QUANTUM TRANSPORT IN
SUPERCONDUCTING, FERROMAGNETIC AND NORMAL NANOWIRES

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ABSTRACT

Electrons in superconductors condense to form pairs known as Cooper pairs [1]. The characteristic decay length of the wavefunction of this pair (or the “size” of a Cooper pair) is the superconducting coherence length $\xi$. When any of the 3 physical dimensions of a superconducting system become comparable to this characteristic length the effect of fluctuations become important and superconductivity is predicted to be destroyed [2]. In 1D systems (nanowires with diameter $< \xi$) the limit at which superconductivity is quenched and the mechanism by which it is quenched is an active field of study. Fluctuations and changes in boundary conditions lead to many novel phenomena in 1D nanowires. Experimental exploration of these novel effects forms the basis of this dissertation.

Metallic 1D nanowires have been fabricated using template-based electrodeposition and evaporation. Availability of nanowires of different morphologies helps in performing comparative experiments to isolate effects due to disorder from true 1D physics. The electronic transport properties of superconducting, ferromagnetic and normal nanowires with superconducting and normal electrodes have been studied in various measurement geometries.

Experiments on aluminum nanowires studying the counterintuitive anti-proximity effect (APE) [3] have been performed. The results of these experiments appear to bring a complete understanding of the phenomenon and have resolved a number of puzzles in the early experiments. In addition, measurements of a single resistance reading found switching from the superconducting to the normal state close to $T_c$ of the wire and at low temperatures in the APE regime. The switching at low temperature is triggered by individual quantum phase slips. These results indicate that the low temperature APE regime offers a clean platform for the observation of individual quantum phase slips, a goal eluded in numerous experiments.
Systematic studies on crystalline and granular ferromagnetic cobalt and nickel nanowires sandwiched between superconducting electrodes have been performed. A very long-range proximity effect (~ 600 nm) was found. This range is two orders of magnitude larger than that measured for bulk superconductor-ferromagnet systems. The superconducting transition was foreshadowed by a large peak in resistance dubbed the ‘critical peak’. Possible explanations of these counterintuitive effects have been discussed.

In earlier experiments on crystalline gold nanowires contacted with superconducting tungsten electrodes, a mini-gap state along with magnetoresistance oscillations indicating individual vortex trapping were found [4]. The experiment has been repeated here with different electrodes and different nanowire morphologies. The mini-gap state persists in these samples demonstrating it is a robust state independent of nanowire and electrode morphology.
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Many systems undergo ‘phase transitions’ in which they go from a less ordered state to a more ordered state as temperature or some other parameter of the system is changed. A prime example of this is freezing, in which the molecules of a liquid get greater order in space as they freeze into a solid. To describe such transitions, an order parameter for the system can be defined. The order parameter goes from zero in the disordered state to a non-zero value in the ordered state. For example, in a paramagnet (disordered) to ferromagnet (ordered) transition, the average magnetization of the system is the order parameter. The order parameter characterizing the transition from a resistive state to a superconducting state is slightly subtler.

When a material transitions from a normal to a superconducting state, electrons with opposite spins pair up \[1\]. The pair is called a ‘Cooper pair’. Once part of a Cooper pair, the two electrons can be described by a single quantum mechanical wave function \( \psi = |\psi| e^{i\phi} \). The spatial extent of this wavefunction is known as the coherence length (\( \xi \)) and the order parameter associated with superconductivity is given by \( \Delta = \psi^* \psi \). \( \Delta \) is non-zero in the superconducting state. This state, characterized by the complete absence of resistance to the flow of electricity and complete expulsion of magnetic fields, is an example of quantum mechanics on a macroscopic scale. If the superconducting state is made possible by electrons ‘holding hands’ to form Cooper pairs, what happens to the superconductivity when one or more dimensions of the sample are smaller than the size of a Cooper pair (\( \xi \))? Do the Cooper pairs break up and is superconductivity
destroyed in these quasi 2D, 1D or 0D systems? This question can be rephrased in the language of phase transitions to ask what happens to this long range ordered state (superconductivity) when the dimensions of the system are lowered. According to the Mermin-Wagner theorem [2], no long range order is possible systems of 2 or less dimensions. In these systems therefore, fluctuations should destroy the superconducting state.

Fortunately, this conclusion turns out to be somewhat premature. In the case of 2D systems (1 dimension < \( \xi \)), for example, the Berezinskii-Kosterlitz-Thouless (BKT) transition occurs [5,6] and a superconducting state is known to be possible. The question then reduces to whether the superconducting state can survive in quasi 1D systems also (2 dimensions < \( \xi \)). The answer to this question is of both fundamental interest and practical importance. On one hand, with the miniaturization of circuitry (there are already nanoscale transistors on computer chips) new horizons for applications of superconducting nanocircuits are opening up. On the other hand superconductivity in nanoscale systems can behave entirely differently from bulk systems, revealing a plethora of novel physics.

One little known aspect of superconductivity in nanoscale systems is the large role environmental factors, like the electrodes used for measurement, play. The goal of our research is to explore quantum transport (viz. superconductivity) in quasi 1D (diameter < \( \xi \)) nanowires with a focus towards the effect of the measurement electrodes. We have conducted experiments on superconducting, ferromagnetic and normal nanowires with superconducting and normal electrodes. In this chapter we briefly review the theoretical foundations for superconductivity and discuss the aspects of it important to our experiments. Since a lot of the theory of superconductivity is phenomenological, we will reference past experiments that have helped to shape this theory wherever necessary.
1.1 Theoretical Foundations

After the discovery of superconductivity in mercury by Kammerlingh Onnes in 1911, the first phenomenological theory to be widely accepted was given in 1935 by Fritz and Heinz London [7]. Many theoretical constructs and experimental evidences of the existence of an energy gap ($\Delta$) and a coherence length ($\xi$) existed at this time. However, a microscopic theory to understand the phenomena related to superconductivity remained lacking. The Bardeen Cooper Schrieffer (BCS) theory of superconductivity, discussed in section 1.1.1 [1], filled this gap. The BCS theory is however, difficult to work out for systems with non-homogeneity, which make up most real world systems of interest. These systems can be analyzed using the Ginzburg Landau (GL) theory, which though lacking microscopic foundations, is extremely intuitive and insightful. This theory is discussed briefly in section 1.1.2.

1.1.1 Bardeen Cooper Schrieffer Theory

The BCS Theory revolutionized the understanding of superconductivity by providing a microscopic approach to understanding and predicting measurable quantities like the superconducting energy gap. We will briefly overview the salient points of the theory here that allow us to understand concepts like $\xi$ and $\Delta$. More detailed descriptions and calculations can be found in reference [8].

The basic idea of the theory is that even a weak attraction ($V$) can bind pairs of electrons into a set called a ‘Cooper Pair’. For classic (non-high $T_c$) superconductors this attraction is provided by the electron-phonon interaction and leads to the existence of a state in which electrons that are paired have lower energy than the Fermi sea. This makes the Fermi sea unstable
against the formation of a Cooper pair and the electrons condense in pairs till an equilibrium point is reached. This point is reached when the state of the system is so greatly changed from the Fermi sea that the binding energy for an additional pair is zero.

Since we expect the lowest-energy state to have zero total momentum, the two electrons making up the Cooper pair must have equal and opposite momenta. Also, the total wavefunction of the Cooper pair including the space and the spin parts must be antisymmetric. We expect the space part to have a co-sinusoidal dependence on \((r_1 - r_2)\) where \(r_1\) and \(r_2\) are the locations of the two electrons because this dependence will give larger probability amplitude for \((r_1 - r_2) \rightarrow 0\) (i.e. electrons to be near each other). Therefore we take the spin part to be singlet (s-wave - |↑↓ - ↓↑\rangle) with electron spins pointing in opposite directions. It is important to note that choice of space and spin wavefunctions is not necessary although it does describe most classic superconductors like Zn, Al, Sn, Pb etc. The BCS pairing model is not inimical to p-wave (triplet) or d-wave pairing. In fact, the model may also be adaptable to systems in which electron-phonon interactions are not the basis of the attractive potential between the electrons. In our studies, with the possible exception of the ferromagnet-superconductor proximity effects, we assume classic s-wave superconductors and will therefore limit the following discussion to this case with the understanding that this is not the only possibility.

The wave function for this ground state is most easily expressed in the language of second quantization. A creation operator \(c_{k\uparrow}^*\) when acting on a state with a vacancy in the \(k,\uparrow\) state creates an electron there. If it acts on a state with the \(k,\uparrow\) state full, it gives 0. If the probability of a pair existing in momentum state ‘k’ is \(|v_k|^2\) and the probability of momentum state being without a pair is \(|u_k|^2\), the BCS ground state wavefunction can be written as:
\[ |\psi_G\rangle = \prod_k (u_k + v_k c_{k\uparrow}^\dagger c_{k\downarrow}^\dagger) |\varphi_0\rangle \] (1)

where, \( |\varphi_0\rangle \) is the vacuum state with no particles present. To make the wavefunction more explicit, we want to find appropriate values for \( u_k \) and \( v_k \). This is done by writing down the pairing Hamiltonian as:

\[ H = \sum_{k,\sigma} \xi_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k,l} V_{kl} c_{k\uparrow}^\dagger c_{l\downarrow}^\dagger c_{-l\uparrow} c_{-k\downarrow} \] (2)

where, \( \xi_k \) is the single particle energy relative to the Fermi sea and \( V_{kl} \) is the interaction potential. \( V_{kl} \) is taken to be \(-V\) if \(|\xi_k|\) and \(|\xi_l| < \hbar\omega_C\) (where \( \omega_C \) is a cutoff frequency of the order of the Debye frequency) and 0 otherwise. This just means that only electrons within \( \hbar\omega_C \) of the Fermi level contribute to pair formation. On applying the variational approach one can obtain:

\[ u_k = \sin \theta_k, v_k = \cos \theta_k \] (3)

\[ \Delta = -\frac{V}{2} \sum_l \sin 2\theta_l \] (4)

\[ E_k = (\Delta^2 + \xi_k^2) \] (5)

\[ \tan 2\theta_k = -\frac{\Delta}{\xi_k} \] (6)

\( E_k \) can be shown to be the excitation energy of a quasi-particle of momentum \( \hbar k \) which makes \( \Delta \) the minimum excitation energy or energy gap. This energy gap also comes up in the GL theory where it plays the part of the order parameter. From (6) and (4) we obtain the self-consistency condition:

\[ 5 \]
upon further simplifications and conversions of the summations to integrals one obtains:

\[ \Delta = 2 \hbar \omega_c e^{-1/N(0)/\nu} \]

(8)

\[ \nu_k^2 = \frac{1}{2} \left( 1 - \frac{\xi_k}{E_k} \right) \]

(9a)

\[ u_k^2 = \frac{1}{2} \left( 1 + \frac{\xi_k}{E_k} \right) \]

(9b)

N(0) here is the density of single electron states at the Fermi level. The calculations so far have been done at 0 temperature. To link the calculated quantities to physically measurable quantities we have to translate this to a finite temperature calculation. Since \( E_k \) has been identified as the excitation energy of a fermion quasi-particle, the probability that it is excited in thermal equilibrium is the Fermi function \( f(E_k) = (e^{\beta E_k} + 1)^{-1} \) (\( \beta = 1/k_B T \), where \( k_B = \text{Boltzmann constant} \) and the self-consistency condition (7) is modified to:

\[ 1 = \frac{V}{2} \sum_k \frac{1}{E_k} \]

(7)

\[ 1 = \frac{V}{2} \sum_k \frac{\tanh(\frac{\beta E_k/2}{\nu})}{E_k} \]

(10)

Simplifying this in a manner similar to equation (7) and comparing the result with (8), one obtains:

\[ \frac{\Delta(0)}{k_B T_c} = 1.764 \]

(10)
The superconducting gap that has emerged from the theory and is a measurable quantity is therefore linked to the critical temperature $T_c$ which is also a measurable quantity. Any source of energy that can allow pairs to cross this gap can destroy superconductivity. Other than temperature, such energy can be provided by a magnetic field, leading to a critical field ($H_c$) or a current leading to a critical current ($I_c$).

A second concept we can understand from this calculation is that of the coherence length. If $\xi_0$ is the characteristic size of a Cooper pair (coherence length at $T = 0$ K) and $\Delta$ is the characteristic energy determining the range of values involved in forming the Cooper pairs, from Heisenberg uncertainty principle we know that $\xi_0 \frac{\Delta}{v_F} \sim \hbar$ where $v_F$ is the Fermi velocity. In conjunction with (10), this gives us an expectation of a characteristic size of $\xi_0 \sim \frac{\hbar v_F}{k_B T_c}$. In addition to this, the BCS model can be used to understand the electron tunneling and how tunneling experiments can measure the superconducting gap, transition probabilities for quasiparticle excitations and electrodynamic effects like magnetic penetration depths ($\lambda$).

1.1.2 Ginzburg Landau Theory

The Ginzburg Landau (GL) Theory [9] offers a way of treating the macroscopic behavior of superconductors in which the overall free energy is important instead of the microscopic details. Although phenomenological in origins, it is derivable as a rigorous limiting case of the microscopic theory [10]. The value of the theory lies in its capability of dealing with many interesting systems like those with spatial inhomogeneity.

In this theory, a pseudo-wavefunction $\psi(r)$ is introduced as a complex order parameter. $|\psi(r)|^2$ represents the local density of superconducting electrons. The theory is developed by
expanding the free energy density \( f \) in powers of \(|\psi|^2\) and \(|\nabla \psi|^2\) and then minimizing \( f \) using a 

variational method. Since the higher order terms are ignored in the expansion of the free energy, the GL theory is only valid provided (1) the system is sufficiently near the critical temperature \( T_c \) so that \(|\psi|^2\) is small and (2) the spatial variations of \( \psi \) and the applied field are not too rapid. The expansion of \( f \) is given by:

\[
f = f_{n0} + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m^*} \left( \frac{\hbar}{i} \nabla - \frac{e^*}{c} A \right) |\psi|^2 + \frac{\hbar^2}{8\pi} \tag{11}
\]

here, \( f_{n0} \) is the free energy of the normal state, \( \alpha \) and \( \beta \) are parameters of the theory, \( m^* \) and \( e^* \) are the effective mass and effective charge of the particles making up the system (since the particles are Cooper pairs, \( e^* = 2e \) and \( m^* = 2m \) can be chosen), \( A \) is the vector potential and \( h \) is the effective field in the system. In the absence of fields and gradients, only the first three terms remain. By differentiating equation 11 with respect to \(|\psi|^2\) one obtains:

\[
|\psi|^2 = 0 \text{ or } |\psi|^2 = -\frac{\alpha}{\beta} \tag{12}
\]

since \( \beta \) has to be positive (else the minimum \( f \) will be obtained at \(|\psi|^2 = \infty\)), the first solution is chosen when \( \alpha \) is positive and the second, non-zero one when \( \alpha \) becomes negative (it can be seen that this solution gives lower \( f \) by substitution into equation 11). By definition \( T_c \) is the highest temperature at which \(|\psi|^2\) becomes non-zero therefore \( \alpha \propto (T - T_c) \).

Substituting \( \psi = |\psi|e^{i\varphi} \) into equation 11 and making comparisons with the London equations \( \alpha \) and \( \beta \) can be related to measureable quantities like the critical field \( (H_c) \) and the
penetration depth ($\lambda$) (page 116, [8]). A differentiation of equation 11 with respect to $\psi$ leads to the GL differential equations:

$$\alpha \psi + \beta |\psi|^2 \psi + \frac{1}{2m^*} \left( \frac{\hbar}{i} \nabla - \frac{e^*}{c} A \right)^2 \psi = 0$$  

(13a)

$$J = e^* |\psi|^2 \left[ \frac{1}{m^*} \left( \hbar \nabla \varphi - \frac{e^*}{c} A \right) \right] = e^* |\psi|^2 v_s$$  

(13b)

The identification of $v_s$, the supercurrent velocity is made here. If the absence of fields ($A = 0$) we can take $\psi$ to be real since all the coefficients of equation 13a are real. Introducing a normalized wavefunction $f = \frac{\psi}{\psi_\infty}$ (where $\psi_\infty$ is the solution to the GL equation in the absence of fields and gradients given in equation 12):

$$\frac{\hbar^2}{2m^* |\alpha|} \frac{d^2 f}{dx^2} + f - f^3 = 0$$  

(14)

from this it is natural to set a natural length scale for variations of $\psi$ as:

$$\xi^2 (T) = \frac{\hbar^2}{2m^* |\alpha(T)|}$$  

(15)

As the relation of $\alpha$ to the measureable parameters of the system has already been established, $\xi (T)$ can now be expressed in terms of these parameters too. Finally, these parameters are related to the coherence length $\xi_0$ of the BCS theory discussed in the last paragraph of section 1.1.1. Therefore, $\xi (T)$ can be shown to be related to $\xi_0$ by (page 119, [8]):

$$\xi (T) = 0.74 \frac{\xi_0}{(1 - T/T_c)^{\frac{1}{2}}} \text{ pure limit}$$  

(16a)
where \( l \) is the mean free path and pure superconductors are those for which \( \xi_0 < l \) and dirty superconductors are those for which \( \xi_0 > l \). For quasi 1d nanowires (diameter \( d < \xi_0 \)), the mean free path is limited by the diameter \( l \sim d \). Therefore, they naturally fall into the category of dirty superconductors and we shall use equation 16b for our calculations.

A magnetic penetration depth \((\lambda)\) that gives the distance a magnetic field remains non zero inside a superconductor can be calculated from the BCS theory. The ratio of this penetration depth to the characteristic coherence length defines the important dimensionless GL parameter \( \kappa = \frac{\lambda}{\xi} \). For dirty superconductors, \( \xi \) can be much smaller than its bulk value leading to a large \( \kappa \).

Since \( \kappa = \frac{1}{\sqrt{2}} \) separates superconductors of type I and II, our samples that are dirty superconductors with \( \kappa \gg 1 \) act as type II superconductors as far as penetration of magnetic fields is concerned.

### 1.2 The Loss of Superconductivity

One of the signature properties of a superconductor is the Meissner Effect [11] in which electromagnetic fields are screened from the interior of a bulk superconductor in a characteristic penetration depth \( \lambda \). The Meissner Effect also implies that superconductivity will be destroyed by a critical magnetic field \( H_c \) that is related to the free energy difference between the normal and the superconducting state in zero field – the condensation energy of the superconducting state:

\[
\frac{H_c^2}{8\pi} = f_n - f_s
\]
An applied current above a critical value $I_c$ can also destroy superconductivity as is apparent from equation 13b. In the following sections we discuss some of the implications of these properties of a superconductor.

