carried out on Fe using an Nb tip. In Fe, $T_{Curie} \approx 1042$ K is two orders of magnitude larger than the temperature range over which the measurement is carried out. Thus for Fe both ferromagnetic spin fluctuations as well as the decrease in exchange splitting is likely to be insignificant. Figure 46(a-c) shows the temperature dependence of the PCAR spectra and best-fit parameters for the Fe-Nb point contact. As expected within experimental errors, the transport spin polarization Figure 46(b) of Fe is constant over the entire temperature range of measurement with $P_T \approx 40\%$. Figure 46(c) shows the temperature variation of $Z$ and $\Gamma$. $Z$ is constant over the entire temperature range. $\Gamma$, on the other hand, remains zero except at temperatures very close to the transition temperature of the superconductor, where it shows a slight increase. This slight increase is in qualitative agreement with the intrinsic decrease of the quasiparticle lifetime of the superconductor as theoretically predicted and experimentally observed in strong-coupling superconductors.

4.4 Studies on isostructural filled skutterudites

To confirm the role of spin fluctuation, further PCAR experiments are carried out on isostructural filled skutterudites. The skutterudites are represented by a general formula $\text{AT}_4\text{X}_{12}$, where “T” is a transition metal and “X” is pnictide. Changing the filler element “A”, magnetic properties of this system can be tuned; substitution of monovalent cation ($\text{K}^+$, $\text{Na}^+$) makes it ferromagnetic, while divalent filler ($\text{Ca}^{++}$, $\text{Yb}^{++}$) makes it nearly ferromagnetic. Accordingly, KFe$_4$Sb$_{12}$ is a ferromagnetic metal with $T_{Curie} \approx 80$ K, whereas CaFe$_4$Sb$_{12}$ and YbFe$_4$Sb$_{12}$ are nearly ferromagnetic metals for which large spin fluctuations are expected to be present even at the lowest temperature.
Figure 47: Normalized PCAR spectra for (a) CaFe$_4$Sb$_{12}$-Nb point contact at 3.5 K. (b) YbFe$_4$Sb$_{12}$-Nb point contact at 2.3 K. (c) KFe$_4$Sb$_{12}$-Nb point contact at 3.5 K. The solid lines are the best fits of the spectra to the m-BTK model. The best-fit parameters are also shown in the figures.
PCAR spectrum on CaFe$_4$Sb$_{12}$ is shown in Figure 47(a). In this case, the PCAR spectra recorded at 3.5 K can be fitted only by incorporating a finite value of $\Gamma$=0.35 meV. The situation is similar for YbFe$_4$Sb$_{12}$ [Figure 47(b)], where the PCAR spectra recorded at 2.3 K can only be fitted incorporating $\Gamma$=0.9 meV. On the other hand, the PCAR data on the ferromagnetic compound, KFe$_4$Sb$_{12}$ [Figure 47(c)] can be fitted as expected with $\Gamma$=0. This is expected, as the measurements are performed at temperatures much below the ferromagnetic transition temperature. Our results are also consistent with the studies$^{109}$ on CaFe$_4$Sb$_{12}$ and YbFe$_4$Sb$_{12}$, where it is shown from magnetization and heat capacity studies that, spin fluctuations are larger in the latter compound. Concomitant with the large increase in $\Gamma$, the superconducting energy gap is reduced from the bulk value for CaFe$_4$Sb$_{12}$ and YbFe$_4$Sb$_{12}$: $\Delta$=1.2 meV for the Nb-CaFe$_4$Sb$_{12}$ contact and $\Delta$=0.85 meV for the Nb-YbFe$_4$Sb$_{12}$ contact.
4.5 Spin fluctuation studies on $Ni_{3\pm x}Al_{1\mp x}$

In earlier sections, I have shown that PCAR spectroscopy can detect the effect of spin fluctuations present on the counter magnetic electrode. In this section, the same technique is applied to study the effects of spin fluctuations in itinerant ferromagnetic system $Ni_{3\pm x}Al_{1\mp x}$. $Ni_{3\pm x}Al_{1\mp x}$ has been widely studied due to its unusual compositional phase boundary around 24-27 at. % Al. Around this composition range, the ground state of this system transforms from a ferromagnet to a paramagnet with large spin fluctuations.

4.5.1 Sample characterization

The parent alloy Ni$_3$Al and its derivatives, in the composition range 27.5-23 at. % of Al, crystallize with a simple cubic structure of the form Cu$_3$Au. In this composition range, $Ni_{3\pm x}Al_{1\mp x}$ exhibits ferromagnetism with moderate Curie temperature in the temperature range ~ 60-72 K. With increased Al concentrations above ~27 at. % of Al it becomes a paramagnet with large spin fluctuation. In this paper, we study the effect of spin fluctuation on the PCAR spectra of $Ni_{3\pm x}Al_{1\mp x}$ with composition range spanning the ferromagnet to paramagnet compositional phase boundary.

$Ni_{3\pm x}Al_{1\mp x}$ samples are prepared through arc melting. Detailed compositional analysis was carried out using electron probe microanalysis. Details of sample preparation and characterization have been described elsewhere. We have chosen three alloys namely Ni$_{76}$Al$_{24}$, Ni$_{74}$Al$_{25}$ and Ni$_{73}$Al$_{27}$ for the purpose of this study. To characterize the sample magnetization measurements are carried out on these samples using a Vibrating Sample Magnetometer (VSM) in the temperature range 2K-300K.
Figure 48: (a-c) shows the temperature ($T$) variation of magnetization ($M$) and inverse susceptibility ($\chi^{-1}$) for Ni$_{76}$Al$_{24}$, Ni$_{74}$Al$_{26}$ and Ni$_{73}$Al$_{27}$ respectively.

Magnetoresistance measurements are carried out up to a field of 12T using a Quantum design Physical Properties Measurement System (PPMS). Figure 48(a-c) shows the temperature dependence of magnetic susceptibility $M(T)$ down to 2K. Ni$_{76}$Al$_{24}$ shows a clear ferromagnetic transition around 72K (determined from the maximum in the double derivative of the $M$-$T$ curve). Ni$_{74}$Al$_{26}$
Figure 49: (a-b) Magnetoresistance (MR) as a function of temperature ($T$) for Ni$_{76}$Al$_{24}$ and Ni$_{73}$Al$_{27}$ respectively. Solid lines are a guide to eye.

also shows a ferromagnetic transition around 60K, but the moment is considerably smaller than Ni$_{76}$Al$_{24}$ and the magnetization does not saturate down to the lowest temperature indicating the presence of spin fluctuations even below $T_{Curie}$. Ni$_{73}$Al$_{27}$ does not exhibit any ordering down to the lowest temperature. However, unlike conventional Pauli paramagnets the magnetization is temperature independent showing a Curie-Weiss like behavior. This shows the presence of large spin fluctuation in the paramagnetic state in that particular sample.