1.2.1 Magnetic Fields, Fluxoid Quantization and Vortices

$H_c$ is the critical field below which the entire sample is superconducting. However, a second field $H_{c2}$ can be defined as the highest field at which superconductivity can nucleate in the interior of a large sample in a decreasing external field. The GL theory yields the following expressions for $H_{c2}$:

$$H_{c2} = \frac{\phi_0}{2\pi\xi^2} = \sqrt{2} \kappa H_c$$  \hspace{1cm} (18)

For bulk type I superconductors, $H_c > H_{c2}$ and on reduction of field the sample goes to the superconducting state in a discontinuous transition. For type II superconductors however, the superconductivity sets in a second order phase transition at $H_{c2}$ with regions becoming superconducting while others are normal with a magnetic field passing through them. Let us think of such a material: mostly superconducting with some normal regions in the presence of a magnetic field. The fluxoid ($\varphi'$) associated with each normal region is given by:

$$\varphi' = \varphi + \int h \cdot da$$  \hspace{1cm} (19)

Where $\varphi$ is the flux due to the applied field and the second term is the flux due to the field generated by the screening supercurrents that are set up to expel the applied field from the superconducting regions. $\varphi'$ is 0 for any path including only superconducting material because for
such a path the applied field and the generated fields are equal. This means that \( \varphi' \) has the same value for any path around a given normal region. In fact, theoretical considerations (page 127, [8]) restrict the values of \( \varphi' \) to a discrete set of integer multiples of \( \varphi_0 = \frac{hc}{2e} \).

This analysis is the basis for the Little-Parks Effect which causes periodic magnetoresistance oscillations in parallel field in a hollow superconducting cylinder [12]. Consider a thin walled cylinder of radius \( R \) with a field \( H \) applied parallel to its axis. In equation 19, \( h \) can be written in terms of the supercurrent \( J_s \) using London equation which can further be written in terms of \( v_s \) using equation 13b to obtain:

\[
v_s = \frac{h}{m^* R} \left(n - \frac{\varphi}{\varphi_0}\right)
\]

(20)

Here, \( n \) is an integer. This relationship implies that the kinetic energy of the cooper pairs is periodic with flux leading to the free energy of the superconducting phase being periodic with the flux. The free energy of the normal phase is independent of flux therefore yielding a \( T_c \) that is periodic with flux. The actual experiment measures the periodic variation of the resistance of the film with changing \( H \). Since the derivation is based on the GL theory, which is valid only near \( T_c \), the effect should be seen near \( T_c \). The Little-Parks effect is discussed in context of our experimental data in sections 4.3.3 and 4.4. The relation in equation 20 also implies an applied magnetic flux in a doubly connected superconductor can be used to control the superfluid velocity. This principle has been used to demonstrate destruction of superconductivity around half-integer flux quanta in ultrathin Al and Au\(_{0.7}\)In\(_{0.3}\) cylinders [13].

The fluxoid quantization is not limited to superconductors with a hollow cylindrical geometry. As discussed earlier, any normal region within a superconductor must have a quantized value of the fluxoid \( \varphi' \). For the case of nanowires, the width and the thickness of the sample are
both very small compared to the penetration depth $\lambda$ of the field. The screening effect of the superconductor is therefore negligible and distinction need not be made between the applied field and the effective field. The fluxoid quantization and flux quantization are therefore interchangeable concepts in this regime. A normal region within a superconductor carrying a quantum of flux is known as a vortex. Within a vortex, the magnetic field equals the applied field and falls off at a distance $\lambda$. The superconducting order parameter $|\psi|$ is 0 at the center of the vortex and regains its normal value $|\psi_\infty|$ within a distance $\xi$ of the center. The size of the normal region caused by vortex penetration is therefore approximately of radius $\xi$. The free energy per unit length of a vortex is given by:

$$\epsilon = \frac{H^2}{8\pi} (\pi \xi^2) 4\ln\kappa \quad (21)$$

This is approximately equal to the condensation energy lost in the core. The screening supercurrent and any externally applied current exert force on a vortex line according to the Lorentz force equation. This force per unit length is given by:

$$f = J \times \frac{\Phi_0}{c} \quad (22)$$

because of this force, the vortex lines move transverse to the current with some velocity $v$ and induce an electric field of magnitude:

$$E = \phi_0 \times \frac{v}{c} \quad (23)$$
which is parallel to \( J \). This acts like a resistive voltage and power is dissipated destroying the zero-resistance state. We go back now to considering a hollow superconducting cylinder as discussed in the Little-Parks case. A field \( B \) is applied in the interior of the cylinder and turned off and a supercurrent \( J \) flows in the superconductor to keep the field trapped within it. If \( \mathbf{r} \) is taken to point radially and \( \mathbf{z} \) axially, the induced emf around the ring in the direction of the current is given by:

\[
V = -\frac{1}{c} \frac{d\varphi}{dt} = -\frac{\Phi_0}{c} \frac{dn}{dt}
\]  \hspace{1cm} (24)

where \( \varphi \) has been expressed in terms of the flux quantum and \( \frac{dn}{dt} \) is the rate at which vortices leak out or the rate at which the fluxoid quantum number of the circuit is decreasing. The integrated phase change of \( |\psi|e^{i\varphi} \) around a path through the cylinder \( \Delta \varphi = \oint \mathbf{A} \cdot d\mathbf{s} = 2\pi n \) where \( n \) is the fluxoid number. Substituting this in equation 24 we obtain:

\[
2eV = h \frac{d\Delta \varphi}{dt}
\]  \hspace{1cm} (25)

This is one form of the Josephson frequency relation which will be further explored in the next section. A voltage \( V \) is induced around the ring each time a vortex containing a flux quantum passes across it. An important thing to remember in this case is that the motion of the vortex is important for inducing this voltage. The resistive state of a thin superconducting film with width larger than magnetic penetration depth \( \lambda \) results from movement of vortices due to transport current. The velocity of the vortices is determined by the balance of the Lorentz force produced by the current and the viscous force due to pinning centers in the material. On the other hand, the resistive state of narrow superconducting channel with widths below the length \( \xi \) is one-dimensional in nature and results from the creation of phase slip centers [14]. Structures with
intermediate widths have dynamics involving both vortex motion and phase slip lines. A vortex with infinite velocity in such a superconductor will correspond to a phase slip line. In the 1D regime relevant to this study a phase slip can be viewed as a vortex, with its normal core, passing across the wire [15]. Phase slip events are discussed in more detail in the next section.

1.2.1 Josephson Effect and Phase Slips

A Josephson Junction (JJ) [16,17] is made up of two superconducting electrodes separated by a thin (L < \(\xi\)) “weak link”. The weak link may be an insulating layer or a normal metal layer or a short, narrow constriction in otherwise continuous superconducting material. These three cases are referred to as S-I-S, S-N-S or S-c-S junctions. The bulk electrodes on both sides have a well-defined phase of the superconducting wave function and both wave functions leak into the weak link. There is a phase difference \(\Delta \phi\) between the two electrodes and Josephson made the prediction that a zero voltage supercurrent \(I_s = I_c \sin(\Delta \phi)\) should flow across the weak link.

Suppose the phase difference between the two electrodes is cranked up in some way (for example by applying a DC current - from equation 13b, \(J \propto \nabla \phi\)), the phase within the weak link winds tighter. The increasing of the current corresponds to increasing the supercurrent velocity \(v_s\) in equation 13b. But, we know there is a critical current/critical velocity \(v_c\) beyond which the superconducting state breaks down. Thus, this picture must break down when \(v_s\) reaches \(v_c\) if not before. This happens via a process known as phase slip [18,19].
In a phase slip event the local amplitude of the superconducting order parameter (\(|\psi|\)) goes to zero at some point in the weak link (figure 1-1). At this point the phase becomes ill defined for a small amount of time. When the amplitude recovers, the phase takes on a value such that \(\nabla \varphi\) is changed from the earlier value by \(2\pi\). Each time a phase slip occurs, the order parameter spiral (figure 1-1) representing the supercurrent unwinds. The unwinding of the spiral corresponds to dissipation of the supercurrent in the weak link given by the Josephson relation:

\[
\frac{d\Delta \varphi}{dt} = \frac{2eV}{\hbar}
\]  

(26)

Every time a phase slip event occurs, a finite voltage and hence a finite resistance appears across the weak link. Since going through a phase slip changes the phase of the superconducting order parameter by \(2\pi\), same as the phase change in going through a vortex, a phase slip can be viewed as a vortex with its normal core passing through the weak link.

Figure 1-1: The phase slip process in a weak link or a 1D superconductor. The plots represent the superconducting order parameter within the weak link. The x direction is along the length of the weak link and bulk superconductors fix the phase at either end.
A physical JJ can be modeled as an ideal one shunted by a resistance $R$ and a capacitance $C$. The equation for evolution of phase in this JJ can be written as:

$$
\left(\frac{\hbar}{2e}\right)^2 C \frac{d^2 \varphi}{dt^2} + \left(\frac{\hbar}{2e}\right)^3 \sqrt{\frac{C}{L_c}} \frac{d \varphi}{dt} = \frac{\hbar}{2e} (I - I_c \sin \varphi)
$$

(27)

where $C$ is the shunting capacitance, $I_{c0}$ is the critical current, $Q$ is the “quality factor” given by $Q = \sqrt{\frac{2eI_{c0}C}{\hbar}} R$ and $R$ is the shunting resistance. The equation is the same as the equation for motion of a particle of mass $\left(\frac{\hbar}{2e}\right)^2 C$ moving along the $\varphi$ axis in an effective potential $U(y) = -\frac{\hbar}{2e} (I_{c0} \cos \varphi - I \varphi)$ and subjected to a damping $\left(\frac{\hbar}{2e}\right)^2 \frac{1}{R} \frac{d \varphi}{dt}$. This is a particle sliding down a tilted washboard potential (figure 1-2) which is commonly used to model JJ. Depending on the value of the factor $Q$, the junction can be overdamped ($Q << 1$) or underdamped ($Q > 1$). In an underdamped junction, small fluctuations can cause the particle to start sliding down the potential...
at a terminal velocity never retrapping. Thus in an upward current sweep searching for the critical
current, the system can acquire a finite resistance (corresponding to the velocity of the particle
sliding down) at currents lower than \( I_{c0} \). This leads to a reduction in the observed \( I_c \) from \( I_{c0} \). This
also leads to hysteresis as the current needs to be reduced to an \( I_r \) even lower than \( I_c \) to retrap the
particle. In an overdamped junction however, the hysteresis is not expected. The physics of JJ is a
well-developed and much studied field. Let us go on to see how the concepts used for
understanding JJs are relevant in the case of superconducting nanowires which are a constriction
between two superconducting bulk electrodes but typically have the condition of \( L \gg \xi \).

In reference [20] a nanowire of finite length is considered as a circuit element with the
rest of the circuit modeled as a resistor parallel to the nanowire and the entire setup is connected
to a current source (voltage source in series with a resistor much larger than the parallel resistor).
It is found that the low energy physics of the nanowire closely resembles that of a JJ.
Reference [21] goes further to show that the Hamiltonian of a superconducting nanowire and a JJ
are exactly dual to each other with respect to the exchange of the canonically conjugated quantum
variables, phase and charge. A voltage biased JJ is found to be equivalent to a current biased
nanowire and a current biased JJ is found to be equivalent to a voltage biased nanowire. The
nanowire Hamiltonian transforms into the JJ Hamiltonian with the following parameters:

\[
\frac{2eV_c}{2\pi} \rightarrow \frac{hI_{c0}}{2e}, \quad \frac{\phi_0^2}{2L} \rightarrow \frac{(2e)^2}{2c}; \quad I \leftrightarrow \frac{V}{R_q}; \quad Y(\omega) \leftrightarrow \frac{Z(\omega)}{R_q}. \]

For our particular measurement geometry, \( V_c \) is the critical voltage of the nanowire, \( L \) is the inductance effectively in parallel with the nanowire, \( I \)
is the applied current and \( Y(\omega) \) is the frequency dependent admittance in parallel with the
nanowire. For the corresponding JJ, \( I_{c0} \) is the critical current, \( C \) is the capacitance in series with
the JJ, \( V \) is the applied voltage and \( Z(\omega) \) is the frequency dependent impedance in series with the
JJ. In particular, the resistance in series with the nanowire in the measurement geometry, on
modeling as a JJ transforms to a resistance that shunts the JJ. For nanowires the inductance $L$ is small leading to a small $C$ in the corresponding JJ. This means $Q \ll 1$ (defined after equation 27) implying that the case of a superconducting nanowire corresponds to that of an overdamped JJ. Now that the relationship between a finite length superconducting nanowire and the JJ is established, we go back to discussing phase slips in either of these systems.

### 1.2.3 Activation of Phase Slips

![Figure 1-3](image)

Figure 1-3: A representation of the (a) thermally activated phase slip where thermal energy allows the system to go over the energy barrier separating two energy minima in the washboard potential, (b) quantum phase slips that allow the system to tunnel from one superconducting state to the other even at low temperatures. The two superconducting states in question have the phase difference between the two ends of the superconductor ($\Delta \phi$) different by $2\pi$.

Different energy minima in the washboard potential for the JJ correspond to different phases. A phase slip corresponds to the system going from one energy minima to another. In order to do this, the system can use energy provided by thermal fluctuations and go over the
barrier (figure 1-3(a)). This process is known as a thermally activated phase slip (TAPS) and is found to be significant only close to $T_c$. The system can also tunnel through the barrier (figure 1-3(b)). This process is known as a quantum phase slip (QPS) and persists all the way to low temperature.

Thermal phase slips were first theoretically discussed by Langer, Ambegaokar, McCumber and Halperin (LAMH) in terms of a thermally activated process in the presence of a weak current [18,19]. The path through function space between two uniform solutions with different number of turns of the phase with the lowest free energy barrier was found. The value of this barrier was found to be:

$$
\Delta F = \frac{8\sqrt{2}}{3} \frac{H_c^2}{8\pi A^2} \xi
$$

(28)

where $A$ is the cross-sectional area of the conductor. This is very plausible since it is of the order of the condensation energy in length $\xi$ of the conductor. The current through the wire tilts the washboard (figure 1-2) and makes the jumps in one direction more probable than the other. The changed barrier heights $\Delta F_+$ and $\Delta F_-$ are different by an amount $\delta F = \hbar l/2e$. Including an attempt frequency as a prefactor $\Omega$, the mean net phase slip rate is:

$$
\frac{d\varphi}{dt} = \Gamma_{TAPS} = \Gamma_+ - \Gamma_- = \Omega \left[ \exp \left( -\frac{\Delta F_0 - \frac{\delta F}{2}}{k_B T} \right) - \exp \left( -\frac{\Delta F_0 + \frac{\delta F}{2}}{k_B T} \right) \right]
$$

(29)

at low currents the expression for resistance becomes:

$$
R = \frac{\pi \hbar^2 \Omega}{2e^2 k_B T} e^{-\frac{\Delta F_0}{k_B T}} e^{\frac{\Delta F_0}{k_B T}}
$$

(30)
The value of the prefactor $\Omega$ was found by McCumber and Halperin by using the time-dependent GL theory to be:

$$\Omega = \frac{L}{\xi(T)} \left( \frac{\Delta F_0}{k_B T} \right)^{1/2} \frac{1}{\tau_{GL}},$$  

(31)

where $\tau_{GL} = 8k_B(T_c - T)/\pi\hbar$ and $\xi(T) = \xi_0 \sqrt{\frac{1 - \left(\frac{T}{T_c}\right)^4}{1 - \left(\frac{T}{T_c}\right)^2}}$.

In the case of large excitation currents, this formulation has to be modified somewhat. The prefactor $\Omega$ becomes different for $+$ and $-$ and the $+$ jumps are exponentially rarer than the $-$ jumps [22]. The following expressions are used for fitting data in these cases:

$$I_-(I, T) = \Omega_-(I, T) \left[ \exp \left( -\frac{\Delta F_-(I, T)}{k_B T} \right) \right]$$  

(32)

$$\Delta F_-(I, T) = C_1(T) \left( \frac{8}{3} \sqrt{2} \sqrt{1 - 3k^2} - 8k(1 - k^2) \tan^{-1} \frac{\sqrt{1 - 3k^2}}{\sqrt{2}k} \right)$$  

(33)

here $C_1$ is given by:

$$C_1(T) = \frac{3\sqrt{3}}{8} \frac{\hbar}{2e} I_c$$  

(34)

and $k$ is the solution to the equation:

$$\frac{I}{I_c(T)} = k(1 - k^2)$$  

(35)

the $I_c(T)$ is given by:
the prefactor $\Omega$ is calculated from $\Omega$ given in equation 31 using:

$$I_c(T) = 92\mu A \frac{LT_c}{R_n \xi_0} \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]^{3/2}$$  \hspace{1cm} (36)$$

This process can be used to calculate the phase slip rate. If the phase slip rate is known, the expected $I_c$ can be calculated using the reverse process as outlined in reference [23] along with the expression $\Delta F(I) = \Delta F(0) \left( 1 - \frac{I}{I_{cb}} \right)^{5/4}$ [24].

Many experiments confirming the existence of TAPS and their conformity to this form have been performed [25]. However, the resistance due to thermal phase slip is expected to die out within a few millikelvins of $T_c$. In an experiment by Giordano [26], a long resistive tail persisting to low temperatures was found. Giordano introduced a phenomenological model of phase slips by macroscopic tunneling which he called QPS. Whether the observation of Giordano was actually caused by QPS is disputed [27]. However, the possibility of such a phenomenon occurring is widely accepted and a number of experiments claiming to see QPS have been performed [15,28,29] even though the conclusions remain controversial. The form for phase slip rate due to QPS follows the form for TAPS except that the temperature $T$ in expressions 32 and 37 is replaced by an effective temperature $T_{\text{eff}}$ which can act as a fitting parameter. In this study $k_B T_{\text{eff}}$ is taken to be $\sim \hbar/\tau_{\text{GL}}$ following references [23,26].
1.3 The Effect of the Environment

The phenomenon of superconductivity affects and is affected by environmental factors like proximity to other materials. As long as the superconducting elements are macroscopic and the length and diameter can be assumed to be infinite, these effects may not be significant compared to the overall behavior of the system. However, with finite length and diameter, any modification of the boundary conditions can significantly alter the physics of the superconducting nanowire. Moreover, in any application, superconducting nanowires always have to be connected to external circuitry, which makes an understanding of these phenomena relevant. In this section we review Charge Imbalance and Andreev reflection that helps in understanding what happens to a current at a normal-superconductor (N-S) interface. With a good understanding of the Andreev Reflection process, we go on to discuss the Proximity effect that is very important for the experiments described in this dissertation. Finally we discuss the interaction between a superconductor and the environment it is coupled to in section 1.3.3.

1.3.1 Andreev Reflection and Charge Imbalance

When an electron from a normal metal seeks to enter a superconductor as part of a current flow across the N-S interface, it needs to find an empty energy level to go into in the superconductor. If the bias voltage is lower than $\Delta$, the electrons cannot enter the superconductor as quasiparticles as there are no available energy levels in the gap. Therefore, the current is converted directly into a supercurrent of Cooper pairs, consisting of two electrons of charge $e$ with opposite spin. This is accomplished by the reflection of a hole back into the normal metal. This process is known as Andreev Reflection [30]. Thus for Andreev reflection $2e$ is transferred.
across the interface giving a differential conductance twice that in the normal state. If the bias voltage \( V \) across the interface is higher than the superconducting gap \( \Delta \), electrons can pass from the metal into the superconductor as quasielectrons or holes, which relax into the Cooper-pair condensate over the charge imbalance length (\( \Lambda_Q \)).