To confirm further the presence of spin fluctuations, we have measured the temperature variation of magnetoresistance at $H$=12 T on the two extreme compositions i.e. the ferromagnetic Ni$_{76}$Al$_{24}$ and the spin fluctuating paramagnetic Ni$_{73}$Al$_{27}$. The
magnetoresistance is defined as

$$\text{MR} = \frac{\Delta \rho}{\rho} = \frac{\rho(H,T) - \rho(0,T)}{\rho(0,T)}$$  \hspace{1cm} (4.2)$$

The MR for Ni$_{76}$Al$_{24}$ and Ni$_{73}$Al$_{27}$ are shown in Figure 49(a-b). The MR is negative over the entire temperature range for both the samples. For Ni$_{76}$Al$_{24}$, the absolute value of the MR (|MR|) is low for $T<T_{\text{Curie}}$ and shows a maximum close to $T_c$. This can be understood, since presence of strong ferromagnetic spin fluctuation around $T_{\text{Curie}}$ increases the resistance $\Delta \rho$. On the other hand, in Ni$_{73}$Al$_{27}$, the |MR| keeps increasing with decreasing temperature showing the presence of strong spin fluctuations down to the lowest temperature.

4.5.2 PCAR studies on Ni$_{3\pm x}$Al$_{1\mp x}$

PCAR measurements are performed on Ni$_{3\pm x}$Al$_{1\mp x}$ with a superconducting Nb tip at liquid He temperatures using standard four-probe lock-in technique. Representative PCAR spectra for Ni$_{76}$Al$_2$, Ni$_{74}$Al$_{26}$ and Ni$_{73}$Al$_{27}$ are shown in Figure 50 (a-c). These spectra are analyzed within the mBTK formalism$^7$ using $\Delta$, $P_t$, $\Gamma$ and an effective barrier potential ($Z$) as fitting parameters. The values of $P_t$, $\Delta$ and $\Gamma$ extracted from the mBTK fits is shown as a function of at. % of Al in Figure 50 (d). With increasing concentration of Al, the transport spin polarization ($P_t$) decreases and as expected is zero for the paramagnetic compound Ni$_{73}$Al$_{27}$. The broadening parameter $\Gamma$ is zero for the ferromagnetic Ni$_{76}$Al$_{24}$ sample and increases gradually with Al content. The superconducting energy gap $\Delta$, on the other hand, decreases with increasing Al content as one goes from the ferromagnetic to the spin fluctuating regime. This is consistent with the earlier results on NdNi$_5$, where we have shown that the proximity of the
superconductor to large spin fluctuations drastically decreases the superconducting quasiparticle lifetime ($\tau$) and the superconducting energy gap ($\Delta$).

To cross check the uniqueness of the fits and the influence of individual parameters on it, PCAR spectrum for the ferromagnetic Ni$_{76}$Al$_{24}$-Nb and spin fluctuating Ni$_{73}$Al$_{27}$-Nb are investigated further in greater detail. In case of the ferromagnetic Ni$_{76}$Al$_{24}$, we try to simulate the best fit [red line in Figure 51(a)] assuming $P_t=0$ and a finite $\Gamma$. The fit (green line) is poorer in all respect. In the case of spin fluctuating Ni$_{73}$Al$_{27}$, we again try to simulate the best fit [red line in Figure 51(a)] assuming $\Gamma=0$ and a finite $P_t$ [green line in Figure 51(b)]. The fit is considerably poorer particularly at voltage values above the superconducting energy gap. This indicates that

Figure 50(a-c) PCAR spectra for Ni$_{76}$Al$_{24}$ and Ni$_{74}$Al$_{26}$ and Ni$_{73}$Al$_{27}$ with mBTK fits (solid red line). (d) Variation of $\Delta$, $\Gamma$ and $P_t$ with Al concentration.
the fitting parameters are independent and unique. Thus, the large decrease in $\tau$ (increase in $\Gamma$) as seen in Ni$_{73}$Al$_{27}$-Nb contacts can be related to the increased spin fluctuations in the same, which is developing with increased Al concentration.

To further explore the effect of spin fluctuations on $\Gamma$, we have done detailed PCAR studies on the two extreme compositions of this compound viz. the ferromagnetic Ni$_{76}$Al$_{24}$ and the spin fluctuating Ni$_{73}$Al$_{27}$. Different PCAR spectra are recorded by engaging the Nb tip several times on them at different places. These spectra correspond to the same sample tip combinations but have statistically different values of $Z$. The variation of $P_t$ with the barrier potential $Z$ for the ferromagnetic Ni$_{76}$Al$_{24}$ is shown in Figure 52(e). As has been shown before, the value of $P_t$ decreases with increasing $Z$ due to the presence of magnetic dead layer in the F-S interface, where spin flip scattering depolarises the electron, thereby decreasing the value of the transport spin polarization. Similar studies [Figure 53(a)-(d)] on Ni$_{73}$Al$_{27}$ reveal a systematic variation between $Z$ and $\Gamma$ [Figure 53(e)], with increasing $Z$, $\Gamma$.

Figure 51. PCAR spectra of (a) Ni$_{76}$Al$_{24}$; red line is the mBTK fit to data. Green line is the simulated spectra for the same. (b) Ni$_{73}$Al$_{27}$; red line is the mBTK fit to data with Green line is the simulated spectra for the same. Fitting parameters are mentioned in these figures.
Figure 52. (a-e) PCAR spectra for different Ni$_{76}$Al$_{24}$-Nb contacts. (f) Variation of $P_t$ with $Z$ at 2.3 K for the same.

decrease. This is expected, since a larger barrier parameter at the interface implies that the two electrodes are less strongly coupled to each other. Therefore, the influence of spin fluctuation would be less on the superconducting electrode. Consequently, there is also an inverse correlation between $\Delta$ and $\Gamma$ extracted from contacts [Figure 53(f)] with
Figure 53. (a-d) The variation of $P_t$ with $Z$ at 2.4 K for different Ni$_{73}$Al$_{27}$-Nb contacts. 
(e) Variation of the extracted value of $\Gamma$ with $Z$ at 2.4 K for different contacts. (f) Variation of $\Delta$ with $\Gamma$. Solid lines are a guide to eye.

different $Z$, the smaller the lifetime of the quasiparticle, the smaller is $\Delta$ for the superconductor. This inverse correlation between $\Delta$ and $\Gamma$ provides a valuable consistency check of intrinsic nature of proximity effect between a superconductor and a spin fluctuating metal.
4.6 Summary

PCAR spectroscopic studies on ferromagnets (NdNi$_5$, Fe, KFe$_4$Sb$_{12}$), nearly ferromagnetic metals (CaFe$_4$Sb$_{12}$, YbFe$_4$Sb$_{12}$) and itinerant ferromagnetic (Ni$_{3\pm x}$Al$_{1\mp x}$) systems are done. In NdNi$_5$, temperature variation of spontaneous magnetization ($M_s$) follows closely the temperature variation of transport spin polarization ($P_t$). I have also shown that the superconducting quasiparticle lifetime ($\tau$) extracted by fitting the PCAR spectra show a minimum close to the ferromagnetic transition temperature of NdNi$_5$. Through a detailed comparison with measurements carried out on the ferromagnet Fe and the nearly ferromagnetic compounds CaFe$_4$Sb$_{12}$ and YbFe$_4$Sb$_{12}$, we attribute this decrease in the quasiparticle lifetime to the effect of large spin fluctuations close to the critical temperature of the ferromagnet. To establish these new findings, further, I have investigated the effect of spin fluctuations in the itinerant ferromagnet Ni$_{3\pm x}$Al$_{1\mp x}$ using transport, magnetization and PCAR spectroscopy, where the ground state evolves from a ferromagnet to a spin fluctuating paramagnet with increase in Al. Our study shows that PCAR spectroscopy can detect the signature of spin fluctuations through a decrease of the superconducting quasiparticle lifetime and superconducting energy gap due to proximity effect. The central observation is that while a static moment has negligible effect on the superconducting quasiparticle lifetime and superconducting energy gap extracted from PCAR spectra, spin fluctuations decreases both the lifetime of the quasiparticle and the superconducting energy gap. This study shows that PCAR can be a valuable tool to explore spin fluctuations along with the measurement of transport spin polarization in different magnetic systems and its effect on superconductivity.
Chapter 5

Scanning tunneling microscopy (STM) and spectroscopy (STS)

5.1 Quantum mechanical Tunneling:

The principle on which STM\textsuperscript{112,113} operates is based on the quantum mechanical tunneling\textsuperscript{114}. In the simplest 1D model, an electron with mass $m$ is considered to be incident on a rectangular potential barrier of width $\alpha$.