If an electron-like or hole-like excitation is added to a superconductor a charge imbalance is created [31]. Charge imbalance is important because it creates a measurable steady state voltage in a superconductor and also because it provides a tool for measuring various electron relaxation rates. The total charge in the region of a superconductor using the BCS theory is given by:

\[
Q_{tot} = \frac{2}{V'} \sum_k \left[ u_k^2 f_k + v_k^2 (1 - f_{-k}) \right]
\]  

(38)

here \( V' \) is the volume of the superconductor and the other quantities have been discussed extensively in section 1.1.1. The quantity in square brackets is the probability that state \( k \) is occupied ad the factor of 2 is for the spin degeneracy. The first term is the product of the probability that the pair state \( (k, -k) \) is not occupied by a Cooper pair and the probability that the quasiparticle state \( k \) is occupied. The second term is the product of the probability that the pair state is filled and the quasiparticle state is empty. Equation 38 can be regarded as the sum of the superconducting fraction contribution:

\[
Q_s = \frac{2}{V'} \sum_k v_k^2
\]  

(39)
this is the definition of charge imbalance per unit volume. A quantitative understanding of charge imbalance stems from an experiment performed on a superconducting Sn film with tunneling injection of quasiparticles at voltage $V > \Delta$. The quasiparticle potential is sensed by a second normal metal film coupled via a normal tunnel junction to the superconducting film in the injection region [32]. Theoretically it was shown that the measured potential was related to the charge imbalance by [33]:

$$V = \frac{Q^*}{2eN(0)g_{NS}}$$

(41)

where $N(0)$ is the density of states for electrons of one spin and $g_{NS}$ is the measured normalized conductance of the normal probe junction. Since the quasiparticle injection rate $\dot{Q}^*_i$ is known, the quasiparticle relaxation time $\tau_Q$ can be calculated using:

$$\tau_Q^{-1} = \frac{\dot{Q}^*_i}{Q^*} = \frac{F^* I_i}{2N(0)e^2V'g_{NS}V}$$

(42)

the quantities $I_i$, $V'$, $g_{NS}$ and $V$ are measured in the experiment and $F^*$ is easily calculated as it is the factor that differentiates injection current $I_i$ from $\dot{Q}^*_i$. In a diffusive 1D NS junction with diffusion constant $D$ (as is the case of a superconductor around a phase slip center), the charge imbalance length can be defined as

$$\Lambda_Q = \sqrt{D\tau_Q}$$

(43)
and the diffusion constant is given by $D = \frac{1}{3} v_f l$ where $l$ is the mean free path that can be calculated from the resistivity of the sample using a constant value of $\rho l$ for a given metal. For aluminum the $\tau_Q$ was measured in a recent experiment [34] to be $\sim 5 \times 10^{-9}$ seconds. We have used a theoretical estimate for $\tau_Q$ for our fits following reference [35]. The concept of charge imbalance is relevant for our experiments because the length of our nanowires is $\sim \Lambda_Q$. Within a distance $\Lambda_Q$ from a phase slip center or from a normal electrode a quasiparticle current exists. Since the total current applied is constant for our measurements, this reduces the supercurrent in a significant length of the nanowire changing the physics of the system.

1.3.2 Proximity Effect

The proximity effect is the occurrence of superconducting-like properties in non-superconducting materials placed in electrical contact with a superconductor. In the 1960s, the propagation of superconductivity through an N-S interface was analyzed within the framework of the Ginzburg-Landau (GL) theory [36]. Since it derives from the GL theory, this treatment has the limitation of only being valid close to $T_c$. In the case of an N-S interface with an applied voltage an understanding of the proximity effect is provided by the Blonder-Klapwijk-Tinkham (BTK) theory [37]. In this theory, the barrier between the NS interface (either due to some oxide layer or because of different Fermi velocities associated with different metals) is modeled by introducing a delta function of strength $Z$ at the interface. The Bogoliubov equations are solved to find the probability of various outcomes for an electron of energy $E$ incident on the interface as a function of $Z$. However, this theory is only valid in the special case of ballistic electrons. As such, perhaps it could be applied to the proximity effect seen in crystalline Co and Au nanowires.
However, the range of the proximity effect seen in these cases is the same as that seen in polycrystalline/granular Ni/Co/Au nanowires. The polycrystalline nanowires as well as some crystalline nanowires have strong impurity scattering and are thought to be in the ‘dirty limit’. In this limit the electron motion is diffusive. Therefore, a different theoretical approach needs to be used in order to understand the proximity effect in our experimental system.

The case of large drops in resistance in diffusive wires in contact with superconductors can be understood from a unified point of view [5–7] based on the theory of “nonequilibrium superconductivity” [8]. Although in principle, this approach applies to mesoscopic superconductivity, it is typically very cumbersome. For a more practical approach quasiclassical techniques (Eilenberger equations) are used. In particular to analyze the proximity effect in the diffusive limit, the Usadel equations are commonly used. The Usadel equations are given in terms of a function from which all measurable quantities can be derived by summing over the Matsubara frequencies.

These equations are used to study the proximity-induced superconductivity in S-N interfaces. In a finite sized normal structure of thickness $d_N < \xi_S$ and length along the x axis placed next to an infinite superconductor a ‘mini-gap’ smaller than the superconducting gap but independent of x is predicted [38]. Such a gap is also found experimentally using scanning tunneling spectroscopy studies [39]. The gap magnitude is predicted to get smaller with increasing thickness $d_N$. The range of the proximity effect is predicted to be $\xi_N(T) = \left(\frac{\hbar D}{2\pi k_BT}\right)^{1/2}$ where D is the diffusion constant of the normal metal. In our experiments on AuNWs some of these theoretical predictions are verified via transport measurements.

The electron transfer mechanism is same in S-N and S-F systems. However, since ferromagnetism favors a parallel spin alignment, the injection of spin polarized electrons from S
into F will lead to a stronger pair-breaking effect than in the case of S-N structures. The exchange field of a ferromagnet can be thought of as an applied magnetic field. In the absence of the field, two electrons with opposite momenta $+k_F$ and $-k_F$ and opposite spins $\uparrow$ and $\downarrow$ form a Cooper pair. The resulting momentum of the Cooper pair is 0. In a magnetic field, because of Zeeman’s splitting, the Fermi momentum of the electron with spin $\uparrow$ shifts from $k_F$ to $k_1 = k_F + \delta k_F$ and with spin $\downarrow$ shifts from $-k_F$ to $k_2 = -k_F + \delta k_F$ where $\delta k_F = \mu_B H / v_F$ and $v_F$ is the Fermi velocity. Then, the resulting momentum of the Cooper pair will be $k_1 + k_2 = 2\delta k_F$. Using the generalized Ginzburg Landau functional a Cooper pair wavefunction that has an oscillatory decay within the ferromagnet is obtained [40] in analogy to the inhomogenous state predicted long ago by Fulde, Ferrell, Larkin and Ovchinnikov [41,42]. If the electron scattering mean free path is small, the Usadel equation can be used to yield a characteristic length scale within the ferromagnet of $\xi_f = \frac{D_f}{\sqrt{H}}$ where $D_f$ is the diffusion length in the ferromagnet and $H$ is the exchange field. However, several experiments on nanoscale S-F systems have reported proximity effect on length scale considerably longer than the theoretical value. It must be noted here that in the ballistic limit, this analysis is no longer valid. In reference [43], the Eilenberger equation in 1D (with boundary conditions of a bulk superconductor on either end) has been solved to show that in this regime, the superconducting wave function shows an oscillatory behavior with no damping. In our experiments we show that the long-range proximity effect persists in diffusive 1d ferromagnets and a different theoretical approach is needed to understand the phenomenon.
1.3.3 Coupling to a Dissipative Environment

In this section, we discuss the effect coupling to a dissipative environment has on quantum tunneling. A physical way of looking at it is that the system cannot do anything quantum mechanical while the environment is looking at it. For example if we take the “system” to be a quantum particle in a double well potential, and the external world to be made up of air molecules that intermittently bump into it. Since after the collision each air molecule possesses information about where it found the particle any quantum fluctuation must take place faster than the timescale of interactions with the environment and fluctuations slower than this are suppressed. Mathematically the problem is set up by the Caldeira Leggett model of quantum dissipation [44].

Caldeira and Leggett originally used their model to calculate the probability of tunneling in a double well. In an isolated system, the tunneling probability is given by the WKB approximation to be $P \sim e^{-\int \frac{\sqrt{V-E}}{\hbar} dx}$ where $V$ is the potential energy and $E$ is the energy of the particle. In the presence of an Ohmic dissipation characterized by $\eta$, the probability of tunneling becomes $P \sim e^{-\frac{A\sqrt{V-E} + B\eta a^2}{\hbar}}$ where $A$ and $B$ are dimensionless constants $\sim 1$, and $a$ is the potential barrier between the two potential minima ($V \sim (x^2-a^2)^2$). The tunneling is therefore suppressed by the presence of a dissipative environment. Any effect that suppresses tunneling between degenerate minima favors symmetry breaking. Although this analysis is done at zero temperature, the results can be extended to finite temperatures also.

Translated into terms of Josephson Junctions, the probability of tunneling through a double well potential becomes the probability of a QPS (section 1.2.1). The coupling to the dissipative environment is represented by a parameter $K = R_q/R_p$ where $R_q$ is the quantum resistance and $R_p$ is the shunt resistance in the RCSJ model. A strongly conducting shunt with $K$
> 1 relaxes the strain on the junction and suppresses the QPS, while a low conductance \( K < 1 \) leads to the proliferation of QPS. Having already seen the mapping between JJ and superconducting nanowires, it is easy to translate this to the case of a superconducting nanowire with normal or superconducting electrodes as has been done in reference [20]. This forms the theoretical basis for the anti-proximity effect that has been extensively discussed in this dissertation.
2 Experimental Procedure

2.1 Synthesis of Nanowires

Two methods of nanowire synthesis have been used for making the nanowires used in the experiments described in this dissertation:

1. template based electrodeposition
2. e-beam assisted evaporation on masks patterned using e-beam lithography

The first technique was used to yield single-crystal or polycrystalline nanowires (depending on various parameters) while the other was used to obtain granular nanowires. A detailed description of these techniques follows.

2.1.1 Template Based Electrodeposition

This method, when used for the synthesis of metallic nanowires, involves the electrodeposition of the metal into the pores of an inert, non-conductive porous membrane which acts as a template [45–47]. Track etched polycarbonate membrane (PCM), anodized alumina membrane (AAM) and other polymers, carbons and solids can be used as membranes for this process. In the experiments described here, PCM and AAM are the two porous membranes used.
(a) Templates

*Polycarbonate Membrane (PCM)*

The PCM, purchased commercially from it4ip, Belgium, is manufactured by irradiating polycarbonate films with energetic heavy ions. The irradiation leads to the formation of linear open channels perpendicular to the surface of the film and parallel to each other (with a dispersion of 17°). By appropriate wet-etching polycarbonate films with nanopores are fabricated. Figure 2-1 shows an SEM image of the membrane. The pore density is between $1.0 \times 10^4 - 1.0 \times 10^8$ per cm$^2$, but the pores are randomly distributed. The membranes come in pore diameter sizes of 30 nm and 50 nm and are 20 µm in thickness. The pore diameter determines the diameter of the nanowire and the membrane thickness determines the length of the nanowire. For other pore diameters, commercially manufactured PCM can be purchased from Structure Probe Inc., USA. These membranes are 6 µm thick and come in quoted pore diameters of 10 nm, 30 nm, 50 nm and 80 nm. The actual pore diameters, determined from the diameter of the nanowire formed within the pores are found to be 40 nm, 70 nm, 100 nm and 160 nm respectively. There are several advantages to using PCM for nanowire growth. PCM are flexible and resilient and therefore well suited for handling and electronic transport measurements involving squeezing of the membrane between electrodes. They are also easy to dissolve in an organic solvent to release the nanowires. On being dissolved they do not leave much residue, which yields cleaner single nanowire samples. One of the downsides to using PCM is that they are hydrophobic. Most solutions used for electrodeposition are aqueous and do not wet the membrane well leading to uneven deposition or deposition on the surface. The PCM are soluble in many organic solvents limiting their use in electrodepositions from non-aqueous electrolytes too. Finally, because of the
small width of the commercially available PCM membranes, the length of the resulting nanowires is small limiting the design of the electrodes to be patterned onto them. For these reasons, it is often feasible to use anodized alumina membranes.

Anodized Alumina Membranes (AAM)

Porous AAM are formed by anodization of high purity aluminum foils in an acidic electrolyte [48]. In comparison to the pores of the PCM, carefully synthesized AAM have well aligned pores with a very high pore density of $10^{11}$ pores/cm$^2$. Varying the parameters of the anodization process can control the diameter and density of the pores, as well as the thickness of the membrane. The steps involved in the synthesis of an AAM are shown in Figure 3-2.

A very high purity (99.999% pure) Al plate is purchased from either Aldrich or Alfa Aesar. The plate is 100 mm x 100 mm x 0.5 mm in dimensions. The surface of the plate, though smooth, is not smooth enough for direct anodization and two steps of polishing are required to prepare the plate. In the first step, the plate is mechanically polished by hand using a wet silicon carbide sand paper and washed with acetone, isopropyl alcohol and water. In the second step,
electrochemical polishing, an electrochemical cell using a freshly prepared solution of 60% by volume sulphuric acid and 40% by volume phosphoric acid is set up. The solution is heated to 75° – 80° C and uniform temperature is ensured by constant stirring with a magnetic bar. The mechanically polished Al plate is used as an anode and a Pb plate of area similar to the Al plate is used as the cathode. Both the plates are dipped in the solution, clamped in place and connected to a current source. The current is slowly ramped up and maintained at ~ 12 ± 2 A. It is essential to ramp up the current slowly and also to monitor the temperature to avoid pitting of the Al plate surface. If the temperature exceeds 80° C, the process is temporarily stopped and the solution is left to cool itself. The process is restarted when the desired temperature of the solution is reached. This electrochemical polishing is carried on for 30-40 minutes, till the plate surface is smooth and a visual inspection shows a haze free mirror-like finish. The Al plate is now ready for anodization.

Anodization is carried out in a cooled acid bath at temperatures close to 0° C. The glass beaker, containing the acid solution is cooled by immersion in an insulated box full of ice. A little cold water is also poured into the insulated box to ensure good thermal contact between the beaker and the surrounding ice. The anodization is only started once the solution temperature reaches 1-2° C. Uniform temperature is maintained by using a magnetic stirrer and temperature is continuously monitored. A stable and uniform temperature is necessary to prevent irregularities and pitting in the Al plate. The electrochemically polished Al plate is dipped in the solution and clamped in place to be used as an anode. A clean Pb plate, similar in area to the Al plate, is also dipped in the solution and clamped for use as the cathode. Both the plates are electrically contacted above the solution level using alligator clamps and connected to a DC voltage source. Since both sides of
the Al plate are exposed to the solution, the anodization occurs on both sides. The applied potential is then slowly ramped up to the desired value.

![Diagram](image)

**Figure 2-2**: Schematics of the procedure of synthesis of anodic alumina membrane. The figure is reproduced from Dissertation: Kumar, N. (2009) *Electrical Properties of Superconducting and Hybrid Superconductor-Ferromagnet Nanowires*, Pennsylvania State University.

The value of the applied potential plays an important role in pore structure and barrier layer width. Therefore, any sudden changes in potential can cause preferential anodization in one location and make lift off difficult. It can also result in boring a hole through the plate in one location rather than uniform anodization. It is therefore important that the ramping up of the potential be done very slowly with frequent pauses to allow the current to stabilize. Once the desired potential is reached, the current stabilizes and is found to change very little during the anodization process. The important parameters of the final membrane which are the pore diameter
and membrane thickness can be controlled by anodization parameters namely – the choice of the acid bath, the applied voltage and the time. In this study, the 50 nm pore size membranes have been prepared by anodization in a 6% by weight H$_2$SO$_4$ solution at a voltage of 20 V. The pore size can be made larger by increasing the anodization potential. The thickness of the membrane depends on the time of anodization. A 50 µm thick membrane is obtained by letting the process go on for ~ 24 hours. 70 nm pore size membranes have been prepared by anodization in a 0.3 M Oxalic acid solution at a voltage of 40 V. A 50 µm thick membrane is obtained by letting the process go on for ~ 18 hours. The anodization process is made up of two separate processes taking place simultaneously. The aluminum plate is oxidized to alumina in the presence of the acid and the electric field makes holes in the alumina to convert it to a porous matrix. There is always a ‘barrier layer’, which is alumina without pores between the bottom of the pores and the non-oxidized aluminum plate. The thickness of the barrier layer is usually between 10 – 100 nm depending on the anodizing potential (figure 2-2 (d)). This barrier layer is insulating and blocks the conduction path between the pores and the aluminum plate required for DC electrodeposition. After the required membrane thickness is achieved, the anodization process needs to be halted. A sudden reduction in potential at this stage makes separation of the membrane from the aluminum plate very difficult. Hence, the potential is decreased in logarithmically spaced steps of ~ 3 minutes in duration. The step-wise reduction in potential leads to a branching of the pores, thinning of the pore wall thickness and reduction in the barrier layer thickness (figure 2-2 (e)) [49–51]. For the ‘lift-off’ of the AAM membrane from the aluminum plate, the anodized aluminum plate is then soaked in a 20 % by volume sulphuric acid solution for 60 – 90 minutes. The acid etches the alumina. The etching is more in the region of the branched pores because of larger surface area exposed. As a result, the pores in the AAM are slightly enlarged and the
porous alumina membrane is detached from the underlying aluminum plate (figure 2-2 (f)). The detached AAM is thoroughly rinsed 3-4 times in water to get rid of residual acid and then washed in acetone and isopropanol (IPA). The remaining aluminum plate is left smooth and polished by the lift-off process and can be used for subsequent membrane synthesis without the mechanical and electrochemical polishing described earlier. The subsequent AAM membranes made from the same plate are also higher in quality than the first one. This might be because of higher smoothness as well as impressions of pore arrays left over from previous membranes. A single aluminum plate is good for the synthesis of several AAM membranes and can be used repeatedly till it becomes too thin and fragile to handle.

Figure 2-3: Scanning electron micrograph of transverse cross-section of a anodized aluminum oxide membrane (left) and longitudinal cross section of anodized aluminum oxide membrane (right). The figure is reproduced from M. Tian et al., APL 83, 1620 (2003).

The quality of the AAM membrane can be judged from visual inspection. Poor quality AAM membranes are cloudy, brittle and curl up on drying whereas good quality membranes are clear, relatively sturdy and do not curl up on drying. The pore sizes and properties are found by examination by a field emission scanning electron microscope (FESEM) Jeol 6700F. Figure 2-3
right panel shows a cross sectional view and left panel top view of an AAM membrane made with the process described above [48]. The nanopores are uniform in diameter, parallel to each other and ~ 25 nm in diameter.

As mentioned earlier, this process leads to AAM membranes ~ 50 µm in thickness. AAM membranes from 30 – 50 µm in thickness are sturdy enough to be lifted off and handled. Membranes thinner than 30 µm are too fragile to be used freestanding. To synthesize these membranes a slightly modified version of the technique described above is used to obtain thin AAM membranes supported by a silicon substrate [48].

PCM and AAM templates can be used to obtain various kinds of nanowires by electrochemical deposition [46,47,52–54] into the pores, chemical vapor deposition [55], electroless deposition [56,57], sol gel chemistry [52], sputtering and other techniques. The technique used for the experiments described in this dissertation is electrochemical deposition.

(b) Electrochemical Deposition

Template based Electrochemical Deposition is a widely used technique for nanowire synthesis. The technique has the advantages of being inexpensive, flexible and having high yield. Electrochemical Deposition or ‘electrodeposition’ involves the reduction of metallic cations from a solution onto a negatively charged ‘working’ electrode. A schematic of the setup for template based electrodeposition at constant voltage into the nanopores of a PCM/AAM membrane is shown in figure 2-4. The electrochemical cell consists of a working electrode, a counter electrode and a reference electrode (Ag/AgCl) connected to a potentiostat (Princeton Applied Research 263A). The potentiostat maintains a definite voltage between the reference and working electrodes by varying the current through the counter and working electrodes (figure 2-4). The
electrodeposition can also be done without the reference electrode in a two-electrode cell. The disadvantage of this is that the voltage at which the deposition occurs depends on the geometry of the cell. Finally, the electrodeposition can be done at constant current. The constant current setup also consists of just the counter and the working electrodes between which a current source is connected. In this study, a platinum wire is used as the counter electrode, an Ag/AgCl reference electrode is used and the working electrode is a thermally evaporated film of either silver or gold.

For electrodeposition to occur in any of the modes described above, a conducting working electrode is required. Since both the PCM and the AAM membranes are insulating, a layer of conducting metal is thermally evaporated on the back of the membranes before putting them in the electrochemical cell as shown in figure 2-4. In this study the conducting metal is composed of 3 layers – chromium, gold and silver. A thin layer (~ 10 nm) of chromium is evaporated onto the PCM/AAM membrane first to aid in adhesion of the following layers. This step is essential in case of the PCM membranes and optional for the AAM membranes as adhesion to AAM membranes is easier. After this, a 40-50 nm layer of gold is evaporated onto the membrane followed by a layer of silver. The thickness of the evaporated silver depends on the diameters of the nanopores on the membrane. As a rule of thumb, the thickness of the evaporated silver is made to be slightly greater than twice the diameter of the nanopore. This is done to ensure that the pores are completely blocked off by the evaporated metal. In the electrochemical cell, the metal ions ‘M’ with valency ‘n’ in the solution move to this evaporated metallic layer and get reduced to their metallic form as:

\[ M^{n+} + ne^- \rightarrow M \]  

(44)

This process leads to the deposition of metal into the nanopores of the PCM/AAM membrane.
Different electrolyte solutions can be used to deposit different nanowires. The details of the electrolyte compositions for the different nanowires are given in sections 3.2, 4.2 and 5.2. In addition to pure metallic nanowires, this technique can also be used to electrodeposist intermetallic nanowires [58] and axially modulated nanowires with subsequent segments of different metals like copper/cobalt [59,60]. The voltage of the electrodeposition and the size of the nanopore can be varied to change the crystallinity of the nanowire from single crystalline to granular [61,62].

To obtain freestanding electrochemically deposited nanowires, the evaporated metal on the back of the membranes is removed using either ethanol or HNO₃ depending on the nature of the nanowire. The membranes are then dissolved in a solvent that leaves the nanowires unaffected. PCM membranes are dissolved in CH₂Cl₂ and the dissolution is rapid. The AAM membranes on the other hand are dissolved in a 6% H₃PO₄, 1.8% CrO₃ (both by weight) solution heated to 60°C. The AAM may take upto 24 hours to dissolve completely. The more conventional choice of NaOH to dissolve the AAM membranes is not used because in the case of Al

Figure 2-4: Schematics of an electrochemical cell used for template based electrodeposition at constant potential.
nanowires, the NaOH dissolves away the oxide layer on the nanowire surface, creates a further oxidation layer and dissolves that, until finally the entire wire is dissolved away.

The nanowire suspension in CH$_2$Cl$_2$ or H$_3$PO$_4$/CrO$_3$ solution cannot directly be dispersed on the substrate since both these solvents will leave a residue on evaporation. To clean the wires and change the suspending solution from the solvents to isopropanol (IPA), the suspension is centrifuged. The nanowires are precipitated at the bottom of the centrifuging tube. The solvent is pipetted out and discarded and IPA is added to the tube. To disperse the nanowires in the IPA, the centrifuge tube is ultrasonicated for a few seconds. The process of centrifuging, dilution with IPA and ultrasonication is repeated 3-4 times till clean wires suspended in IPA are obtained.

2.1.2 E-beam Lithography

This method has the advantage of being more flexible than the template-based electrodeposition method in terms of nanowire diameter and the materials accessible. It is also more expensive and has lower number of nanowire yield. When the nanowire is evaporated with the help of an e-beam onto a mask created using e-beam lithography (EBL), as done in this study, it yields granular nanowires. However, the nanowire can potentially be deposited onto the mask with other methods like sputtering to yield single crystalline nanowires.

The steps of the lithography process (optical or e-beam) are shown in figure 2-5. The substrate (most often doped silicon coated with an insulating layer of silicon oxide or silicon nitride) is spin coated with a photo resist or e-beam resist. The choice of resist depends on the resolution required, spacing of features and thickness of metal to be evaporated post lithography. The resist is then baked for hardening. In case of optical lithography a hard mask with the required pattern made on it and in case of EBL a ‘soft’ mask drawn using computer software like
L-Edit is used. The areas within the pattern are exposed to either UV light for photolithography or an electron beam for EBL. The exposure time or beam-current used depends on the resolution required and the feature size. The exposure of the resist causes it to undergo a chemical reaction. The substrate is then soaked in a developer.

Figure 2-5: A schematic of the lithography process for making nanostructures (a) a layer of resist is spin-coated on the substrate, (b) the resist is exposed to either UV radiation in case of photolithography or an electron beam in case of electron-beam lithography through a mask which has the required pattern cut out from it, (c) the substrate with the resist is soaked in a developer which removes the parts of the resist that were exposed to radiation earlier (in case of positive resist) or parts that were not exposed to radiation earlier (in case of negative resist), (d) material is evaporated onto the substrate with the resist acting as a mask, (e) the substrate is soaked in a solvent that dissolves the remaining resist and also the layer of evaporated material on the resist. This ‘liftoff’ process only leaves behind the material evaporated directly on the substrate in step (d).

In case of positive resist (as depicted in figure 2-5), the parts of the resist exposed to the beam and chemically altered, are dissolved by the developer. For negative resist, the parts not exposed to the beam are dissolved away. The substrate is now left with resist everywhere except for places where the pattern should be. The required material is now evaporated on the substrate. This material fills the blanks left by the dissolved resist and also covers up the
remaining resist. The substrate is then taken for the ‘lift-off’ process where it is dipped in a solvent that dissolves away the remaining resist. The material covering the resist is stripped away with the resist, and only the material in the pattern remains on the substrate.

(a) Alignment Markers

Before the patterning of nanowires by e-beam lithography, it is necessary to pattern alignment markers onto the substrate so that the nanowires can be found for making electrical contacts onto. The alignment markers are made using optical lithography. A 300 µm thick lightly n(Sb)-doped silicon substrate is coated with a 150 nm thick silicon nitride film on both sides using low pressure chemical vapor deposition (CVD) technique. The substrate has to be slightly conducting to minimize charging during the lithography process or other processes like scanning electron microscopy. The insulating silicon nitride layer is necessary to electrically isolate the patterned nanowires and electrodes from the conducting substrate. The substrate is cleaned with acetone and IPA and resist Lor 2A is spin coated at 4000 rpm for 45 sec and baked at 170° C for 2 minutes. A second layer of resist 1813 is spin coated at 4000 rpm for 45 sec and baked at 110° C for 90 seconds (corresponds to figure 2-5(a)).
The hard mask for optical lithography is made of quartz coated with a chrome layer with the chrome layer etched away in the desired pattern to make a transparent pathway for light to travel through the mask. The process of making the mask is a separate optical lithography step. This mask is put 40 µm away from the substrate coated with the photoresist and the resist is exposed to UV light for 7 seconds (corresponds to figure 2-5(b)) using a Karl Suss aligner with a UV light source. The substrate is soaked in developer CD-26 for 45 seconds and washed with water (corresponds to figure 2-5(c)). A 35 nm thick layer of gold is now thermally evaporated onto the patterned substrate (corresponds to figure 2-5(d)). The substrate is soaked in acetone followed by CD-26 for liftoff (corresponds to figure 2-5(e)) and then thoroughly washed with water. The figure drawn on the L-Edit software to obtain the mask for optical lithography is shown in figure 2-6. The 20 µm x 20 µm gold squares placed ~ 1 mm apart are used as markers for the EBL tool to align the sample. The smaller gold patterns (not visible on the figure) are used for identifying where the nanowire is with respect to the 20 µm gold squares.
(b) Nanowires

For nanowire synthesis, the substrates with the alignment markers are spun coated with a layer of MMA/MAA EL 6 at 5000 rpm for 45 seconds and baked at 150° C for 3 minutes. A second layer of 950 PMMA A3 is coated at 4000 rpm for 45 seconds and baked at 150° C for 3 minutes. The bilayer structure ensures easy liftoff. The lower layer thickness determines the maximum possible thickness of evaporated metal (maximum evaporation thickness is \( \frac{1}{2} \) of the thickness of the lower layer) and the upper layer thickness determines the resolution of the patterning (thinner upper layers give better resolution). With this recipe, a lower layer thickness of \( \sim 150 \) nm and an upper layer thickness of \( \sim 80 \) nm is obtained. A 10 nm layer of Au is thermally evaporated on the two spin layers to ensure height measurements in the EBL instrument. The sample is then placed in the EBL instrument (Leica EBPG5-HR). The nanowires are drawn with the help of L-Edit software and are written on the substrate with a 100 KeV beam. At this stage, it is possible to use the alignment markers and write the wires at definite places to avoid having to find them for making electrical contact. The nanowires can also be patterned at random places without using an alignment process. Their positions with respect to the alignment markers can later be mapped with an optical or scanning electron microscope for making electrical contact. Both these techniques are used in this study depending on the particular circumstances. The dose and the spotsize are optimized to obtain thin and well-defined wires. The narrowest nanowires obtained with a bilayer resist (MMA/MAA EL6, 950 PMMA A3) are \( \sim 60 \) nm in diameter with a beam spot size of 15 nm and a dose of 1200 \( \mu \text{C/cm}^2 \). The sample is developed in mixture of MIBK:IPA in a ratio of 1:3 for 1 minute followed by immersing in IPA for 15 seconds. The sample is then washed with deionized water and IPA. Nanowires of thickness upto 80 nm can be evaporated on the substrate using thermal/e-beam evaporation or sputtering. If
the evaporated layer is too thin, one may obtain separated islands instead of a continuous film. This sets the lower limit to the nanowire thickness. For this study, cobalt, nickel, aluminum and gold nanowires have been synthesized this way. A layer of protecting material like gold or aluminum oxide can be evaporated on nanowires to prevent oxidation. However, the total thickness of the nanowire material and the protecting layer should be less than half the thickness of the lower resist layer. Also, the protecting layer may affect the transport properties of the nanowire. The substrate is then soaked in acetone for a few minutes for lift-off and washed with IPA and deionized water.

In case of the nanowires grown by the EBL followed by evaporation technique, no special preparation is needed for contacting. However, since these nanowires are much fewer in number than the nanowires which are electrochemically grown, finding them with the SEM is more difficult and care needs to be taken to make markers on the substrate to aid in locating them.

2.2 Structural Characterization

Nanowires synthesized by electrochemical deposition are characterized by using X-ray diffraction (XRD) to determine the crystalline properties of a large number of nanowires. For detailed characterization like physical dimensions and extent of oxidation, transmission electron microscopy (TEM) was performed. The granular nanowires are characterized for dimensions, composition and grain size using scanning electron microscopy (SEM). The three techniques and their relative merits are described below.
2.2.1 X-Ray Diffraction

X-rays are electromagnetic radiation with typical energies between 0.1 – 100 keV. For diffraction purposes, short wavelength x-rays (hard x-rays) with energies between 1 – 100 keV are used. The wavelength (\(\lambda\)) of an x-ray photon is given by \(\lambda = \frac{hc}{E}\) where \(h\) is the Planck’s constant, \(c\) is the speed of light and \(E\) is the energy of the photon. Since the wavelengths of x-rays in the 1 – 100 keV range are close to the size of atoms in a lattice, they provide an ideal instrument for probing the structural arrangement of atoms and molecules. The x-rays interact with electrons in an atom and get scattered. In a diffraction experiment, the x-rays that get scattered without losing any energy (elastically scattered) are collected for analysis. The scattered x-rays interfere with each other and the resulting interference pattern allows us to deduce the structural arrangement of atoms.

X-rays can be generated using vacuum tubes or by synchrotron radiation. In this study, measurements were done using a Philips X’pert X-ray Diffractometer equipped with a vacuum tube generating Cu K\(\alpha\) radiation of wavelength 1.54 Å. The AAM or PCM template with the electrochemically grown nanowires embedded in them are prepared for XRD by carefully removing the evaporated metal layer that acted as cathode during electrodeposition. This can be done by wiping the back of the membrane with either nitric acid (if the nanowires are unaffected by nitric acid) or ethanol. The sample is then placed in a zero background holder and set for measurement inside the diffractometer. The sample is held stationary by the diffractometer while the incident beam and detector are rotated over a specified range of angles and intensity as a function of scattering angle is plotted. If the atoms are regularly arranged as in a crystal, there are sharp maxima in the interference pattern at angles given by the Bragg condition \(2d\sin(\theta) = n\lambda\) where \(\theta\) is the scattering angle, \(n\) is the peak index and \(d\) is the interplanar spacing. An example of
such a sharp intensity peak at a given angle for a crystalline material can be seen in figure 3-3. This spectrum corresponds to 50 nm diameter Al nanowires embedded in AAM. The peak corresponds to the [110] planes of a face centered cubic Aluminum lattice. From this measurement it can be concluded that the Al nanowires are single crystalline with a face centered cubic structure and a strong preference to grow in the [110] direction.

XRD is a very useful tool for characterizing crystalline samples. It gives information about sample crystallinity and growth direction and since x-rays examine a large segment of the sample, XRD gives information about the whole sample. Techniques like TEM and SEM on the other hand are limited to examining a very small fraction of the nanowires. The limitations of XRD for our samples are that it cannot give information about sample dimensions and extent of oxidation.

2.2.2 Transmission Electron Microscopy

The resolution of optical microscopes is limited by the wavelength of visible light which is ~ 400 nm. The de Broglie wavelength of an electron accelerated to 100 keV is found to be 0.004 nm. The idea behind the creation of the transmission electron microscope (TEM) was to exploit the smaller wavelength of electrons to improve the resolution of microscopy [63]. Although far from this theoretical limit because of limitations of electron lenses, TEMs today are capable of resolving individual columns of atoms in a crystal. Besides high resolution, another advantage of TEM over traditional microscopy is that electrons are a type of ‘ionizing radiation’. This means that they are capable of removing one of the tightly bound inner shell electrons from an atom. Ionizing radiation also produces a wide range of secondary signals from the specimen among which are – elastically scattered electrons, inelastically scattered electrons, secondary
electrons, backscattered electrons, auger electrons, characteristic x-rays etc. Depending on the requirement, different parts of the secondary signals can be captured and analyzed to yield a wide range of information. A detailed description of the instrument and its applications can be found in the book [64].

![TEM Imaging](image)

**Figure 2-7:** (a) A transmission electron micrograph of 50 nm diameter gold nanowires. (b) A high resolution transmission electron micrograph of a 50 nm diameter gold nanowire. The atoms can be seen clearly in the nanowire and the absence of an oxidation layer can also be noticed. The inset shows an electron diffraction pattern from the same nanowire. Indexing of the pattern yields the information that the preferential direction for nanowire growth is [111].

TEM imaging was done using Philips EM-420T operating at 120 keV. High resolution imaging was done with JEOL EM-2010F microscope equipped with a field emission gun operating at 200 keV. Since the TEM relies on transmitted electrons that have interacted with the sample for imaging, a TEM sample needs to be reasonably electron transparent. This makes nanowires with their small diameters good candidates for TEM imaging as electrons only have to traverse a small path through them. The sample is prepared for TEM imaging by dissolving the membrane containing the nanowires to obtain a suspension of nanowires. The nanowires are cleaned by successive cycles of sonication and centrifuging and finally a suspension in isopropanol is obtained. A drop of this solution is dispersed on a lacey carbon coated copper grid.
(purchased from SPI Supplies Inc.). The grid is allowed to air dry and then loaded onto a sample holder and introduced into the TEM sample chamber for characterizations.

Figure 2-7 (a) shows a TEM image of 50 nm diameter gold nanowires. A high resolution TEM image showing atoms of a single gold nanowire from the same sample set is shown in figure 2-7 (b). As mentioned before, the TEM is a powerful and versatile tool. In addition to imaging, we have used it to obtain diffraction patterns by capturing the elastically scattered electrons (figure 3-6 (b) inset). From the diffraction pattern, the preferred growth direction and crystal structure of the wire can be found to be FCC and [111] respectively. Both the Philips and the JEOL TEM are equipped with energy dispersive x-ray spectroscopy (EDX). This technique relies on capturing the characteristic X-rays emitted by the sample on interacting with the electron beam. The characteristic X-rays are used to analyze the chemical composition of the sample. Since the electron beam in the TEM can be focused to a small point, the detailed chemical composition of the nanowire can be found by sweeping this point along the length of the wire.

2.2.3 Scanning Electron Microscopy

A scanning electron microscope (SEM) also uses a beam of electrons to interact with a sample and form an image. Either a thermionic or a field effect source is used to produce electrons ranging in energy from 0.2 – 40 keV. The major difference from the TEM is that the SEM uses a convergent beam of electrons to scan the sample in a raster scan pattern. The TEM uses a parallel beam of electrons to illuminate the sample unless it is being used in scanning mode as a scanning TEM. The electron beam in the SEM also generates a wide variety of secondary radiation. For forming the image, the back scattered electrons and the secondary electrons are used. The emitted characteristic X-rays can be used to study chemical composition. The SEM has
extremely high resolution and can image objects ~ 1nm depending on the electron beam energy.

The magnification in an SEM depends on the ratio of the raster on the sample to the raster on the display device. Therefore, the SEM can be used to produce a wide range of magnifications from 10 – 500,000 times.

SEM imaging was done using a LEO 1530 field emiss

Figure 2-8: (a) A scanning electron micrograph of a 120 nm diameter aluminum nanowire contacted with 8 aluminum electrodes (b) A higher magnification image of an aluminum film in which the aluminum grains making up the sample can be seen.

SEM imaging was done using a LEO 1530 field emission SEM. This instrument uses a field emission source and operates between 0.2 – 30 keV giving a resolution of ~ 1.2 nm. The SEM does not require the sample to be transparent to electrons. Therefore this instrument enables us to image samples already dispersed on a silicon substrate that cannot be put on a TEM grid. SEM samples need to be conductive since the electron beam can lead to charging otherwise. Since most of the nanowires we image are metallic, this does not present a problem. The samples used in this study do not need any special preparation for imaging by an SEM. The silicon/silicon nitride substrate with the sample and electrodes patterned onto it is taped down with copper tape onto the sample holder and loaded into the vacuum chamber.