![Figure 54. Tunneling through 1D rectangular potential barrier of width $\alpha$.](image)

One needs to calculate the probability for the electron to penetrate from the right side of the barrier. For this, the Schrödinger equation needs to be solved:

$$\left( -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x) = E \psi(x)$$

For an electron with energy $E$ less than the barrier potential $V_0$, the wave functions for the regions I, II and III are:

$$\psi_I(x) = e^{ikx} + Re^{-ikx}, \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\psi_{II}(x) = Ae^{\kappa x} + Be^{-\kappa x}, \quad \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$
\[ \psi_{III}(x) = Te^{-ikx} \]  

(5.4)

The coefficients R, T, A, B are determined from the boundary conditions and the requirements that the wave function and the derivatives should be continuous across the boundary. Then transmission probability becomes

\[ |T|^2 = \frac{(2k\kappa)^2}{(k^2 + \kappa^2)^2 \sinh^2 2\kappa\alpha + (2k\kappa)^2} \]  

(5.5)

This model is used to describe the STM tunnel junction for barrier heights of the order of the work function of the metal and the barrier width (~4eV) corresponds to the tip-sample distance (~5Å). When \( \kappa\alpha \gg 1 \), \( \sinh(2\kappa\alpha) \to \frac{1}{2} e^{2\kappa\alpha} \) and eqn.(5.5) becomes

\[ |T|^2 \rightarrow \left( \frac{4\kappa k}{k^2 + k^2} \right)^2 e^{-4\kappa\alpha} \]  

(5.6)

In region II, the particle behaves as an evanescent wave of range \( 1/\kappa \) and for \( \alpha \leq 1/\kappa \), the particle has considerable probability of crossing the barrier through “tunnel effect”. This exponential dependence on the barrier width (for small enough width) is common to all tunneling problems. The wave function of the tunneling electron decays exponentially within the barrier so that the probability of the electron to tunnel is very strongly dependent on the separation \( (d) \) between the two metal electrodes. The current measured across the tunnel barrier is given by

\[ I \propto e^{-\kappa d} \]  

(5.7)

This exponential dependence on the separation distance between the two metal electrodes allows the extreme sensitivity of scanning tunneling microscope.
5.2 Principle of operation:

The essential components of a STM consists of a sharp probing tip; a piezoelectric scanning unit, that controls the vertical and lateral movement of the tip; a coarse positioning unit, which brings the tip-sample separation to within the tunneling range (~5-10 Å); a vibration isolation stage and a set of control electronics. The STM digital feedback controller takes the output signal from the current pre-amp, compares the signal level with the preset value and sends the feedback voltage through an analog to digital converter to the high-voltage amplifier, which then magnifies the input signal to drive the piezo scanner. The controller communicates with the computer to change the experimental settings, such as the bias voltage, the tunneling current set point, the scanning range, scanning speed and the proportional/integral (P-I) gain for the feedback algorithm. On the other hand, it also transfers the feedback signal and tunneling current signal back to the computer to generate topographic images and tunneling spectra. During topographical image scanning, the output voltages from the feedback loop to

Figure 55. Schematic of STM and its operating principle from ref. 116.
the z-electrode of the piezo tube are converted to deduce the vertical position of the tip as a function of its lateral position, z(x, y). To initiate the tunneling process, the STM tip is brought to within several angstroms from the sample surface by the coarse approach piezo walker so that their wave functions overlaps significantly; then application of a bias voltage between them gives rise to a quantum mechanical tunneling current that varies exponentially with distance.

5.3 STM construction

To perform spectroscopy measurements with an STM several instrumentation challenges has to be addressed. First, the coarse approach mechanism has to bring the probing tip into the tunneling range (~5 Å) without crashing onto the sample. Secondly, the tip-sample separation has to remain constant to within ~0.1 Å throughout the measurement. To ensure this, mechanically the design of the STM should be rigid enough to prevent vibrational couplings from changing the tip-sample distance. The mechanical disturbance from the environment and acoustic vibrations should be decoupled as much as possible from the STM head. Electronically, tunneling currents generally range from ~pA to ~ nA. To avoid artifacts in tunneling spectra due to noise contamination, the electronics must be well shielded from ambient electromagnetic sources. Ground loops must be avoided, and cross-talk between the high-voltage piezo driving signals, the temperature controller output and the low-level tunneling/bias signals need be minimized. In the cryogenics part, the STM should have good thermal stability, low thermal drift and good thermal isolation when operating at variable temperatures. This section describes the design of our STM head, the cryogenics, and the vibration isolation methods.
5.3.1 Scanner Design and Operation

Piezoelectric scanners for STM are usually fabricated from lead zirconium titanate or PZT. Piezoelectric materials are ceramics that change dimensions in response to an applied voltage. Conversely, they develop an electrical potential in response to mechanical pressure. Piezoelectric scanners can be designed to move in x, y, and z by expanding in some directions and contracting in others. These piezoceramic tubes have electroplating divided into 4 quadrants on the outside and one on the inside. The inside quadrant gives overall elongating or shrinking of the tube length — z motion, and the 4 outer quadrants give shearing motion to the tube along a perpendicular plane — x-y motion. The tip is attached to the center of this tube using a copper holder and is well

![Figure 56. Operating principle of the scan piezo tube.](image-url)
isolated from all the piezo quadrants that carry high voltages. A schematic of the operating principle of the piezo is given in Figure 56. This behavior of the piezo tube can be expressed as follows. The motion along the X-Y and the Z-direction is described by

\[
\Delta Z = \frac{d_{31}}{t} V L,
\]

(5.8)

\[
\frac{\Delta X}{\Delta Y} = 0.9 d_{31} V \left( \frac{L}{d_m t} \right),
\]

(5.9)

where

- \(L\)=Length of the tube,
- \(OD\)= Outer diameter of the tube,
- \(ID\)= Inner diameter of the tube,
- \(t\) (Wall thickness)= OD-ID,
- \(d_m\)= (OD+ID)/2
- \(V\)= Applied voltage on piezo,
- \(d_{31}\)= Piezo electric charge constant (≈ 250 x 10^{-12} m/V)

We have used the piezo ceramics from Staveley sensors (EBL#2) with the following dimensions: \(L=0.5 \text{ inch}, \ OD=0.25 \text{ inch}, \ ID=0.24 \text{ inch}, \ d_{31} = -1.73 \text{ Å/V(293K), -0.31 Å/V(4.2K).}\) Table below shows the specifications of the scan piezo at various temperatures.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>293K</th>
<th>4.2K</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔX, ΔY</td>
<td>155.7Å/V</td>
<td>27.95Å/V</td>
</tr>
<tr>
<td>ΔZ</td>
<td>86.7Å/V</td>
<td>15.54Å/V</td>
</tr>
</tbody>
</table>
5.3.2 Head design

The STM built as part of this thesis work is intended to operate at variable cryogenic temperatures and in high vacuum. There is a variety of distinct STM designs. In general, they differ in how the coarse approach is implemented and in their rigidity against vibrations. In our design, we have employed ANC 150 piezo walker from Attocube systems for the coarse approach. The schematic of the STM head is shown in Figure 57. The STM head is made of Titanium metal. The metallic tip holder is attached to the center of the piezo-tube scanner with copper holder using stycast 2850-FT. The piezo scanner is glued in a Ti cylinder with Epotech epoxy and the whole

![Figure 57. Photographs of the STM head assembly.](image)
assembly sits on the Attocube piezo walker. All the materials used to assemble the STM head are non magnetic (Ti, Cu) and high vacuum compatible. The sample sits on the top of the STM head with the help of a vertical manipulator, making it possible to replace the sample in situ. The STM head is designed to be concentric with the tip and sample located at the center. Therefore, it minimizes thermal drifting and enhances the STM performance at variable cryogenic temperatures.
5.3.3 Variable temperature insert and Dewar assembly

The STM probe used in this thesis work is designed in house. A charcoal pump is installed at the bottom of the vacuum can to absorb the residual gas from any virtual

Figure 59. Schematic of the variable temperature insert.
leaks of the STM head at low temperatures. Next, we minimize the thermal conduction of the electrical wires. Twisted pairs of constantan wires from Lakeshore with low thermal conductivity are used for wiring the piezo-tube scanner, heater and the Cernox temperature sensor. For the tip and sample connection, we have used CC-SS-25 flexible coaxial cables form Lakeshore. The STM head is attached to the 4K pot at the end of the VTI using M3 screws. The thermal link between the 4 K pot and the STM head is maintained using several strips of Cu wires firmly anchored between the two, thus providing good cooling power for the entire STM head. After the installation of heat links, base temperature significantly improves to ~4.8 K.

5.4 Noise reduction

Due to the extremely close tip-sample distance of only few Å and the exponential distance dependency of the tunneling current, a scanning tunneling microscope is very sensitive to vibrations. Vibration noise\textsuperscript{115} can affect the STM measurement two ways: (1) change in the tip-sample separation, which is amplified exponentially in the tunneling current, and (2) motion of the wire carrying the tip current, which capacitively couples to its environment and therefore causes current spikes when moved. The latter issue can be addressed by carefully clamping all of the wires in place, so that they cannot move with respect to each other due to helium boiling vibrations or external building vibrations. Selective measures must be taken to avoid these noise problems. Below we list different sources of vibrations\textsuperscript{115},
**Figure 60.** STM unit with vibration isolators.

**Figure 61.** Sample preparation chamber for the STM.
Sources of vibration:

1. Low frequency (0.1-50 Hz) building vibration.
2. Table chambers have resonance frequency 30-100 Hz that can be driven by persons walking, acoustic waves etc.
3. Acoustic noises are in range 100 Hz to 1 KHz.
4. Line frequency noise of 50 Hz and its harmonics.
5. 0.1-20 Hz: Frames, walls, floors of building.
6. 20-200 Hz: motors, AC line freq(50 Hz), acoustic noise.
7. 200-1 kHz: piezo resonances.

Figure 62. Velocity profile of the noise level on the ground measured with a HP 35665-dynamic-signal-analyzer.
Our STM lab is located in the ground floor where the floor vibration is comparatively low. The room in which STM operates is radio frequency (RF) shielded. Nevertheless, as we set up the accelerometer and physically measure its noise spectrum, several sharp resonant peaks below 100 Hz are found [Figure 62]. To suppress the coupling to these resonance modes, we have employed two main stages of vibration isolation using a passive Newport air damper and an active Halcyonics vibration isolator [Figure 60]. The dewar holding the STM VTI is placed on the four-post Newport air damper, which serves as a low-pass filter against the floor vibrations. Additional lead bricks are placed around the table to increase the loading and suppress the corner frequency of the air damper. When the table is inflated, most of transmitted vibrational noises at the high

Figure 63. Velocity profile of the noise level on the STM table with Newport air legs floated, measured with a HP 35665-dynamic-signal-analyzer.
frequencies are suppressed to less than 10% of its original amplitude at the resonant frequencies as shown in Figure 63.

In the second stage of isolation, the Halcyonics active vibration isolation takes effect right at 0.5 Hz and its efficiency considerably increases from this frequency upward [Figure 64]. Above 10 Hz, Halcyonics system isolates 99.0% of the floor vibration. A major advantage of active vibration isolation systems is that they do not have any natural resonance frequency, which is responsible for most of the problems encountered with passive vibration isolation systems, especially in the low-frequency range below 5 Hz.

**Figure 64.** Velocity profile of the noise level on the STM table with Newport air legs and Halcyonics active vibration isolator operating simultaneously, measured with a HP 35665-dynamic-signal-analyzer.
Another type of vibrational noise is transmitted through acoustic coupling. The acoustic noises that plague the STM system mostly come from the room ventilation motors. This type of low frequency noises are generally difficult to remove because they either drive the plaster wall or indirectly couple through the ceiling to vibrate the whole lab. We have covered all of the sidewalls of the STM room with sound proof shields to minimize these effects.

Apart from vibrational noise, the largest source of noise is electronic noise. Our STM holds the tip at virtual ground, and applies a bias voltage to the sample. The tunneling current is measured from the tip. To minimize the contamination of tunneling current signals through cross talks and environmental electromagnetic interference and capacitive couplings, we run wires of different purposes through separate thin-wall SS tubes; the latter serve as additional shielding. As a result, the high voltages driving the piezo-tube are decoupled from the low-level bias voltage and the tunneling current leads. The coaxial cables carrying the bias and the tunneling signal are passed through a room-temperature low pass filter (1.5 KHz) before being connected to the STM head.

![Figure 65. Filter characteristic showing (a) gain and (b) phase of the filter response with frequency (f).](image-url)
Apart from this, additional low pass filters (1.5 KHz) are also employed before the high voltage piezo lines to minimize the high frequency noise. The characteristic of the piezo filter are shown in Figure 65. Furthermore, all grounding and shielding wires are carefully arranged to avoid ground loops, which is a major source of 50Hz line noise and its harmonics.

5.5 Tip preparation

Electrochemical etching of a metal wire\textsuperscript{117} (W) is used to generate good STM tips. The basic idea is to dip a small diameter metal wire into an electrolyte solution, in which a counter electrode is sitting. Then apply an A.C or D.C voltage between these two electrodes and the metal wire ends up in a sharp tip. The choice of the electrolyte and the applied voltage depends on the material used to make the tip. In general, using tungsten (W) wire extremely sharp STM tips can be obtained\textsuperscript{118} in a single electrochemical step with mild chemicals. The drawback is that due to its poor resistance to oxidation, the tungsten tip will most likely undergo surface contamination. However, a proper annealing treatment in UHV can provide a quick and efficient solution to this problem. We also prepare tips from 0.25 mm thick platinum-iridium (Pt-Ir) (85:15 wt.\%) wire from Alfa Aesar by cutting it at certain angle, this reduces the chance of surface oxidation.