Figure 2-8 shows an SEM image of a 120 nm wide aluminum nanowire contacted with several aluminum electrodes on a silicon substrate. Figure 2-8(a) has a low magnification image

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in which the entire sample can be seen, figure 2-8(b) contains a high magnification image in which the grains of aluminum making up the sample are visible.

2.3 Measurement of Electrical Transport

Measurement of electrical transport is a reliable and easy way to study superconductivity in nanowires. Making good electrical contact to the nanowires for such a measurement presents a challenge and several methods have been developed to make such contact possible. Conventionally, most electronic transport measurements use a four-probe configuration as shown in figure 2-9. Since the voltage probes have negligible amounts of current passing through them, the measured voltage does not have contributions from contact resistance between the wire and the electrode. To achieve measurements in this geometry however, nanowires have to be extracted from the membrane and dispersed. Most nanowires being measured in this study like Zn, Al, Co and other elemental nanowires are prone to oxidation on exposure to atmosphere. The oxide layers are insulating and prevent good electric contact between the nanowires and the electrodes. In some cases, the entire wire may also be oxidized and insulating. To bypass this problem, one needs to achieve one of three things: (1) synthesize nanowires that do not oxidize as readily (2) develop a technique for electrical measurement without exposing the nanowires to atmosphere and (3) develop a technique for contacting the nanowires after getting rid of the oxide layer. The first of these methods is not feasible for our studies since we are interested in quasi 1d nanowires whose diameter \( d < \xi \) (superconducting coherence length). With our current synthesis techniques we can synthesize nanowires of minimum diameter \( \sim 20 \) nm. Therefore we need materials with large coherence lengths and are limited in our choice of materials to elemental superconductors like Al and Zn. The second method - called quasi-4 probe method - involves
transport measurements while the nanowires are still embedded in and protected by the PCM/AAM membrane. This method is discussed in section 2.3.1. The third method has been developed using focused ion beam system and e-beam lithography and will be discussed in more detail in section 2.3.2.

![Figure 2-9: Schematics of a 4-probe measurement on a single nanowire.](image)

### 2.3.1 Quasi 4-probe Measurements

In this technique, the nanowires are not released from the membrane. Since, they are not exposed to atmosphere, they do not get oxidized. Two small copper blocks ~ 5mm x 3mm are threaded through so that they can be fastened together with stainless steel screws (Figure 2-10). Small pieces of sapphire are glued to the inner surface of both the blocks to insulate the blocks from the measurement electrodes. Sapphire is a good thermal conductor, so thermal contact to the sample puck is ensured. One of the blocks is glued onto the sample puck and the other one is screwed on top of the first one. Two small lengths of wire of some soft material like In are put on both sapphire pieces and the membrane with the nanowires embedded in it is finally inserted
between these wires and mechanically squeezed (labeled ‘S’ in the figure). The screws on the copper piece can be tightened or loosened to achieve some degree of control over the number of nanowires contacted [3,29,65]. The wires of soft material which are now connected to the top and bottom of the membranes are attached to voltage and current measurement circuitry as shown in figure 2-10. In a slight variation of the technique, the electrodes can also be evaporated on both sides of the membrane before introducing the membrane between the sapphire pieces.

This technique is quite successful in measuring transport properties of nanowires. However, it does have a few limitations. The first is the mechanical stress of being squeezed between bulk electrodes that may alter the nanowire properties. The second is that the number of nanowires being contacted can only be controlled approximately. One possible way around this is found by evaporating a thin layer of material on the top surface of the PCM/AAM membrane before electrodeposition is started. The current is monitored carefully during the electrodeposition process. The current decreases steadily (as the wires grow in the pores) and then shows a sharp

Figure 2-10: Schematics of a quasi 4-probe measurement on an array of nanowires. S stands for the bulk measurement electrode which is generally a superconductor.
increase as soon as the fastest growing wire reaches the top and makes contact with the thin layer of evaporated metal. At this point the deposition is stopped. This technique, though ingenious, is not completely failsafe. The third and perhaps most serious problem with this technique is that the contact resistance is present in the resistance measurements. This prevents any features in the measurement from being conclusively attributed to the nanowires and may also obscure possible quantum mechanical effects at low temperatures. To circumvent this problem to some extent, it is ensured that that the material used to squeeze the nanowires between the copper blocks is superconducting. Also, both sides of the membrane are cleaned and all evaporated layers removed to ensure that the superconductor is contacting the nanowire. Below the transition temperature ($T_c$) of the bulk measurement electrodes, the resistance of the electrodes becomes 0 Ω. In addition, it is hoped that the proximity effect (discussed in section 1.3.1) drives the interface superconducting reducing the contact resistance to 0 Ω. The 2-probe measurement does not have any contribution from the resistance of the electrodes or that of the contact and can therefore be dubbed a ‘quasi 4-probe measurement’. This technique has been successfully used to measure the transport properties of a wide variety of nanowires like Zn, Sn, AuSn, Au, Pb, In amongst others. The transport measurements done on Al nanowires in this configuration are described in section 3.3.

2.3.2 4-probe Measurements

The problems with the quasi 4-probe measurements described in the previous section make a true 4-probe measurement desirable. Such measurements have been made on crystalline nanowires grown using template-based electrodeposition (section 2.1.1 (b)) and granular nanowires grown using e-beam lithography followed by evaporation (section 2.1.2 (b)). The
crystalline nanowires have to be released from the membranes to allow such a measurement. The chief challenge consists of removing the oxidation layer that forms on the nanowire. This can be achieved in a number of ways as described below.

(a) Focused Ion Beam

Focused ion beam (FIB) systems are used for site specific ablation, deposition and imaging of materials. The principle behind the imaging aspect of the tool is similar to the SEM except that an ion beam is used instead of an electron beam. The FIB instrument used for this study is an FEI Quanta 200 3D dual beam FIB/SEM system. The dual beam means that in addition to an ion beam, it also contains an electron beam for imaging and deposition. The quoted resolution of the electron beam images is 3.5 nm and the quoted minimum size of the gallium ion beam is 10 nm. A schematic of an FIB instrument is shown in figure 2-11. The instrument consists of a vacuum system, an electron column, an ion column, imaging detectors and one or more gas injection systems. The vacuum system maintains a pressure of ~ $10^{-6}$ torr in the region of the sample and a much lower pressure ~ $10^{-8}$ torr in the columns. The electron column is identical to the electron column in an SEM and consists of a thermionic emission electron gun along with accelerating fields and lenses. The ion column consists of a liquid metal ion source (LMIS). The most commonly used source, which is also present in this system, is a Ga source with acceleration voltages from 5 – 30 keV. An applied field extracts and ionizes the Ga from the LMIS. The rest of the column is in principle the same as the electron column. The FIB system can be coupled to a number of detectors. The one used in this study is equipped with secondary electron detector for imaging. The gas injection needles are connected to hydrocarbon precursor
gases. In general W, Pt or C can be deposited. For this particular system W and Pt are available. Table 2.1 shows the details of the gases and the parameters used for deposition.

![Schematics of a focused ion beam system equipped with a electron column and two gas injection systems.](image)

**Figure 2-11:** Schematics of a focused ion beam system equipped with an electron column and two gas injection systems.

The FIB system can be used to mill away parts of the sample by using the highly focused Ga ion beam. To achieve localized deposition of material, the precursor hydrocarbon gas is first introduced into the chamber. The electron or ion beams are then rastered across the area where the deposition is required. The secondary electrons generated by the interaction of the ion beam with the sample or the electron beam crack the hydrocarbon precursor gas leading to local deposition of the conducting material. The milling due to the ion beam continues even as the deposition occurs. However, for our samples, this is an advantage rather than a disadvantage as the milling removes the insulating oxide layer from the nanowires and enables good ohmic contact to the deposited electrode.
FIB deposited Pt and W are not pure metals but an amorphous mix also containing Ga and C. The Pt resistance does not show typical metallic behavior and this has been attributed to the presence of Ga and C. The FIB deposited W is a superconductor with a transition temperature of ~ 4.8 K and critical field of ~ 8 T [66]. Several groups have successfully performed 4-probe measurements on metallic nanowires using FIB deposited Pt contacts [67, 68] but, our group is the first to report measurements using superconducting W electrodes on nanowires [69]. Detailed transport properties of the FIB deposited W and Pt can be found in reference [70].

**Substrate Preparation**

The substrate used for FIB must be slightly conducting to avoid charging. We therefore use 300 µm thick n (Sb)-doped Si substrate. The doping makes the substrate slightly conducting. It is necessary to coat it with an insulating layer to isolate the sample from the substrate. A 150 nm thick insulating Si₃N₄ layer is grown on both sides of the substrate using a low-pressure chemical vapor deposition process. An optical lithography process is then carried out to make large contact pads on the wafer. The process was similar to that described in section 2.1.2(a) except that the photoresist used was BPRS-100, the mask had a different pattern from the one shown before and only acetone was used for the liftoff. Figure 2-12 shows the Si substrate after photolithography, Au evaporation and lift off using acetone. The wafer can be cleaved into small

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pt Deposition</th>
<th>W Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor Gas</td>
<td>C₂H₅(PtCH₃)₃</td>
<td>W(CO)₆</td>
</tr>
<tr>
<td>Temperature</td>
<td>30°C</td>
<td>55°C</td>
</tr>
<tr>
<td>Current Density</td>
<td>2 – 10 pA/µm²</td>
<td>50 pA/µm²</td>
</tr>
</tbody>
</table>

Table 2-1: Parameters for FIB assisted Pt and W deposition
cells. A single cell is shown in Figure 2-12 (b) with four Au contact pads that are meant to act as measurement electrodes after the FIB process is completed.

![Image](image.png)

**Figure 2-12**: (a) SEM image of a die containing several cells of a substrate prepared for FIB assisted deposition of nanowire contacts. The lighter portions are evaporated Au and the darker are the Si/Si$_3$N$_4$ wafer. (b) SEM image of a single cell from the same die. A nanowire is found in the middle of the four large gold pads and FIB assisted deposition is performed to connect the nanowire to the four pads.

**Sample Preparation**

The growth, separation and cleaning of the electrochemically grown nanowires has been described in section 2.1.1 (b). A drop of the solution of isopropanol containing dispersed nanowires is put on a substrate prepared as described in the previous section. The isopropanol is allowed to evaporate. The substrate is then glued onto a sample puck with a carbon tape and loaded into the sample chamber of the FIB system. A single nanowire is found in the window between the four gold pads using the SEM feature of the FIB system. The wires grown using e-beam lithography do not need any preparation since they are already on the Si/Si$_3$N$_4$ substrate. One needs to be mindful to make markers to locate the nanowire during the e-beam process so that the individual wires are easy to find.
Making the electrodes

Once a nanowire is chosen, some feature near the nanowire is used to focus the microscope, correct astigmatism and set eucentric height all using the electron beam. The preferred voltage is 15 keV and the preferred current is 1 nA. The nanowire itself should not be used for this process to minimize damage to the nanowire. After this the sample stage is rotated to an angle of 52° to ensure it is facing the ion column (refer to figure 2-11). The sample is imaged using the ion beam at a 30 keV voltage and a current of 10 pA. Minor adjustments are made to the position of the stage using the X and Y knobs of the ion beam to ensure that the electron beam and ion beam are pointing at the same area of the sample. If the eucentric height has been properly adjusted, this process should be fairly easy. Again, one must avoid looking at the actual nanowire with the ion beam for as long as possible. After the adjustments, the gas-injecting needle (Pt or W) is inserted into the chamber. Four electrodes, typically 10 µm x 100 nm x 200 nm are patterned onto the nanowire connecting it to the large Au pads. The electrodes are deposited at a current of 10 pA for Pt and 30 pA for W. In case a substrate without pre-patterned Au pads is being used, these 4 electrodes are connected in the next step to larger FIB assisted electrodes, which are in turn connected to larger ones. The current for deposition of the larger electrodes in the subsequent steps depends on the area of the electrodes. The aim is to obtain a current density close to that reported in table 2-1. The largest electrodes, whether they are the pre-patterned Au pads or FIB assisted W or Pt electrodes, are ~ 0.5 mm apart. Figure 2-13 shows SEM images of a 50 nm diameter electrochemically deposited Ni nanowire contacted using FIB assisted W electrodes.
Wiring the sample

After the patterning is completed, the sample is taken out from the chamber and glued on with GE varnish (to obtain thermal coupling) to the sample puck. In dots 0.008 inches in diameter (purchased from Indium Corporation of America) are squeezed onto each of the four largest electrodes by using a wooden stick sharpened to a point. Very thin Au wires of diameter 8 mils (~0.02 mm) are pressed into these indium dots and connected to the 4 electrodes of the sample puck. During the whole procedure, great care is taken to protect the sample from electrostatic discharge and a grounding wrist strap is worn while connecting the Au wires. The sample is then loaded onto a dilution refrigerator (DR), He\(^3\) refrigerator (He3R) that are put into a physical property measurement system (PPMS) or is directly inserted into the PPMS. The three can achieve minimum temperatures of 50 mK, 350 mK and 1.8 K respectively.

This technique offers a reliable and simple way to contact nanowires. The disadvantages of the technique include uncontrolled milling, Ga ion contamination and lower resolutions than e-beam lithography. The spreading of the electrodes outside the boundaries drawn by the software

Figure 2-13: (a) SEM image of a 50 nm diameter Ni nanowire contacted with FIB assisted W electrodes connected to Au pads made using optical lithography (b) A larger magnification SEM image of the same sample showing details of the wire, the electrodes and the relevant lengths.
for the parameters used in this study was found to be ~ 300 nm for W and ~ 100 nm for Pt. An additional disadvantage is that only Pt, W or C electrodes can be made this way.

(b) E-beam Lithography

The technique and substrate preparation for EBL has already been described in section 2.1.2. In this section we will describe the process of contacting nanowires that are already dispersed on or written on a Si/Si$_3$N$_4$ substrate using the procedures described in section 2.1.

**With Alignment**

Images of the nanowires are obtained using an optical microscope and the exact location in terms of cell number and the location of the small Au squares is noted. Care is taken to get at least 5 of the small Au squares in the image. The image is imported onto the L-Edit software, resized, rotated and moved until the Au squares in the image lie exactly on top of their counterparts in the file used to make the alignment markers (see figure 2-14).

Electrodes are then drawn on the nanowire image. The smallest electrodes are ~ 1 µm x 50 µm in area. Successively larger electrodes are made and the largest electrodes are 200 µm x 50 µm in area. Depending on the size of the electrode, different beam diameters are used to write them. Therefore the smallest electrodes are put on a different layer from all the larger ones. The layer for the smaller electrodes is fractured at a resolution of 50 or 100 nm depending on the separation between the electrodes and the layer for the larger electrodes is fractured at 200 nm.

The resist recipe used for making electrodes is generally a lower layer of MMA/MAA EL 11 spun at 2000 rpm for 45 seconds and baked at 150$^\circ$ C for 3 minutes and an upper layer of PMMA A3 spun at 4000 rpm for 45 seconds and baked at 150$^\circ$ C for 3 minutes. A 10 nm layer of
Au is thermally evaporated to ensure height measurements in the EBL instrument. The amount of material that can finally be evaporated on the mask is determined by the thickness of the lower layer. Since the lower layer is very thick for this recipe, it allows us to evaporate metal up to 75 nm thick even after 3-4 minutes of milling. The beam spot size used for writing the smaller electrodes is 50 or 100 nm depending on the fracture resolution and for the larger electrodes is 200 nm. A dose of 400 µC/cm² is used for this particular resist recipe for both sets of electrodes.

![Figure 2-14](image.png)

Figure 2-14: The left panel shows an optical image of a substrate with Ni nanowires dispersed on it. The Au squares in the image are made by optical lithography as described in section 2.1.2 (a). This image is taken and placed on the L-Edit file which was used to make the optical lithography pattern so that the Au squares in the image and the Au squares on the file are exactly aligned as shown in the middle panel. The electrodes are then drawn on the L-Edit file and written with the e-beam lithography tool in the correct location using the alignment squares. The final sample where the Ni nanowire has been contacted with Al electrodes is shown in the right panel.

After the electrodes have been written, the substrate is developed for 60 seconds in a solution of MIBK:IPA::1:1 followed by IPA for 15 seconds. It is then washed with deionized water and IPA. The substrate is then put in an evaporator equipped with thermal and e-beam evaporation capabilities and an argon ion mill (custom made by the Kurt J. Lesker company). The nanowire is milled for 1-3 minutes depending on the expected thickness and hardness of the oxide layer. The milling removes the oxide layer. This is followed by evaporation of the required electrode (generally Au or Al) on the pattern. Since the e-beam resists used have very low
melting points (~ 150°C), only low melting metals like Au, Al, Sn, Pb or In can be used for electrodes.

After the evaporation, the sample is immersed in acetone at room temperature for a few minutes for liftoff. It is then washed with water and isopropanol and dried in a nitrogen stream. An optical image of a completed sample is shown in right panel of figure 2-14.

**Without Alignment**

This technique is identical to the one of contacting nanowires with alignment except that in this technique the nanowires and electrodes are made in the same step therefore no alignment is required. Since the nanowires and electrodes are also co-evaporated, the problem of the oxidation of the nanowire is no longer present and no ion milling is required. However, since the nanowires are made in the same step as the electrode, the resist recipe has to be changed slightly from that of the previous section to accommodate the need for increased resolution. The same recipe as that described in the nanowire synthesis section 2.1.2 (b) is used. A layer of MMA/MAA EL 6 is spun at 5000 rpm for 45 seconds and baked at 150°C for 3 minutes. A second layer of 950 PMMA A3 is coated at 4000 rpm for 45 seconds and baked at 150°C for 3 minutes. A 10 nm layer of Au is thermally evaporated on top of the two spin layers to ensure height measurements in the EBL instrument. The nanowire is drawn on a layer separate from that of the small and large electrodes. This smallest layer is fractured at a resolution of 10 nm and the beam spot size used is 15 nm. The fracturing resolution and beam spot size for both the small and large electrodes remains the same as that in the previous section - ‘with alignment’. For this resist combination, the dose for the electrodes is 700 µC/cm² and the dose for the nanowires is ~ 1200 µC/cm². After writing, the pattern is developed for 60 seconds in MIBK:IPA::1:1 followed by 15 seconds in isopropanol. After this it is washed with isopropanol and deionized water and placed in an evaporator. The
required material is evaporated and the liftoff is performed by dipping the sample in acetone at room temperature for a few minutes. No ion-milling is required in this process. The resist limits the maximum thickness of evaporated metal to ~ 50 nm. An SEM image of aluminum nanowires made and contacted this way is shown in figure 2-8.

The advantage of the technique is that every part of the sample is written in the same step and therefore the interfaces are clean and ohmic. A disadvantage is that the nanowires obtained are granular. This makes morphology important to understanding the physics of the sample.

The wiring of the sample to the refrigerator pucks is the same as that for the FIB samples (see section 2.3.2 (a)).