5.5.1 Electrochemical Etching

The experimental setup we use for the electrochemical etching of W tips is shown in Figure 66. We have employed a cut off circuit (Figure 67) to control precisely the etching process. In the etching set up, the tip wire can be moved vertically using a
Figure 66: Etching assembly for tip preparation.

Figure 67. Diagram for the cut off circuit used in the etching process.
Figure 68. Illustration of the drop-off method. (a) shows the formation of the meniscus. (b) – (e) Illustrate the flow of WO$_4^{2-}$ towards the lower end of the wire, the formation of a dense layer of WO$_4^{2-}$ around the bottom of the wire and the necking phenomenon in the meniscus. (f) The lower part breaks off: the drop-off has occurred.

micrometer differential screw; it is thus possible to easily control the length of the wire immersed in the solution, as the length of the immersed wire plays an important role in determining the final shape of the tip. The shorter the meniscus, the smaller the aspect ratio of the resulting tip and a small aspect ratio is desirable to limit the vibration of the tip in a STM experiment. Details of the etching procedure are tabled below:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH concentration</td>
<td>2 Molar</td>
</tr>
<tr>
<td>Immersion depth</td>
<td>1 mm</td>
</tr>
<tr>
<td>Wire diameter</td>
<td>0.25mm</td>
</tr>
<tr>
<td>Voltage applied to the circuit</td>
<td>15 Volt</td>
</tr>
<tr>
<td>Etching current</td>
<td>43 mA</td>
</tr>
<tr>
<td>Etching time</td>
<td>12 minute</td>
</tr>
</tbody>
</table>

The overall reaction for this particular electrochemical etching$^{119}$ is the following

\[
\text{cathode: } 6H_2O + 6e^- \rightarrow 3H_2(g) + 6OH^- \\
\text{anode: } W(s) + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^- \\
W(s) + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2(g)
\]

The etching takes place at the air/electrolyte interface and the tungsten undergoes an oxidative dissolution to form tungstate anions (WO$_4^{2-}$), which are soluble in water. The
reaction also involves the reduction of water; bubbles of gaseous hydrogen and OH$^-$ ions are thus produced at the cathode. The shape of the meniscus plays a very important role in determining the final shape of the tip as the etching rate at the top of the meniscus is a lot slower than at the bottom. This can be explained by the presence of a concentration gradient due to the diffusion of OH$^-$ ions to the tip. Furthermore, the soluble tungstate produced during the reaction flows towards the lower end of the tip wire, generating a dense viscous layer, which prevents this region from being etched away. At some point, this part of the wire becomes so thin its tensile strength cannot sustain the weight of the lower end of the wire; the latter breaks off and a sharp tip is left behind. This “drop-off” method is illustrated in Figure 68. Once the etching is completed, the tip is cleaned immediately in an ultrasonic bath by carefully dipping it for a few seconds in distilled water, acetone and ethanol respectively. The purpose of this step is to remove residues left by the etching process.

In the electrochemical etching process, when the lower part of the wire drops off and a sharp tip is formed, the electrolytic current decreases suddenly. After this moment the tip apex still remains in the electrolyte. Because the etching voltage is still applied, a very little residual current exists and the apex of the upper part will continue to etch resulting in a blunt tip as shown in Figure 69(a). In order to get a tip as sharp as possible, the residual current must be cut off immediately after the tip on the upper part is formed. The circuit diagram described in Figure 67, cuts off the current upon reaching a threshold value and prevents any further etching of the tip apex immersed in the electrolyte. The resulting tip using this cut off circuit is extremely sharp as can be seen from the high-resolution SEM images in Figure 70. However, all these tips prepared by electrochemical etching contain oxide layers on its surface, which needs to
**Figure 69.** SEM images of W tip (a) without cut off circuit, (b) with cut off circuit.

**Figure 70.** SEM images of W tips, prepared with cut off circuit.

**Figure 71:** SEM image of a mechanically cut Pt-Ir tip.
be cleaned before the experiment. Another easy way to obtain good oxide free STM tips is to cut Pt-Ir wire in some angle. Figure 71 shows the SEM image of such a tip. For most of our STM studies we have used mechanically cut Pt-Ir tips.

5.5.2 Tip cleaning with field emission

In field emission, under the influence of a high electrostatic field, electrons are emitted from a metallic surface into the vacuum. The electrons in a metal reside in a potential well, mainly because of their attraction to the positive ions. In an electrically neutral metal, this barrier can be crudely represented by an abrupt potential step that electrons cannot surmount, as illustrated in Figure 72. The step height, as measured from the metal’s Fermi level $\mu$, is equal to the work function $\Phi$. The work function is defined as the minimum energy required to remove an electron from a metal surface. Since the atoms at the surface of the metal do not have as many nearest neighbors as the atoms in the bulk, the charge distribution at the surface is quite different than in the bulk.

**Figure 72.** Potential energy diagram for electrons in a metal. The step height, calculated from the Fermi level $\mu$, is equal to the metal’s work function $\Phi$. 
Moreover, once the electron has exited the metal, it will experience an interaction with its image charge on the surface. The strength of these surface electrostatic potentials varies with the surface structure, which explains why the work function for a particular metal differs from one crystallographic plane to another. Typical values of $\Phi$ for metals are around 3 to 5 eV. Field emission occurs when the applied external electrostatic field induces such a strong deformation in the potential barrier that unexcited electrons can tunnel through it.

The STM tip prepared either by electrochemical etching or by mechanical cutting is cleaned using field emission to remove the oxide layers and other external impurities those reside on the tip apex. In general, the field emission is done on single crystals of Au/Cu/Ag. In the process, the tip is bought very close to the sample, such that in 10-12 steps one can enter the tunneling regime. The sample is grounded and a negative bias is applied to the tip. A 10/100K Ohm resistor in series is placed in the circuit to limit the current. First we apply voltage in steps to 100-200V until a small current (1-2 $\mu$A) is detected. Now we slowly increase the tip sample distance and increase the voltage in small steps such that around 300-400V we get a current $\sim$ 20-30 $\mu$A. At this point, the system is kept in this configuration for $\sim$30 minutes or until one obtains a stable current. If the field emission is successful, the current drops suddenly to zero; this implies that the tip has changed, which we intended. After successful filed emission, it is useful to check the distance dependence of the current (i.e. withdrawal of the tip by a step results in the decrease in tunneling current and vice versa) to verify the vacuum tunneling.
5.6 Mounting the tip and the sample

For practical purpose, we normally use the Pt-Ir tip for STM experiments. After external cleaning with isopropanol and acetone, the tip is inserted into the tip holder, which is a hypodermic tube. We bend the tip in the middle while inserting, so that the tip is held in place due to its spring force. After loading the tip, we close the copper can with indium seal and put the VTI into the cryostat. The VTI is pumped to \(\sim 10^{-6}\) mbar of vacuum before we load the sample. The sample is loaded on the copper sample holder using silver epoxy. For thin films grown on non-conducing substrates, it is necessary to make an electrical contact with the Ag paste from one corner of the film to the Cu sample holder. Once the sample is loaded, we insert it to the STM head using a vertical manipulator without breaking the vacuum. At this stage, we are ready to start the experiment.

To prepare the sample, normally we first anneal it (at times) in the sample preparation chamber (Figure 61) attached to the VTI on the STM table (Figure 60). It is necessary to prepare different single crystals (Au/Ag/Cu/Nb) by anneal them before we do field emission to prepare the tip. The time and temperature of the annealing process varies for different samples. Normally, for Au, we heat it at 400\(^\circ\)C for 4 hours in high vacuum. Then using the horizontal and vertical manipulators we place it in the STM head at the end of the VTI, without breaking the vacuum. After the field emission, we verify the tip condition with the surface topography/STS data on the sample. This annealing treatment is sometimes necessary to get good surface topography and STS data on the sample.
5.7 STM control electronics and data acquisition

The STM control and data acquisition electronics form RHK technologies consist of a high-gain low-noise current preamplifier (IVP 200), a digital P-I feedback controller, a set of high-voltage amplifiers that control the piezotube scanner. The low-noise current pre-amp has a variable gain up to $1 \times 10^{10}$. We operate the pre-amp mostly at a gain of $1 \times 10^9$ for data acquisition with a frequency bandwidth of 1.5 KHz. While engaging the tip to the sample we employ the automated feedback detect mode using RHK-Attocube interface. In this mode of operation, the tip is brought within the tunneling range using the Attocube piezo walker. Initially the piezo scan tube retracts fully and the piezo walker takes single steps towards the sample; during each step it tries to detect the tunneling current and repeats the process until 50% of the current set point (typically 1 nA) is measured. Once it detects the tunneling current, the automated approach is stopped. Now the RHK controller takes the amplified current signals from the pre-amp, performs the P/I feedback algorithm and, finally, outputs a voltage signal to the z-electrode of the piezo-tube to maintain a constant tunneling current. Overall, the speed of the coarse approach is limited by the bandwidth of the feedback to $\sim 1$ step/sec. It uses slip-stick mechanism for the approach. Typical step size of the walker is 0.025μm at 300K and 10nm at 4.2K. At room temperatures, it takes an hour to move the tip $\sim$1mm forward into tunneling range with applied voltage of 20-30V at frequency of 500Hz. At helium temperatures (4.2K), because of the reduced piezo coefficient, it usually takes $\sim$8/9 hours to reach the tunneling range; the applied voltage is 50-60V with a frequency of 600Hz.
5.8 STM experiment

5.8.1 Modes of operation

STM are designed to scan a sample in either of two modes: constant-height or constant-current mode, as shown in Figure 73. In constant-height mode, the tip travels in a horizontal plane above the sample and the tunneling current varies depending on topography and the local surface electronic properties of the sample. The tunneling current measured at each location on the sample surface constitutes the data set, i.e. \( I(x,y) \) at \( z \) with a constant applied voltage \( (V) \) gives the topographic image. In constant-current mode, STM use feedback to keep the tunneling current constant by adjusting
the height of the scanner at each measurement point. For example, when the system detects an increase in tunneling current, it adjusts the voltage applied to the piezoelectric scanner to increase the distance between the tip and the sample. In this mode, the motion of the scanner constitutes the data set, i.e. $z(x,y)$ at constant $I$ and $V$. If the system keeps the tunneling current constant to within a few percent, the tip-to-sample distance will be constant to within a few hundredths of an angstrom. Each mode has advantages and disadvantages. Constant-height mode is faster because the system does not have to move the scanner up and down, but it provides useful information only for extremely smooth surfaces. Otherwise, the tip may crash in to the sample. Constant-current mode can measure irregular surfaces with high precision, but the measurement takes more time. In our STM, we follow the constant current mode of operation.

5.8.2 Spectroscopy

Now we are in a position to proceed for the experimental aspects of the STM. First, one needs to ensure the stability of the STM head against various noises. Earlier I have

![Power Spectrum](image)

**Figure 74.** Current noise profile measured with RHK data acquisition system at 300K.
shown the noise profile of our STM measured using an accelerometer, which showed reasonable damping of the vibrational amplitudes using two stages of vibrational isolators. However, it is also essential to verify the effect of electromagnetic coupling to the noise profile before we take the data. We have measured both the current and topographic noise levels in our system, in situ, when the tip and sample are in tunneling range using RHK’s data acquisition system and they are shown in Figure 74 and Figure 75 respectively. The low noise level ensures the stability of the STM head against vibrational and electromagnetic noises.

5.8.3 Topography of a surface

When the tip and sample are within tunneling distance (~5 Å) we are ready to scan the surface of the sample. To calibrate the STM we have used Au thin films on glass. The topographic studies show grains of the Au film with sizes ~25 nm, this is confirmed with the atomic force microscope (AFM) studies on the same. Figure 76 and Figure 77 show some of the topographic images on Au film and freshly cleaved HOPG surface.
**Figure 76.** Topographic images of Au on glass at 300 K with $V_{Bias}=-25\text{mV}$, $I_{Set}=40\text{pA}$.

**Figure 77.** Topographic images of HOPG at 300 K with $V_{Bias}=-100\text{mV}$, $I_{Set}=50\text{pA}$.
Using Pt-Ir tip at room temperature. Using our STM we can precisely track some particular feature on the surface over a larger scan area (Figure 78), as this is very much essential while studying the spectroscopic properties on a surface. These studies ensure that the calibration of the piezo is proper; also, it indicates the stability of the STM scanner against vibration and thermal drifts.

5.8.4 Current (I) – Voltage (V) spectroscopy

At this point the system is ready to acquire single point data captures. This is done simply by selecting a single location from the topographic image within the scan area.

**Figure 78.** Topographic images of Au on glass at 300 K with $V_{\text{Bias}}=-10\text{mV}$, $I_{\text{Set}}=25\text{pA}$. 
The tip then scans to the location while implementing the feedback loop to maintain constant current in the same way as when imaging. When the tip reaches the desired location, the feedback is turned off and the voltage is ramped at a constant tip-sample separation to measure the current-voltage characteristic of the sample at that particular point. The I-V curve measured on Au thin film and HOPG samples at 300K performed with a Pt-Ir tip are shown in Figure 79 and Figure 80 respectively. We normally take a large number of I-V data on a particular point and average them to get the final spectra.

**Figure 79.** Current (I)-voltage (V) profile of Au film using a Pt-Ir tip at 300K.

**Figure 80.** Current (I)-voltage (V) profile of HOPG using a Pt-Ir tip at 300K.
5.8.5 Current vs. Tip/Sample Separation (I vs. Z)

In conventional tunneling spectroscopy the tunneling current is measured as function of the applied bias voltage, thus providing a measure of the sample DOS. The major uncertainties in such experiments are the unknown effective barrier height and width of the tunneling barrier. However, it is possible to probe directly the effective tunneling barrier by measuring the dependence of tunneling current on the tip-sample separation, at constant applied bias voltage. Since the tunneling probability amplitude is an exponential function of the tip-sample separation [eqn.(5.7)], the value of the tunneling current is extremely sensitive to the sample surface corrugation [Figure 81]. For instance, an increase in separation (δz) of 1 Å decreases the tunneling current (δI) by a factor of $e^{2\sim 7.4}$. This exponential dependence of the tunneling current on both tip/sample separation can be measured performing $I$ vs. $Z$ spectroscopy. In this mode of operation, the current is recorded while the tip is slowly withdrawn several Angstroms from the sample surface. If the tunnel junction is a good vacuum barrier, then the

\[ I \propto e^{-2\kappa \delta z}, \quad \kappa = \frac{\sqrt{2m\Phi}}{h} \]