The synthesis, characterization, contacting and wiring techniques described in this chapter are used to study the electronic transport in a number of combinations of nanowires and electrodes. The motivations behind these studies and their results are discussed in detail in chapters 3, 4 and 5.
In general, the presence of a superconductor induces partial superconductivity in or enhances the superconductivity of any material placed in proximity to it. This is known as the ‘proximity effect’ and has been discussed in section 1.3.2 as well as in chapters 4 and 5. In superconducting Zn nanowires (ZnNW) however, the presence of bulk superconducting electrodes was found to weaken or destroy the superconductivity of the nanowires [3]. This counterintuitive phenomenon was named the ‘anti-proximity effect’ (APE). Understanding the APE offers more insight into the proximity effect and perhaps even into the nature of superconductivity in quasi 1D systems. It is also important to understand the regime in which it becomes important because superconducting nanostructures in proximity to superconducting bulk structures are likely to be widely used in possible future applications, for example in superconducting qubits.

Since its initial discovery, a number of experimental studies on the APE have been performed. A few theoretical models also exist. We will briefly discuss these in section 3.1. Detailed descriptions of the theoretical models are given in section 3.6. The synthesis and characterization of Al nanowires (AlNW) used for this study is described in section 3.2. Sections 3.3, 3.4 and 3.5 contain experimental results and analysis of measurements on AlNW arrays, crystalline single AlNWs and granular single AlNWs respectively. In section 3.7 we summarize the result of the most recent experiments and point out some possible directions for future endeavors.
3.1 Historical Background

The anti-proximity effect was first discovered in 40 nm diameter single crystal ZnNW arrays embedded in PCM membranes and squeezed between superconducting Sn electrodes [3]. The measurement geometry is shown in figure 3-1(c) and described in section 2.3.1. The $T_c$ and $H_c$ for the ZnNW are 1 K and 2700 Oe respectively while the $T_c$ and $H_c$ for the bulk Sn electrodes are 4.8 K and 300 Oe respectively. In the $R$ vs. $T$ as a function of $H$ (figure 3-1(b)) for the 40 nm diameter, 6 µm long ZnNW array, at 0 Oe field, the Sn electrodes are superconducting as evidenced by the drop in resistance at 4.8 K. The ZnNWs show no superconducting transition. When a field of 300 Oe is applied, the Sn becomes normal and the superconducting transition of
the ZnNWs is recovered. The superconductivity of the bulk electrode therefore suppresses the superconductivity of the superconducting nanowire. This effect was named the APE.

The right panel of figure 3-1(b) shows the V vs. I at 0 Oe (Sn electrodes superconducting) and at 300 Oe (Sn electrodes normal) for the 40 nm diameter ZnNW array. The critical current ($I_c$) increases from 0 µA to 0.7 µA on the application of a 300 Oe field. This enhancement in $I_c$ is a signature of the APE. The behavior of $I_c$ with field in an APE system is shown in figure 3-1(d). The $I_c$ was measured on a 40 nm diameter, 2 µm long ZnNW array squeezed between superconducting Pb electrodes [71]. The $I_c$ reaches a maximum value as the superconducting electrodes are driven to the normal state by increasing the magnetic field to the critical value. With further increase in the field, $I_c$ decreases. Figure 3-1(a) shows the R vs. T at H and V vs. I at H for a 70 nm diameter ZnNW array contacted with bulk Sn electrodes. For this system, no suppression of superconductivity is seen. The superconducting coherence length ($\xi$) of the ZnNWs was found to be ~ 150 nm. The absence of APE in the 70 nm diameter ZnNWs was used to conclude that the APE was diameter dependent and only appeared when the diameter of the nanowire $d << \xi$.

Experiments were also performed on nanowires of different lengths and with different electrodes (Pb and In) [71]. It was found that the ‘strength’ of the APE was less for longer (35 µm) nanowires. The ‘strength’ here was defined qualitatively as the extent of suppression of the superconducting transition of the nanowire at zero field. The length dependence of the strength of the APE was also discussed in reference [72]. There, the strength of the APE was defined as the magnitude of enhancement of $I_c$. In the reference it was found that the APE was weak for 1 µm long and 20 µm long nanowires and strong for 4 µm long nanowires. It was concluded that the APE was strongest when the length of the nanowire was comparable to the charge imbalance.
length ($\Lambda_Q$). This assertion was also justified on the basis of the mechanism of the APE suggested in reference [73].

![Graph showing the relationship between temperature and resistance for different fields and voltages for Zn nanowire arrays with bulk In and Sn electrodes.](image)

Figure 3-2: Resistance as a function of temperature at different fields and voltage as a function of current at different fields for 40 nm diameter, 6 µm long Zn nanowire arrays with bulk (a) Indium and (b) Tin electrodes. These graphs are reproduced from Tian et al., PRL 95, 4 (2005).

The strength of the APE was also found to depend on the nature of the electrodes. In figure 3-2(a) and (b) the APE in 40 nm diameter, 6 µm long Zn nanowire arrays with bulk In and Sn electrodes respectively is shown. While the Sn electrodes (figure 3-2(b)) completely suppress the superconductivity in the ZnNWs at 0 field, with the In electrodes (figure 3-2(a)), a small residual transition of the ZnNWs at 0.9 K at 0 field can be seen. This result was interpreted as the influence of the Sn electrodes being stronger than that of In and the APE depending on the material of the electrode. We now believe this interpretation to be incorrect and will examine it in more detail in the section 3.4.

Two theoretical models for this effect have been proposed [73,74]. Both are in qualitative agreement with experiments. There are however, a few limitations. The first requires a
magnetic field to be present to see the APE, which is later, found not to be the case. The second model does not make quantitative predictions. Furthermore, neither model explains the dependence on the electrode material.

Additional experiments on evaporated granular ZnNWs with bulk Zn electrodes were performed by Chen et. al [72,75]. The results of these experiments confirm the diameter dependence seen in the earlier experiments. The length dependence was also studied in detail in these experiments. It was found that the APE was strongest when the length of the nanowire was of the order of the charge imbalance length ($\Lambda_Q$). It was found to become weaker at lengths shorter and longer than this length. This also matches with the theoretical predictions from [73]. However, the authors have considered the absolute value of the length and not the length compared to $\Lambda_Q$.

In all the experiments described above, a magnetic field was used to see the APE. This led to controversy about the APE being the effect of a magnetic field or of the measuring electrodes. Furthermore, the universality of the effect needed to be confirmed by seeing it in systems other than Zn. Finally, the nature of the resistive state induced by the APE in the nanowire needed to be studied to understand the mechanism behind it. The experiments described in sections 3.3, 3.4 and 3.5 have been performed with these goals in mind.

### 3.2 Aluminum Nanowires: Synthesis and Characterization

Aluminum nanowires (AlNW) have been a favorite candidate for studying superconductivity in the quasi-1D regime for several reasons. The long $\xi (T)$ of bulk Al, at 1600 nm, makes it easier to access the quasi 1D regime. Al has a thin and stable oxide surface layer, protecting it from uncontrolled oxidation. These two factors make AlNWs ideal candidates for
four probe transport measurements on individual nanowires, enabling systematic investigation of phenomena like quantum phase slips and the anti-proximity effect in quasi 1D systems. Tunneling experiments to explore superconductivity in 1D are also possible on AlNW since the oxide surface layer on these wires is highly insulating. Lastly, AlNWs are possible candidates for electronic circuits in future nanodevices. For these reasons, Al was the choice of material for further APE experiments. Both single crystalline and granular AlNWs have been synthesized.

3.2.1 Crystalline Aluminum Nanowires

Electrochemical deposition of Al into AAM templates (section 2.1.1) was used to synthesize the nanowires. Al, being very active, has to be deposited in a dry atmosphere from an anhydrous electrolyte. In this study, the following technique was developed for the growth of AlNWs [76]. An electrolytic bath composed of 6 M AlCl$_3$ and 0.2 M LiAlH$_4$ in tetrahydrofuran (THF) was prepared. The electro-deposition was carried out inside a glove box (Vacuum Atmospheres Company) in a 99.999% pure nitrogen atmosphere, with less than 1 ppm moisture and, oxygen. 50nm, 80 nm and 200 nm pore diameter membranes were prepared using a constant voltage anodization process described in section 2.1.1. The membranes were coated on one side with a layer (150 nm, 200 nm and 450 nm respectively) of thermally evaporated Ag. This Ag layer acts as a cathode. A Pt anode was used and Al was deposited at a constant current density of 1.3 - 2.5 mA cm$^{-2}$ for 45-60 minutes.

The XRD spectrum of a 50 nm AlNW array embedded in an AAM membrane is shown in figure 3-3. There are two distinct peaks at 44.7° and 99.0° corresponding to the {220} and {440} planes respectively. This indicates that the wires are single crystal with [110] as the preferred direction of growth. The XRD spectrums of 80 nm and 200 nm arrays also show the
same pattern indicating that the crystallinity and growth direction are largely independent of pore size in these diameter regimes.

Figure 3-3: X-ray diffraction spectrum of 50 nm Al nanowire array embedded in an anodic aluminum oxide membrane. The peaks at 44.7° and 99.0° correspond to the \{220\} and \{440\} planes respectively. The inset shows a TEM image of 50 nm Al nanowires after being released from the membrane and dispersed on a carbon coated copper grid. The figure is reproduced from Singh et al., Chem. Mat. 21, 5557 (2009).

To obtain freestanding ANW, the Ag film on the back of the AAM membrane has to be removed and the membrane dissolved. To prevent the HNO₃ used for Ag film removal from damaging the ANW, Au was deposited into the AAM membranes for 2 minutes before the Al electrodeposition. The Ag film could thus be etched away with concentrated HNO₃. After removal of the Ag film, the AAM membrane was dissolved in a solution containing 6% H₃PO₄ (by weight) and 1.8% CrO₃ (by weight), heated to 60°, for several hours. The ANWs suspended in the solution obtained were cleaned by washing several times with isopropyl alcohol (IPA), alternating with centrifugal separation.
Clean ANWs in IPA were dispersed on a Cu grid for structural characterization using transmission electron microscopy, high-resolution transmission electron microscopy and selected area electron diffraction (SAED) in a field emission TEM (described in section 2.2). The inset of figure 3-3 shows a transmission electron micrograph of 50 nm diameter freestanding AlNWs. An HRTEM image of a 50 nm thick wire is shown in the left panel of figure 3-4. The HRTEM image shows an amorphous oxidation layer ~10 nm in thickness on the surface of the wire. The oxidation layer makes the diameter of the nominally 50 nm nanowire effectively 30 nm. The thickness of the oxidation layer decreases with increasing nanowire diameter and is stable with time. The oxidation layer on the nanowires is significantly thicker than the oxidation layer on amorphous aluminum nanowires. This may be caused by the aggressive etching procedure employed to release the ANW from the alumina membrane. The crystallinity of the wire, as
shown by the XRD pattern, is also confirmed by the HRTEM. The SAED pattern (right panel of figure 3-4) has hexagonal symmetry. For FCC ANW with [110] as the growth direction and [\( \overline{1}10 \)] as the beam direction, this is the pattern that would be expected. The needle inserted to block the direct beam obscures the sixth spot in the inner hexagon. The TEM and XRD results for 80 nm ANW are similar to that shown in figure 3-4 for the 50 nm wires.

The transport measurements on these nanowires were performed in two separate configurations. In the quasi four-probe configuration, the nanowires were not extracted from the AAM membrane and were squeezed between In electrodes as described in section 2.3.1. The results of these measurements are given in section 3.3. For true four-probe measurements on individual nanowires, the nanowires were extracted from the membrane using the technique described in the sample preparation for TEM. The nanowires were dispersed on a Si/Si$_3$N$_4$ substrate and contacted with Pt or W electrodes using a FIB system (details can be found in section 2.3.2). The results of these measurements are given in section 3.4.

### 3.2.2 Granular Aluminum Nanowires

The granular nanowires were patterned using e-beam lithography (section 2.1.2). To obtain small diameter nanowires a bilayer resist (MMA/MAA EL6, 950 PMMA A3) was used according to the recipe given in section 2.1.2 (b). The AlNWs and the electrodes were all written in the same step of lithography to minimize contact resistances. The nanowires were defined to be 25 nm wide in the L-Edit software and were written with a beam spot size of 15 nm and a dose of 1200 \( \mu \text{C/cm}^2 \). The smallest electrodes were defined to be 1 \( \mu \text{m} \) wide and 50 \( \mu \text{m} \) long and written with a beam spot size of 100 nm and a dose of 700 \( \mu \text{C/cm}^2 \). The other electrodes, larger than 1 \( \mu \text{m} \) wide were written with a beam spot size of 200 nm and a dose of 700 \( \mu \text{C/cm}^2 \). The sample
was developed in mixture of MIBK:IPA in a ratio of 1:3 for 1 minute followed by immersion in IPA for 15 seconds. The sample was then washed with deionized water and IPA. A 50 nm thick layer of Al was evaporated with the help of an e-beam at 0.5 - 1 Å/s. Changes in the evaporation rate and the vacuum level in the evaporator while evaporating the Al can change the grain size and the impurity level thereby affecting the superconducting critical temperature ($T_c$) of the Al [77]. The evaporation is done at a slow rate and breaks are taken every 5 minutes to prevent overheating and melting of the PMMA layer. These precautions have to be taken since the evaporator used in this study is water-cooled. Perhaps higher rates can be used for liquid nitrogen cooled evaporators. For some of the samples a 5 nm thick Au layer is evaporated on top of the Al layer at a rate of 1 Å/s. The original intent for doing this was to protect the AlNWs from oxidation. However, it was found, that the AlNWs are very robust and only oxidize on the surface, the interior remaining relatively unaffected by exposure to atmosphere. Some samples without the Au protection layer were made. These samples typically had higher $T_c$s and $H_c$s than the samples with the Au protection layer. This could be because of one of two reasons. The first and more likely possible reason is that the samples without the Au layer oxidize to a larger extent. The disorder in the Al samples tends to increase the $T_c$ and $H_c$ [77–80]. The second possible reason is that the proximity effect due to the normal Au nanoparticles on the surface suppresses the gap in the superconducting Al nanowire. There have been many experimental and theoretical studies on the effect on the gap of the superconductor and the normal metal close to an N-S interface in mesoscopic systems [81–83]. However, in all of these studies, the focus is towards finding the evolution of the gap in the normal metal and the dimensions of the superconductor are larger than its superconducting coherence length. Therefore, an estimate of the magnitude of the suppression of the gap in the Al in this particular geometry could not be found. If we use measurements made in the regime where the dimensions of both the superconductor and the
normal metal are several times larger than the superconducting coherence length [83], we obtain that the Al gap is smaller than the bulk gap upto a distance of $\xi$. This is likely to be an overestimation. The evaporation of a Au layer significantly reduced the $I_c$ of the AlNW. Since many of the measurements in this study were done at excitations close to $I_c$, having low $I_c$ was a desirable property and a Au layer was evaporated on some of the later samples with the intent of lowering $I_c$.

Figure 3-5: A scanning electron micrograph of an aluminum nanowire with aluminum electrodes made using e-beam lithography followed by evaporation. Even though the nanowire and electrode are evaporated simultaneously, the grain size in the electrode is larger than the grain size in the nanowire.
The nanowires and the electrodes were characterized using SEM (figure 3-5). The grain size, in addition to being dependent on the evaporation rate, was found to be affected by the lateral confinement resulting in smaller grains in the nanowire than in the electrodes. In figure 3-5, a few grain boundaries in the nanowire and the electrode are outlined in red to see this effect clearly. The average grain size in the nanowire is ~ 20 nm whereas the average grain size in the electrodes is ~ 100 nm. This effect has also been studied using SEM in evaporated Zn nanowires where the grain size in the nanowires was found to be of the order of the wire diameter [72]. From these studies, we can conclude, that even though the nanowire and the electrodes are co-evaporated, the grain sizes in the two are significantly different. Since, the $T_c$ and $H_c$ of the superconductor are known to depend on the grain size [77], the electrodes and nanowires have different $T_c$s and $H_c$s. This result is confirmed in transport measurements in which the $T_c$ and the $H_c$ of the nanowire ( ~ 1.4 K and 4000 Oe) are much higher than bulk Al. The $T_c$ and $H_c$ of the electrodes ( ~ 1.0 K and 300 Oe) are very close to bulk. The nanowire and the electrode therefore, can be treated as if they are made of separate superconducting materials.

A description of how the samples are connected to electronic transport measurement circuitry and placed in the refrigerator is given in a section titled ‘wiring the sample’ within 2.3.2 (a).

### 3.3 Quasi Four-Probe Transport Measurements

In the first set of experiments, transport measurements are made on crystalline AlNWs of diameter 80 nm and 200 nm still embedded in a porous AAM membrane. The membrane was squeezed between superconducting In electrodes (as described in section 2.3.1) and cooled in a Dilution Refrigerator. The In electrodes have a $T_c$ of 3.2 K and an $H_c$ of 300 Oe. The AlNWs
had $T_c \approx 1.2 - 1.4$ K and $H_c \approx 2000$ Oe – 1 T depending on the diameter of the nanowire being measured. These values are enhanced compared to the corresponding values for bulk Al because of surface effects [79,80].

Figure 3-6: (a) Resistance as a function of temperature at different applied fields for a 200 nm diameter Al nanowire array embedded in a anodic aluminum oxide membrane. The geometry of the measurement can be seen in the inset of (b). (b) The voltage as a function of excitation current for the same array.

Figure 3-6 (a) shows the R vs. T as a function of H for an array of 50 µm long ANWs of 200 nm diameter still embedded in the membrane. The wires are directly in contact with a bulk In dot 1 mm in diameter on one side of the membrane. On the other side, the bulk In electrode is squeezed onto an evaporated Ag film (250 nm thick) covering the membrane. The geometry of the measurement, with the applied magnetic field parallel to the nanowires is shown in the inset of figure 3-6 (b). At 0 Oe field, two steps in the resistance can be seen. The step at $\sim 3.2$ K corresponds to the In electrodes becoming superconducting. The step at $\sim 1.1$ K corresponds to the AlNWs becoming superconducting. A field of 1000 Oe destroys the superconductivity of the In electrodes ($H_c = 300$ Oe). The sharp drop at 3.2 K therefore disappears. At a field of 2000 Oe the superconducting transition of the AlNWs also disappears indicating that the $H_c$ is $\sim 2000$ Oe.
The V vs. I measurements at different H at 0.1 K are shown in figure 3-6 (b). In the absence of a magnetic field, when the In electrode is superconducting, the $I_c$ of the nanowires is 47 $\mu$A. An externally applied magnetic field of 300 Oe (the critical field for bulk In is 300 Oe) drives the In electrode normal, as seen by the non-zero resistance at low currents, and the $I_c$ of the nanowires decreases. This decrease in the $I_c$ of the nanowires in the presence of an external magnetic field is consistent with expectations for macroscopic Al: the superconducting behavior of the wires is insensitive to the state (normal or superconducting) of the In contacts. The APE is absent in these nanowires.

![Graphs](image)

Figure 3-7: (a) Resistance as a function of temperature at different applied fields for a 80 nm diameter Al nanowire array embedded in a anodic aluminum oxide membrane. The geometry of the measurement can be seen in the inset of figure 3-6 (b). (b) The voltage as a function of excitation current for the same array.