**Figure 81.** Theoretical I-Z spectrum showing the exponential dependence of tunneling current on the tip-sample separation.
Figure 82. (a) I-Z and (b) ln I-Z spectra for Pt-Ir tip with NbN sample. Red line shows linear fit to the data. The slope of the curve gives a work function of 4.5 eV.

current falls exponentially with the displacement, and the slope of the line (on a log-linear plot) reveals the work function ($\Phi$) for the tip-sample system as

$$\Phi (eV) = \frac{\hbar^2}{2m} \left( \frac{d \ln(I)}{ds} \right)^2 \approx 0.95 \left( \frac{d \ln(I)}{ds(\text{Å})} \right)^2$$  \hspace{1cm} (5.10)

We always confirm clean vacuum tunneling with this technique at the outset of an experiment. The relationship between tunneling current $I$ and tip displacement from the surface $Z$ is recorded to confirm the characteristic exponential behavior of vacuum tunneling [Figure 82(a)]. The effective barrier height, which represents the convoluted work function of the tip and the sample, can be extracted from this data. As an example, the results of an $I$ versus $Z$ measurement for a Pt-Ir tip is plotted in log-linear format in Figure 82(b). The linear curve confirms the vacuum nature of the tunneling, and a work function of 4.5 eV is deduced from its slope.
5.8.6 Differential Conductance Spectroscopy

In addition to measuring the work function and topography, the STM also has the ability to measure a much more scientifically interesting property of any conducting material – the electronic density of states (DOS). The differential tunneling conductance, $G(V) = \frac{dI}{dV}|_V$, is simply proportional to the local density of states of the sample at $E = eV$. It can also be obtained by acquiring an I-V characteristic and subsequently taking a numerical derivative of the data. Since numerical derivatives in general add scatter to the data points it is always preferable to employ a lock-in technique capable of considerably less noise and higher energy resolution. Such a measurement is indeed possible via a standard lock-in technique. The key idea is to add a small AC signal ($dV$) to the DC bias voltage applied to the tunnel junction. We typically measure the differential conductance by setting the tip-sample separation, characterized by the junction resistance at a given sample bias, and then turning off feedback so that this separation is fixed. A small, high frequency sinusoidal modulation voltage is applied on the top of the constant DC bias voltage between the tip and the sample. The AC component the resulting current modulation is measured with a lock-in amplifier attached to the output of the current amplifier, with the in phase component directly giving $G(V) = \frac{dI}{dV}|_V$. This can be seen using the Taylor expansion of the current:

$$I(V + dV \sin \omega t) \approx I(V) + \frac{dI}{dV}|_V \cdot dV \sin \omega t \quad (5.11)$$

At a given point on the surface, then, a differential conductance spectrum is obtained by recording the amplitude of the lock-in output, proportional to $dI/dV$ (and hence indicative of the density of states), as a function of applied sample bias (energy). The
modulation frequency must be faster than the closed loop bandwidth of the STM feedback system, which is typically 1-2 KHz. In practice, the optimal modulation frequency is slightly above the cutoff frequency of the feedback loop, and it is set in the frequency range where the induced modulation \( \frac{dI}{dV} \) is independent of frequency.

It should be noted that this current modulation is due to both the resistance and the reactance of the circuit. The resistive component is the \( dI \) that carries the density of states information for the given energy and spatial location. The reactance component of the overall current modulation is out of phase with the resistive component by \( \frac{\pi}{2} \) and can thus be separated out by appropriate choice of the lock-in phase. The phase must be set to measure only the resistive response, and not the capacitive response, of the tunnel junction. This can be accomplished by offsetting the tip out of tunneling range, such that the tip is fully extended and no tunneling current results, and then opening the feedback loop. In this condition, the response is fully capacitive, and the lock-in phase can be set to measure the amplitude of the ac response of the tunnel junction out of phase with the capacitance (i.e., the conductance).
5.8.7 Studies on HOPG

The studies in this section concerns with both topographic and STS measurements on a cleaved Highly Oriented Pyrolytic Graphite (HOPG). Figure 83 shows topography of HOPG sample with visible step edges. We have performed the G(V)-V measurements (Figure 85) on these armchair edges using a Pt-Ir tip at various temperatures. The bump like structure at positive bias in LDOS is possibly due to a local electrostatic potential induced by the tip. Below are some of the images of the same showing the step edges present in HOPG. Figure 84 shows raw conductance spectra on the same, it contains a total of 50 spectrums taken at the same point. While measuring the

![Figure 83. Topographic image of HOPG with Pt-Ir tip at 300K.](image)
Figure 84. Raw $\frac{dI}{dV}$-$V$ spectra for HOPG at 10 K. The data set consists of 50 odd spectra. The bias modulation parameters are $V_{\text{Mod}}=0.4$ mV, $f_{\text{Mod}}=1376$ Hz.

Figure 85. $\frac{dI}{dV}$-$V$ spectra on HOPG at various temperatures with Pt-Ir tip. The bias modulation parameters are $V_{\text{Mod}}=0.4$ mV, $f_{\text{Mod}}=1376$ Hz.

The differential conductance of a sample, we normally take a large number of spectrum and average over them. The spectra shown in Figure 85 are the averaged ones, measured at various temperatures at the same point on the HOPG sample.
5.8.8 The I-V characteristic of semiconductors

The STS measurement often leads to an overestimated gap energy compared to values expected from other measurements. A “tip-induced band bending” is one of the origins which give rise to a large gap value\textsuperscript{121,122}. In an n-type semiconductor sample at positive sample bias voltage, an external electric field from an STM tip penetrates into the sample surface region and bends the energy band near the surface. As a result, the conduction band edge energy increases, and electron tunneling from the STM tip is blocked. The onset voltage of the tunnel current is raised due to the tip-induced band bending. These lead to mid gap states at the Fermi level\textsuperscript{123}, as result, in an n-type semiconductor at positive bias the band bending is increased, and at negative bias the band bending is decreased. The situation is reversed on a p-type semiconductor. We have performed the STS measurement on n-AlGaAs grown on GaAs (100) with the etched W tip at room temperature and high vacuum ~2x10\textsuperscript{-6} mbar. The tunneling spectra obtained from the I–V curves (Figure 86) yields a band gap energy ~1.75 eV, it also shows the band bending effect.

Figure 86. I-V spectrum on n-AlGaAs with a W tip at 300 K.
5.8.9 STM Studies on the superconductor NbN

NbN is a conventional BCS superconductor with moderate high \( T_c \approx 16 \text{K} \). Superconductivity in NbN thin films has been widely studied in connection with superconducting hot electron bolometer and superconducting single photon detectors. The short coherence length (\( \xi < 5 \text{ nm} \)) and large penetration depth (\( \lambda \approx 200 \text{ nm} \)) allows fabrication of few nanometer thick superconducting thin films with moderately high \( T_c \). These films have good mechanical strength, chemically stability in ambient atmosphere, and can be recycled from cryogenic temperatures to room temperature without any detectable degradation in their superconducting properties. These properties of NbN allow us to investigate its superconducting properties using our STM. In this study, thin films of NbN are synthesized through reactive dc magnetron sputtering by sputtering an Nb target in an Ar-N\(_2\) gas mixture. After the deposition, the film is quickly loaded in the STM sample holder and put in the VTI for STM

![Figure 87](image.png)

**Figure 87.** Topograph of NbN at 5.2 K, with \( V_{\text{Bias}} = 50 \text{ mV} \) and \( I_{\text{Set}} = 70 \text{ pA} \).
Figure 88. Conductance spectra on NbN thin film using Pt-Ir tip at liquid He temperature. The bias modulation parameters are $V_{\text{Mod}}=0.1 \text{ mV}, f_{\text{Mod}}=1376 \text{ Hz}$.

measurements. The sample shows [Figure 87] smooth grains with textured surface. To study the superconducting properties, STS experiments are performed [Figure 88] on it using a Pt-Ir tip. The tip is prepared by field emission on an Au single crystal (111) before the actual experiment. The superconducting gap ($\Delta$) comes around 1.6 meV at 5.2 K. Further studies are going on to get a full understanding of the properties of the superconductor NbN.
5.9 Summary

In this chapter, I have described the design and fabrication of a variable temperature (4-300 K) scanning tunneling microscope (STM). The STM is designed and fabricated in our lab at TIFR. RHK’s SPM 8 software module is used for the data acquisition and data analysis. The tips used in the STM experiments are made in the lab using either electrochemical etching process with a cut off circuit or by mechanically cutting high purity wires. In STM experiments noise plays a predominant role. A combination of active and passive vibration isolation systems are used to minimize the noise effect. Finally, I have investigated various systems like HOPG, Au thin films, semiconductors and superconductors like NbN to characterize the spatial and energy resolution of the STM.
Chapter 6
Conclusion

In this thesis, I have used various transports spectroscopic measurements like point contact spectroscopy (PCS), its variant point contact Andreev reflection (PCAR) spectroscopy and scanning tunneling microscopy (STM) and spectroscopy (STS) to investigate conventional, unconventional superconductors and different magnetic systems. All these experimental set ups are designed and fabricated in our lab. The studies reveal energy and momentum resolved information about the electron and their interactions with different elementary excitations close to the Fermi surface in different systems.

Directional PCAR spectroscopic studies are performed on the anisotropic superconductor YNi$_2$B$_2$C along the crystallographic directions $a$ (100) and $c$ (001) using a normal metal Ag tip. From the temperature and magnetic filed variations of the superconducting energy gaps along the two crystallographic directions a clear elucidation of the multiband nature of superconductivity in this material is shown. Band structure calculations also suggest that there exist mainly two types of electrons with anisotropic Fermi velocities that vary by a factor of 6. Further, the evolution of the multiband effects on the upper critical field $H_{c2}$ and the critical transition temperature $T_c$ are investigated by doping non magnetic impurity (Pt) in YNi$_2$B$_2$C. Studies on YNi$_{2-x}$Pt$_x$B$_2$C reveal that the observed anisotropy in $H_{c2}$ and $T_c$ disappears with Pt doping, as it introduces inter-band scattering. Specific heat studies confirms that the Pt doping has no effect on the density of states in YNi$_{2-x}$Pt$_x$B$_2$C ($x=0-0.2$). The scaling of $H_{c2}$ and $T_c$ due to Pt doping is in agreement with the multiband scenario.
PCAR spectroscopic studies on ferromagnets (NdNi$_5$, Fe, KFe$_4$Sb$_{12}$), nearly ferromagnetic metals (CaFe$_4$Sb$_{12}$, YbFe$_4$Sb$_{12}$) and itinerant ferromagnetic ($Ni_{3±x}Al_{1±x}$) systems are done. In NdNi$_5$, temperature variation of spontaneous magnetization ($M_s$) follows closely the temperature variation of transport spin polarization ($P_t$). I have also shown that the superconducting quasiparticle lifetime ($\tau$) extracted by fitting the PCAR spectra show a minimum close to the ferromagnetic transition temperature of NdNi$_5$. Through a detailed comparison with measurements carried out on the ferromagnet Fe and the nearly ferromagnetic compounds CaFe$_4$Sb$_{12}$ and YbFe$_4$Sb$_{12}$, we attribute this decrease in the quasiparticle lifetime to the effect of large spin fluctuations close to the critical temperature of the ferromagnet. To establish these new findings, further, I have investigated the effect of spin fluctuations in the itinerant ferromagnet $Ni_{3±x}Al_{1±x}$ using transport, magnetization and PCAR spectroscopy, where the ground state evolves from a ferromagnet to a spin fluctuating paramagnet with increase in Al. Our study shows that PCAR spectroscopy can detect the signature of spin fluctuations through a decrease of the superconducting quasiparticle lifetime and superconducting energy gap due to proximity effect. The central observation is that while a static moment has negligible effect on the superconducting quasiparticle lifetime and superconducting energy gap extracted from PCAR spectra, spin fluctuations decreases both the lifetime of the quasiparticle and the superconducting energy gap. This study shows that PCAR can be a valuable tool to explore spin fluctuations along with the measurement of transport spin polarization in different magnetic systems and its effect on superconductivity.

Apart from these, the design and operation of a home build variable temperature scanning tunneling microscope (STM) is presented and some preliminary results are
shown, that includes both topographic and spectroscopic studies on various systems. In combination with PCAR spectroscopy, the STM measurements are intended to extend the spectroscopic measurements with spatial resolution.


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Uncertainty in the wave vector $k$ would also arise from the Heisenberg uncertainty relation $\Delta x \Delta p \sim \hbar / 2$. For a typical point contact diameter, this uncertainty is, however, less than 1% of $k_F$, the momentum wave vector at the Fermi level. For further details, see EPAPS. Document No. E-PRBMDO-72-110525. This document can be reached via the EPAPS homepage http://www.aip.org/pubservs/epaps.html.

In principle, one should also take the band structure of the normal metal tip into consideration. However, for silver tip (used in this work) the FS nearly spherical and
isotropic. It is therefore sufficient to take only the anisotropy of the FS of the superconductor into consideration.


84 The statistical variation of the superconducting energy gaps was measured for over 20 contacts in both current directions. For different point contacts the anisotropy ranges from 4 to 7. Similarly, the statistical variation in $\frac{\Delta}{\Gamma}$ ranges from 0.1 to 0.3 for $I||c$ and 0.4 to 0.6 for $I||a$. These distributions are largely from our inability to control the current direction precisely.

85 A. E. Koshelev and A. A. Golubov, Phys. Rev. Lett. 90, 177002 (2003); this calculation assumes that the two bands are in the dirty limit. However, qualitatively the same conclusions are reached when the two bands are in the clean limit (see, ref. 18).


90 Liu Min-Xia, Gan Zi-Zhao, Chinese Physics 16 826 (2007).


92 This is in qualitative agreement with the variation of $H_{c2}$ reported in polycrystalline Pt doped YNi$_2$B$_2$C samples; see G. Fuchs, K. H. Muller, J. Freudenberg, K. Nenkov, S. L. Drechsler, S. V. Sugla, D. Lipp, A. Gladun, T. Cichorek and P. Gegenwart, Pramana: J. Phys 58, 791(2002); G. Fuchs et al., Physica C 408, 107 (2004).

96 Li-Ping Zhou, Sheng Ju, and Zhen-Ya Li, J. Appl. Phys. 95, 8041 (2004).