When the same experiment was performed on an 80 nm diameter nanowire array, however, the behavior of $I_c$ was different. The V vs. I measurements are shown in figure 3-7(b). It is estimated that 15 nanowires are being contacted. The non-zero residual resistance at zero field may be from the Ag film coating the membrane. The $I_c$ of the nanowires when the In electrodes are superconducting (in zero applied field) was 21 $\mu$A. Upon driving the In electrode normal (300
Oe field), the $I_c$ of the nanowires increased to 22 µA. The enhancement in the $I_c$, while it is only 1 µA, was much larger than the instrumental error of 0.01 µA. This is a sign of more robust superconductivity in the ANWs contacted by normal electrodes and a signature of the APE. In this and other similar samples, the $I_c$ of the nanowire increased upon application of a magnetic field and reached a maximum at the $H_c$ of the In electrodes, much like the effect seen in Zn nanowires with Pb electrodes (figure 3-1(d)). The fact that the APE was seen in thin but not in thicker AlNWs is consistent with earlier findings with ZnNWs [3,71] where the APE was seen in 40 nm diameter wires but not in 70 nm wires. The difference in the ‘characteristic’ diameters determining the presence or absence of APE in ZnNWs and ANWs may be a consequence of the different coherence lengths of the superconducting materials. It is also noteworthy that the APE is seen in wires up to 50 µm in length. The APE has also been seen in Zn wires as short as 1 µm in length [72] indicating that the APE is present over a large length range. Figure 3-7 (a) shows the $R$ vs. $T$ at different $H$ for the 80 nm diameter AlNW array. The $T_c$ for this sample is ~ 1.2 K and the $H_c$ is ~ 4000 Oe.

These results establish the ‘universality’ of the APE as they prove that it is not some material dependent phenomenon limited to ZnNWs. Moreover, AlNWs are stable on exposure to atmosphere unlike ZnNWs. Therefore, in this system, we can extract the nanowires out of the membrane and study the APE in single nanowires. The results obtained on single nanowires in true four probe geometry are expected to be easier to interpret as interface resistance, wire diameter variation from wire to wire and the presence of several superconductors in parallel need not be considered.
3.4 Four-Probe Transport Measurements on Crystalline Nanowires

In the second set of measurements, crystalline AlNWs, 200 nm, 80 nm and 50 nm in diameter, were released by dissolving the alumina membrane in a solution containing 6% H₃PO₄ (by weight) and 1.8% CrO₃ (by weight), heated to 60°C, for several hours. The AlNWs suspended in the solution obtained were cleaned by washing several times with isopropyl alcohol (IPA), alternating with centrifugal separation. The resultant suspension of wires in IPA was dispersed on a silicon substrate with a 1 µm thick Si₃N₄ insulating layer. The sample was then transferred into an FIB system. An isolated nanowire was located using the electron microscope and four FIB-assisted Pt or W electrodes were deposited on it for a standard four-electrode measurement (section 2.3.2). During FIB-assisted deposition, the ion beam etches away the native oxide layer on the AlNW to ensure good ohmic contact to the wire. Since the oxide layer on the 200nm, 80 nm and 50 nm diameter AlNWs is 2nm, 5 nm and 7 nm thick respectively, the effective diameters of the individual nanowires are ~ 196 nm, ~ 70 nm and ~ 35 nm respectively. FIB deposited Pt is normal but W is superconducting with a T_c of 4.8 K and H_c of 80000 Oe.

The transport properties of a ~ 200 nm (figure 3-8 (a) and (b)), 70 nm (figure 3-8 (c) and (d)) and 35 nm (figure 3-8 (e) and (f)) diameter AlNW contacted with Pt electrodes are shown in figure 3-8. SEM images of the samples are shown in the insets of the figures. The length of the nanowire being measured (= distance between the voltage electrodes) is ~ 4.5 µm for the 200 nm and 70 nm nanowire and 3 µm for the 35 nm diameter nanowire. The T_c's of the nanowires at 0 Oe applied field are 1.2 K for 200 nm, 1.5 K for 70 nm, and 1.8 K for the 35 nm diameter nanowire. The increase in T_c with decreasing diameter is in agreement with expectations [80]. The enhancement of T_c has been studied in the past for granular Al films and the pattern seen here in single crystal nanowires agrees with the trends seen in granular Al films. Figure 3-8(e) shows the
R vs. T at different H for the 35 nm diameter AlNW. The transition is very rounded compared to the 200 nm diameter nanowire (figure 3-8 (a)). This is because of thermal phase slips. In addition the 35 nm diameter nanowire does not go to a 0 resistance state even at low temperatures. There are two possible ways of interpreting this data. The first is to attribute the resistive tail to quantum phase slips. There are several problems with this interpretation. The resistance has a minimum at 1.1 K and begins to increase with decreasing temperature below 1.1 K.

This increase in resistance cannot be fitted with the quantum phase slip model [80]. Moreover, if we assume that the residual resistance is because of quantum phase slips, the normal state resistance of the wire is \( \sim 5000 \, \Omega \). This gives a resistivity of 160 \( \mu \Omega \)-cm. The resistivity of the 70 nm diameter nanowire on the other hand is \( \sim 3.3 \, \mu \Omega \)-cm. Although the resistivity is expected to increase with decreasing diameter, a 48 times increase is much larger than expected from simulations and studies on granular Al thin films [84]. For comparison, the resistivity of the 200 nm diameter nanowire is \( \sim 0.8 \, \mu \Omega \)-cm. In decreasing the diameter from 200 nm to 70 nm, the resistivity only increases by 4 times. The second way to interpret the data is to conclude the interfacial region where the Pt voltage electrodes contact the nanowire has been sufficiently damaged by the FIB process to make it non-superconducting. The residual resistance is coming from this interfacial region.

The increasing trend in resistance with decreasing temperature is easier to explain with this interpretation, as the temperature dependence of the resistance of this region is likely to follow that of FIB deposited Pt (which increases with decreasing T). Moreover, the resistance contribution from the AlNW is then equal to the resistance drop at 1.8 K (\( \sim 1600 \, \Omega \)). The resistivity of the AlNW would then be 51 \( \mu \Omega \)-cm: that is 15 times larger than the 70 nm diameter nanowire. A 15 times increase in resistivity is not surprising as the resistivity increases by 4 times from 200 nm to 70 nm and the increase is expected to get faster with decreasing diameter [84].
Figure 3-8: (a), (c), (e) Resistance as a function of temperature at different applied fields for 200 nm, 70 nm and 35 nm diameter single crystalline Al nanowire contacted with 4 Pt electrodes (the insets show scanning electron micrographs). (b), (d), (f) Resistance as a function of field at different temperatures for the same three nanowires.
The R vs. H at different T for AlNWs of three different diameters are shown in panels (b), (d) and (f) of figure 3-8. The $H_c$ for the 200 nm, 70 nm and 35 nm diameter AlNWs are 400 Oe, 3000 Oe and 9000 Oe respectively. The multiple steps in both the R vs. T and R vs. H transitions are caused by inhomogeneity in the sample. The wires themselves are very homogenous as seen in the TEM studies (< 1nm variation in a 50 nm diameter nanowire). However, the contacting with the FIB process with Pt electrodes introduces inhomogeneity in the contact region. The size of the inhomogeneity is estimated using reference [85] and found to be ~ 200 nm which is of the order of the width of the Pt electrodes (~ 100 nm). The V vs. I characteristics of the nanowires were also measured. The critical current densities ($j_c$) for the 70 nm diameter and the 35 nm diameter nanowire at 0.1 K were $8.7 \times 10^4$ A cm$^{-2}$, $1.2 \times 10^4$ A cm$^{-2}$. These are three orders of magnitude smaller than the bulk values of $j_c \sim 2.57 \times 10^7$ A cm$^{-2}$ measured for aluminum strips of dimension 3.00 mm $\times$ 0.35/2.5 μm $\times$ 1.24 μm. Reduction of this order in $j_c$ from the bulk value has been seen in other single crystal nanowires like Zn [3] and Sn [47] and hence, is not unexpected. Earlier studies done on amorphous AlNW have reported values of $j_c \sim 8.3 \times 10^3$ A cm$^{-2}$ in nanowires of dimensions similar to the dimensions of the nanowires under study [86]. A possible explanation for the general trend of reduction of $j_c$ in nanowires, is the importance of fluctuations in reduced dimensionality systems [87]. Fluctuations in quasi 1D systems can weaken the superconductivity and enable small currents to completely destroy the long range order.

In summary, systematic four probe transport measurements on single crystalline AlNWs of different diameters show that the superconducting properties of the nanowires are in agreement with expectations. The availability of these AlNWs of controllable diameters, which are surrounded by a stable, insulating oxide layer opens some exciting avenues for individual nanowire measurements on single-crystal wires. We begin by attempting to see the APE in
individual nanowire measurements. Since the wires are contacted with FIB, the materials available for the electrodes are normal Pt and superconducting W. The $H_c$ of the superconducting W is $\approx 8$ T which is much larger than the $H_c$ of the AlNWs. Therefore our usual modus operandi of applying a field to drive the electrode normal and see the enhancement in the $I_c$ of the nanowire cannot be used. Performing the following two experiments solved this problem.

Measurements were made on two different single 70 nm diameter wires, one of which was contacted with four normal Pt electrodes and the other with four superconducting W electrodes as shown in inset of Figure 3-9(a). The distance between the voltage electrodes for both wires was $\approx 2.5$ µm. Figure 3-9(a) shows that the $I_c$ of the wire with the normal Pt electrode was 1.5 µA while the $I_c$ of the wire with superconducting W electrodes was 0.4 µA at 0.1 K. An identical experiment was performed on a 200 nm diameter ANW. The $I_c$ with normal Pt electrodes was 2 µA while the $I_c$ with the superconducting W electrodes was 13 µA (Figure 3-9(b)). The weakening of superconductivity in the presence of a bulk superconductor is again not seen in the thicker 200 nm diameter ANWs. The $I_c$ for the 200 nm wire contacted by W electrodes is actually much higher than that with Pt electrodes. This may be a consequence of the standard proximity effect of the W electrodes on the thick Al wire. As there are no applied magnetic fields in this experiment, this serves to definitively decouple the APE seen in the 70 nm wire from negative magnetoresistance caused by a weak applied magnetic field [88–90]. It is worth noting that even though the length of 70 nm diameter ANW between the W electrodes is only 2.5 µm, the superconductivity of the ANW is not completely suppressed by the W, unlike in the case of 2 µm long ZnNWs with Sn electrodes [3]. An enhancement of $I_c$ rather than a complete suppression of superconductivity by the superconducting electrode is more akin to the behavior of ZnNWs with Pb electrodes [71]. Initially this was thought to point to the APE
strength being dependent on the nature of the superconducting electrode. However, if the results in reference [71] are carefully examined, it is apparent that to see a complete suppression of superconductivity, an excitation current from a particular range of excitation currents has to be chosen. This is also clear from figure 3-1(d) that shows the dependence of critical current of the nanowire on the applied field. If the suppression of superconductivity is to be seen, an excitation current above 1.6 µA has to be chosen (for that particular sample). Therefore it seems that in the samples in which a complete suppression was not seen, both in reference [3] and in figure 3-7, by changing the excitation current to a value closer to $I_c$, such a suppression could indeed have been seen. Let us re-examine the results shown in figure 3-2 in the light of this information. The nanowires contacted with bulk Sn electrodes (panel (b)) show a complete suppression of superconductivity whereas the nanowires contacted with bulk In (panel (a)) do not. This was taken to mean that Sn is stronger than In for the APE. However, if we look at the V vs. I plots for these two samples, we see that the $I_c$ for the sample with In electrodes is higher ($\sim 0.5$ µA) than that of the sample with Sn electrodes ($< 50$ nA). The actual excitation current being used for these measurements was 100 nA, which is in the correct range for the sample with the Sn electrodes but not for the sample with the In electrodes. The absolute value of the $I_c$ depends on a number of parameters like the number of nanowires and is not an indicator of the APE. If a higher current (0.4 µA for example) was used to measure the ZnNWs with bulk In electrodes, a complete suppression might have been seen as in the case of ZnNWs with Pb electrodes in reference [71]. The importance of the excitation current was not realized at the time of these experiments.
With the aim of measuring $I_c$ of the same 70 nm diameter ANW with both superconducting and normal electrodes, a 6 electrode geometry was used (inset of Figure 3-10). Current was introduced using two normal Pt electrodes (#1, #6 in the inset of Figure 3-10) and two superconducting W (#4, #5) and two normal Pt (#2, #3) electrodes were deposited to measure the voltage. Graphs of the normalized resistance measured between two normal Pt electrodes 2 and 3 ($L = 2 \mu m$) and one normal Pt and one superconducting W electrode, 3 and 4 ($L = 2 \mu m$), are shown in Figure 3-10. The $I_c$ for the segment with two Pt electrodes was 0.6 $\mu A$ whereas the $I_c$ for the segment with one Pt and one W electrode was 0.3 $\mu A$. It is not clear why the $I_c$s measured with the 6-lead configuration are different from those shown in Figure 3-9. It is likely that with additional FIB processes the ANW is made thinner than the wires contacted with only Pt or only W electrodes. Nevertheless, this measurement confirms the results shown in Figure 3-9 namely, the superconductivity of the ANW segment close to the superconducting W electrode is
weaker than the superconductivity of the Al NW near the normal Pt electrodes. It must be noted that the current in this experiment is not passing through the superconducting W electrodes. From this result, it can be concluded that the bulk superconductor need not be part of the current circuitry for this effect to manifest. Also, the APE is seen here again in the absence of an external magnetic field, by changing the nature of the electrodes.

![Figure 3-10](image.png)

**Figure 3-10:** The inset shows an SEM image of the sample being measured. A 70 nm Al nanowire is contacted with 6 electrodes. Electrode 1, 2, 3 and 6 are made with normal Pt and electrodes 4 and 5 are made with superconducting W. Electrode 1 and 6 current through the nanowire. Normalized voltage vs. applied current for segment 2-3 between normal Pt electrodes and segment 3-4 between one Pt and one superconducting W electrode is measured at 0.5 K. The length of both the segments is ~ 2 µm and the diameter of the wire is 70 nm.

Although the measurements on crystalline individual AlNWs with FIB assisted electrodes offer much insight into the APE, there are several constraints on the parameters of the systems being studied. The diameters of the nanowires are limited by the pore sizes of the templates available. More importantly, the only superconducting electrode the FIB technique provides is W which has an $H_c$ much higher than that of the AlNWs. To gain access to a larger range of diameters and to superconducting electrodes with smaller $H_c$, it was decided to synthesize...
nanowires and electrodes using e-beam lithography coupled with evaporation. The experimental results are discussed in the following section.

3.5 Four-Probe Transport Measurements on Granular Nanowires

In this section we report on our experimental studies of the anti-proximity effect in granular single aluminum nanowires (AlNW) contacted with bulk aluminum electrodes (the synthesis is described in section 3.2.2). As expected, the AlNW becomes superconducting as the temperature is reduced to its critical temperature \( T_c \) and loses its superconductivity when the temperature is further lowered and the \( T_c \) of the electrode is reached. In this ‘normal’ state induced by the superconductivity of the electrode, the resistance of the nanowire is found to fluctuate between the normal state resistance \( R_N \) and 0 \( \Omega \). The fluctuations point to the fact that the superconductivity is lost due to phase disorder rather than a suppression of the amplitude of the order parameter. The regime of nanowire diameter, the temperatures, the fields and the excitation current at which the APE induced normal state occurs are specified. The disappearance of phase slips as soon as the environment of the nanowire becomes resistive is seen. The measurements are fitted to the presence of current induced phase slips and heating effects and theoretical models explaining the absence of these phase slips with a dissipative environment are discussed.

3.5.1 The Anti-Proximity Effect

A number of AlNWs with different areas of cross section and length were studied in order to explore the parameter space of the APE. At the time of the experiments the important
parameters for seeing the APE were the area of cross section of the nanowire relative to $\sim \xi^2$ and the length $L$ of the nanowire compared to the charge imbalance length ($\Lambda_Q$). Table 3-1 summarizes the dimensions of the samples studied (the thickness of all the samples is 50 nm), the measured $T_c$s, the measured resistivities ($\rho$), the calculated coherence lengths and charge imbalance lengths and the presence or absence of APE. The coherence lengths at 0 temperature shown in the table are calculated using the BCS dirty limit formula $\xi = 0.855(\xi_0 l)^{0.5}$ where $\xi_0$ is the bulk coherence length (~1600 nm for Al) and $l$ is the mean free path. The mean free path is calculated using the measured resistivity of the nanowire and the fact that the product $\rho l$ is constant for a given metal and the constant for Al = $9 \times 10^{-16}$ $\Omega m^2$ [91,92]. In literature other values of $\rho l$ of the same order of magnitude but differing by upto a factor of 3 from each other can be found (from $4 \times 10^{-16}$ $\Omega m^2$ to $15 \times 10^{-16}$ $\Omega m^2$). We have chosen a middle value. For the wires of finite lengths used in the current study, the conventional way of extracting the coherence length from $H_c(T)$ near $T_c$ cannot be used due to complications associated with the alteration of the boundary conditions by the magnetic field. The charge imbalance length is calculated using the formula $\Lambda_Q = (D\tau_Q)^{0.5}$ where $D$ is the diffusion length and $\tau_Q$ is the quasiparticle relaxation time [35]. The diffusion length is given by $D = \frac{1}{3}v_F l$ where $v_F$ is the Fermi velocity ($2.03 \times 10^6$ m/sec for Al) and $l$ is the mean free path. The quasiparticle relaxation time for aluminum microbridges is found to be ~ 50 ns in reference [93]. Another experiments on bulk aluminum has found a smaller relaxation time of 2 ns [94]. However, this number is unusually small compared to many other relaxation time measurements and so we do not use this. We are aware that the relaxation time may change to smaller values in the presence of a current [95] or a field [35]. Since, we are only using the estimated charge imbalance length for a rough estimate of the length to charge imbalance length ratio, these minor changes do not affect our general conclusions.
the table, it seems that the APE is not seen in the samples with the lowest $T_c$s (lower than 1.25 K). These are also the samples with the lowest $\rho$ and hence the highest $\xi$s. A similar pattern was noticed in the Zn nanowire samples in reference [72] where it was commented that no APE was seen in samples with $T_c$s lower than 0.75 K. However, no further analysis of this fact was done in this reference. The fact that the APE here is seen in the samples with the smallest $\xi$s is contradictory to the understanding gained from the crystalline samples for which the APE is only seen in samples with diameter $d < \xi$. In granular samples also, when the width of the sample is increased to 500 nm, the APE disappears. There is definitely diameter dependence to the APE. It may be however, that the condition $d < \xi$ is not the relevant condition for granular samples.

Table 3-1: APE in Granular Al Nanowires

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Length (µm)</th>
<th>Width (nm)</th>
<th>$T_c$ (K)</th>
<th>$\rho$ (Ω-m)</th>
<th>$\xi$ (nm)</th>
<th>$\Lambda_Q$ (µm)</th>
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<td>6</td>
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<td>23.72</td>
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</tr>
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</tr>
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</tr>
</tbody>
</table>

The cross sections of both the granular Zn and granular Al NWs for which the APE is being seen are larger than the corresponding areas of cross section of the crystalline wires. For example, APE is seen in crystalline ZnNWs with cross sectional area 1256 nm$^2$ but, not in crystalline ZnNWs with cross sectional area 3848 nm$^2$ [3]. In contrast, in granular ZnNWs, they are seen for nanowires of cross sectional area 6000 nm$^2$ [72]. The calculated coherence lengths for the crystalline and granular ZnNWs are not very different (~150 nm for crystalline, ~ 200 nm
for granular). One plausible explanation is that by the condition $d < \xi$, none of the granular NWs are in the APE regime. The higher $T_c$ nanowires are the ones with smaller grain size – with higher stresses: either grain size $< \xi$ becomes the relevant condition for these nanowires or the superconducting coupling in the stressed material is changed to yield a higher $\xi$. Either of these conditions would lead to APE in the nanowires with the smaller grain sizes. The samples for which the APE is seen are discussed further below. The other samples are shown in Appendix B.

Figure 3-11: (a) Resistance as a function of temperature at different applied fields for an individual 120 nm wide, 50 nm thick, 3 µm long Al nanowire (sample 1). The excitation current for this measurement is 50 nA. The inset shows an SEM image of the sample along with the 3-electrode measurement geometry. (b) Resistance as a function of applied current at different fields for the same sample. (c) Resistance as a function of temperature at different fields for the same sample at an excitation current of 2 µA. (d) Resistance as a function of field at different temperatures for the same sample at an excitation current of 2 µA.
The inset of figure 3-11 shows a single AlNW prepared using e-beam lithography contacted with bulk Al electrodes (sample1). This setup is similar to the experiment on Zn Nanowires described in [72,75]. A three-electrode measurement (as indicated in the inset) was done to enable simultaneous determination of $T_C$, $H_C$ and $I_C$ of the electrodes and the wire. The wire is 120 nm wide, 50 nm thick and 3 µm long. In the $R$ vs. $T$ measurements (figure 3-11(a)) with 50 nA excitation current two distinct superconducting transitions were seen in the absence of a magnetic field. The transition with $T_C = 1.8$ K corresponds to the AlNW and the transition with $T_C = 1.2$ K corresponds to the electrode. The $H_C$ of the AlNW and the electrodes were found to be 4500 Oe and 280 Oe respectively. It is important to note that at this excitation current, no suppression of superconductivity of the AlNW is seen. Figure 3-11(b) shows the $R$ vs. $I$ behavior of the same sample as a function of the applied field ($H$). Each data point corresponds to an average of 50 resistance measurements made by the instrument at a given $H$ and $I$. In the absence of an external magnetic field, two jumps corresponding to $I_C$s of 1.8 µA and 3.5 µA were seen. At the first $I_{c1}$, the resistance changes from 0 Ω to ~ 427 Ω. At the second $I_{c2}$, the resistance increases to ~ 862 Ω. Both these $I_C$s are significantly lower than the expected $I_C$ of the electrodes (~ 13 mA) at this field [76] and must have their origin in the AlNW. The interesting feature of the measurement is that in the presence of a field of 250 Oe, at which the electrodes become normal, the lower $I_{c1}$ of the wire increases from 1.8 µA to 2.3 µA, an increase of 0.5 µA. This enhancement in $I_C$ when the measurement electrodes are normal is a signature of the APE and has been demonstrated even in the absence of a magnetic field [65]. On revisiting the $R$ vs. $T$ behavior of this sample at an excitation current of 2 µA (figure 3-11(c)) which lies in the regime of enhanced $I_C$ on application of field (figure 3-11(b)) the effect of the electrodes can be seen more clearly. At low temperature at 150 Oe, the electrodes are superconducting, therefore the
AlNW is not completely superconducting. As the temperature is increased, at a $T_c$ of ~ 0.5K, the bulk electrodes lose their superconductivity. The AlNW becomes superconducting. On further increasing the temperature, at a $T_c$ of 0.75 K, The AlNW becomes normal. In the APE induced resistive state, the resistance of the nanowire has fluctuations. These fluctuations persist in all the samples and can also be seen in earlier studies done on the APE [3,71,75].

The fluctuations are even more apparent in figure 3-11(d) in which the resistance is plotted as a function of applied field at different temperatures. At low fields, when the electrodes are superconducting, the wire has a finite resistance. When the field is increased and reaches the critical field of the electrode, the electrodes become normal and the wire becomes superconducting. The resistive state seen at low field has many fluctuations in resistance.

### 3.5.2 Bistability and Switching

A 4-electrode measurement was made on another sample (sample 2) prepared the same way as sample 1. This AlNW was 130 nm wide, 50 nm thick and 5 µm long (inset of figure 3-12(a)). The large difference in resistivity between sample 1 ($2.22 \times 10^6 \Omega\cdot m$) and sample 2 ($3.16 \times 10^7 \Omega\cdot m$) may be because of different average grain sizes caused by difference in evaporation rates. The transport properties of this sample are in agreement with sample 1. The enhancement in $I_c$ on application of field is 0.35 µA. The ‘weaker’ APE might be because sample 2 is longer than sample 1. The R vs. T behavior of the sample at high excitation current (2.5 µA) is shown in figure 3-12(a). It matches closely with that seen in figure 3-11(c). The R vs. H behavior of the sample at high excitation is shown in figure 3-12 (b). This behavior also matches closely with that of sample 1. The fluctuations seen in the APE induced resistive state are very apparent in this sample.
It is important to note that in all the graphs discussed so far, each data point corresponds to an average of 100 resistance measurements made by the instrument at a given T and H by applying DC currents of +2.5 and -2.5 µA alternatingly. The frequency of the square wave current signal was 15 Hz. The resistance was only measured when the current was stable at its final
value. The same measurement was repeated by averaging over just 2 measurements (one with a DC current of +2.5 µA and the other with a DC current of -2.5 µA). The result of this measurement at an applied field of 300 Oe is shown in figure 3-12(c). For this graph only one measurement is made at each temperature. The fluctuations seen in the 50 point averaged measurements as well as the smooth transition from the normal state to the superconducting state disappear.

There is a steady (almost linear) drop in the resistance between 0.9 and 0.7 K and a weak linear dependence is also seen below 0.7 K. This is attributed to the interface region between the AlNW and the Al electrode where the wire merges into the electrode. The total value of the interface resistance (estimated from the drop) is ~ 15 Ω. If this smooth background linear resistance is subtracted from the data, only 3 possible resistance values are seen: the normal state, the zero resistance state and a middle state. The scatter in the values of these resistances is less than 0.2 Ω out of measured resistances of ~ 240 Ω. Using the slopes of the drops in the regions between 0.83 and 0.69 K (60.8 Ω/K) and the region below 0.7 K (8.29 Ω/K), the normal state resistance at 0.28 K (if the wire is normal) can be calculated. The resistance at 0.8 K is 236.4 Ω so the resistance at 0.28 K would be [236.4 Ω – (0.14 K x 2 x 60.8 Ω/K) – (0.4 K x 8.29 Ω/K)] = 214.6 Ω. The superconducting state resistance is = 2.8 Ω (this is because the electrodes are normal at this field of 300 Oe). So, if the instrument measures one of each of these values, the resulting average of the two measurements would be 108.7 Ω. The middle state measured by the instrument has a resistance of 104.5 Ω which is within 4% of the average of the normal and superconducting state. This is quite close considering that the normal state resistance has been quite roughly estimated. In later measurements we will see that the middle state actually agrees much more exactly with the mean of the normal and the superconducting states. Remembering the measurement technique that is averaging two resistance values, the simplest explanation of
the middle state is that it is a result of the averaging of the normal and the superconducting state resistances. Splitting each point obtained in the middle into two separate readings – one of the normal state and one of the superconducting state - the ‘instantaneous’ resistance that would be obtained with just one measurement (no averaging) is shown in figure 3-12(d) as a function of temperature at a field of 300 Oe. It is apparent that the resistance can take only 2 values, at any given temperature and field. Excluding a weak dependence on temperature coming from the interface, these values are: $R_s$ (0 $\Omega$) and $R_N$ (~240 $\Omega$). Near $T_c$, the nanowire shows switching between the normal and superconducting states. As the temperature is lowered further, the nanowire becomes completely superconducting. When the $T_c$ temperature of the electrode is reached (see figure 3-13 for $R$ vs. $T$ behavior of electrode at 300 Oe), the nanowire loses its superconductivity and begins to switch between the normal and the superconducting states again. It is worthwhile to note that the switchings are also seen close to $T_c$. This surprising result leads to a number of questions. The first concern is the presence of the Au coating on the AlNW. Although how the presence of a Au coating will cause this switching is unclear. However, to get a cleaner result, we repeat the experiment on a different sample (sample 3) without the Au coating.

Figure 3-13: Resistance of an Al electrode as a function of temperature at different fields. The constant 420 $\Omega$ resistance is added due to the dilution fridge measurement circuitry.
Before moving on to sample 3, a discussion of figure 3-13 is relevant. Figure 3-13 shows the R vs. T behavior of the sample at 50 nA excitation current. The resistance plotted here is the sum of the one way resistance of the Dilution Refrigerator measurement circuitry (~ 420 Ω), ~ 1 cm long gold wire (negligible), a superconducting In dot (negligible), one of the Al electrodes and the nanowire (0 below ~ 1.4 K at this excitation). At 0 field, the $T_c$ of the electrode is ~ 0.95 K and at 300 Oe field it is ~ 0.38 K (this agrees with the point of upturn of resistance of the nanowire as seen in figure 3-12(a)). This $T_c$ is not expected to change much with excitation current (in the range of currents being used) since the estimated critical current of the electrode is ~ 13 mA. However, increasing the excitation current might affect the area of interface between the electrode and the nanowire and this area is relevant to our results. The increase of ~ 30 Ω in the resistance on the application of the 300 Oe field might be because the In dots pressed onto the Al electrodes to connect them to the Dilution Refrigerator circuitry become normal at this field. The area of the Al electrode close to these macroscopic indium dots might be turning normal with them and contributing to the resistance. The area of the electrode close to the nanowire is far removed from the In dots and remains superconducting.

The third sample (sample 3) is identical to sample 2 in geometry and only differs in the fact that it is not coated with 10 nm of Au. The $H_c$, $T_c$ and $I_c$ of this sample are higher than the corresponding numbers for the Au coated samples. The R vs. T at different fields and R vs. H at different temperatures at low excitation current (50 nA) are shown in figures 3-14(a) and (b) respectively. The $T_c$ for the nanowire is 1.9 K at this current. The $T_c$ for the electrode can be estimated by the shoulder in the R vs. T graphs to be ~ 1.4 K. The $H_c$ for the wire is ~ 3000 Oe and the $H_c$ for the electrode (corresponding to the small central dip in the R vs. H) is ~ 300 Oe. All these numbers have a strong current dependence for the nanowire and a weaker dependence for the electrodes. Although the $I_c$ of the entire electrode must be very high (~ mA), the small area
of the voltage electrodes contacting the nanowire through which the current passes can be more strongly affected by the excitation current.

Figure 3-14: (a) Resistance as a function of temperature at different applied fields for an individual 130 nm wide, 50 nm thick, 5 µm long Al nanowire (sample 2). The excitation current for this measurement is 50 nA. In the measurements shown in this panel, each point corresponds to an average of 50 DC measurements. (b) Resistance as a function of field at different temperature for a 50 nA excitation current. (c) Resistance as a function of excitation current at different fields. (d) Resistance as a function of temperature at 0 Oe at an excitation current of 19.6 µA.

The R vs. I behavior (figure 3-14(c)) of this sample shows the enhancement of $I_c$ from 19.4 µA to 20 µA on the application of a 200 Oe field. When the field is further increased, the $I_c$ decreases. This enhancement of $I_c$ with the application of magnetic field close to the $H_c$ of the electrodes signals the presence of the APE. An excitation current of 19.6 µA, within the range of
the APE is chosen for the R vs. T measurements. The data from the R vs. T scans at a 0 Oe field without averaging is plotted in figure 3-14(d). At each temperature the resistance is measured 30 times. Because of the very high excitation current being used, the Tc of the sample is much lower than that seen in samples 1 and 2 and the temperature scan is therefore limited in range. The Tc of the electrode is higher than the Tc of the nanowire at this field and current. This measurement is therefore akin to the ZnNWs with bulk Sn electrodes and a suppression of superconductivity at all temperatures is expected (figure 3-1(b)). Above ~ 0.45 K, the sample is always normal. Below this temperature, the sample resistance shows three possible values: 445.8 Ω (RN), 223.2 Ω (~RN/2) and 0 Ω. The deviation from these values is within 0.4 % and the middle value is the average of the normal and superconducting state values to within 0.1 %. It is justified to conclude again that the middle state is a result of the averaging of the superconducting and the normal state. Each point in the middle is split into one point of RN and another of RS, while each point of RN and RS counts as two measurements of RN and RS. The resultant R vs. T behavior is plotted in figure 3-14(d). The state below 0.45 K is the APE induced resistive state and it is apparent that it is composed of switchings between superconducting and normal states. Since there is no Au coating on this sample, this phenomenon is clearly not caused by it. On applying a field of 200 Oe (the Hc of the electrodes at this current), the superconductivity of the nanowire is recovered as seen in figure 3-15(a). This is also akin to the ZnNW with Sn electrode measurement (figure 3-1(b)). Each point in figure 3-15 corresponds to a single resistivity measurement. The Hc of the nanowire is very low at this excitation current and at 250 Oe, the entire nanowire becomes normal at all temperatures (figure 3-15(b)).
Other AlNW samples without the Au coating are also found to have very high $I_c$ significantly constraining the parameter space for the exploration of the APE. Therefore, having proved that the APE and the switchings do exist in the Al samples without the Au coating and that their behavior in these regards does not differ from the samples with the Au coating we go back to samples that do have a Au coating.

Samples 4 and 5 are made in the same lithography and evaporation step and are identical in all regards except that sample 4 is 20 $\mu$m long and 100 nm wide and sample 5 is 5 $\mu$m long and 120 nm wide. Both samples 50 nm thick and coated with a 5 nm layer of Au. The transport properties of sample 4 are shown in figure 3-16 and those of sample 5 are qualitatively identical to these. The $T_c$ of both the samples at low excitation is $\sim 1.6$ K and the $H_c$ is $\sim 2500$ Oe. At these excitations the $T_c$ of the electrodes is $\sim 0.8$ K and the $H_c$ is $\sim 400$ Oe (see inset of figure 3-16(a) for R vs. T behavior of one of the electrodes).

Figure 3-15: Panel (a) shows normalized resistance vs. temperature (single measurements) for sample 3 at an applied field of 200 Oe. The superconductivity of the nanowire is recovered (compare to figure 3-14 (d)). (b) Resistance as a function of temperature for the same sample at an applied field of 250 Oe. The nanowire is completely normal at all temperatures.
The R vs. I at different fields (figure 3-16 (c)) shows an enhancement of $I_c$ with applied field from 3 μA at 0 Oe to 4 μA at 400 Oe. If any current from this ‘APE’ range is used, we should see the APE behavior in the R vs. T as we do in figure 3-16(d) (R vs. T for the same sample at an excitation current of 3.2 μA). Figure 3-16(d) shows the average of 50 resistance measurements to obtain each point. It is important to note that the fluctuations at low temperature...
in figure 3-16(d) where each point represents averaging of 50 DC measurements are more than those in figure 3-12(a) where each point represents averaging of 100 DC measurements. It should also be noted that the electrode transport measurement for this sample (inset of figure 3-16(a)) is quantitatively slightly different from figure 3-13. This is not surprising since the $T_c$ and $H_c$ of Al films are known to depend very sensitively on the evaporation conditions including evaporation rate, level of vacuum and level of oxygen in the evaporation chamber, presence of contaminants etc. [77,79].

The single point measurements (obtained as described for samples 2 and 3) at an excitation current of 3.2 $\mu$A are shown in figure 3-17 (a) and (b) for fields of 0 Oe and 200 Oe respectively. The resistance is measured 120 times at each temperature. Near the $T_c$ of the wire the wire switches from the superconducting to the normal state. As the temperature is further lowered, it goes into the superconducting state. Then, when the critical temperature of the electrode is reached (~ 0.8 K for 0 Oe), the wire begins to switch between the normal and the superconducting states. These switchings persist all the way to the lowest temperatures.

Figure 3-17: (a) Normalized resistance vs. temperature (single measurements) for sample 4 at an applied field of 0 Oe. (b) Normalized resistance as a function of temperature for the same sample at an applied field of 200 Oe. The resistance is measured 120 times at each temperature.
The current dependence of the R vs. T for sample 4 at an applied field of 200 Oe is shown in figure 3-18. Excitation currents of both 3.2 µA and 3.7 µA are within the range of currents to see the APE for this sample. The $T_c$ of the nanowire reduces from 0.85 K to 0.6 K on increasing the excitation current. Below these temperatures the nanowire is superconducting until the electrode becomes superconducting at a $T_c$ of ~ 0.32 K. As the electrode turns superconducting the nanowire acquires the APE induced resistive state for both the currents. It is interesting to note that the temperature for the onset of the APE induced resistive state does not change much on changing the current. This is not surprising since both currents are too small to significantly alter the $T_c$ of the electrode. However, the average resistance of the APE induced state is significantly higher with the higher excitation current.

![Figure 3-18](image.png)

**Figure 3-18**: Resistance as a function of temperature at different currents for sample 4 at an applied field of 200 Oe.

It is apparent that the bistability and switching phenomena are controlled by T, H and I. Phase diagrams indicating the regimes of bistability and switching were obtained. The phase diagrams showing the range of currents and fields at temperatures 0.2 K and 0.5 K at which bistability is seen are shown in figure 3-19 (a) and (b) respectively. The behavior of the cross bistability at other temperatures can be extrapolated from these. The plots are obtained by
plotting the normalized resistance (single measurement) as a function of field and current for sample 5. The red dots correspond to the normal state (resistance = $R_N$) and the blue the superconducting state (resistance = 0 Ω). At low currents (below 0.8 μA for 0.2 K and below 1 μA for 0.5 K) the transition from the superconducting state to the normal state is continuous (region I in figure 3-19 (a)). At higher currents, the resistance switches between the normal and the superconducting states near $H_c$ before the wire becomes completely normal, as can be seen in figures 3-19 (a) (region II) and (b). The corresponding oscillations near $T_c$ can be seen in figures 3-17 (a) and (b). There is another region (III in figure 3-19 (a)) of bistability at low temperature and low field (below $H_c$ of the electrodes). This region corresponds to the low temperature bistability in figures 3-19 (a) and (b).

Figure 3-19: Maps of regions of bistability and switchings for sample 5 at (a) 0.2 K and (b) 0.5 K
3.5.3 Control Experiments

To check the validity of the single point measurements before analyzing the data further, a large number of single point measurements were taken and numerically averaged. The results were compared to the averaged measurements obtained by the instrument. The comparison of the numerically averaged (from 120 points at each temperature) and the measured average data (from 50 measurements) is shown in figure 3-20. The comparison at low temperatures for sample 4 at 200 Oe shown in figure 3-20 (a). The comparison is similar at 0 Oe field also. The comparison close to $T_c$ at 0 Oe was obtained for sample 5 and is shown in figure 3-20 (b). The agreement at low temperatures is very good. The $T_c$ from the numerically averaged data however, is consistently higher than that obtained from the measured average. One way to explain this is to remember that the measurement introduces a current into the sample along with $I^2R$ heating. The average measurements take $\sim 1.6$ seconds for each data point whereas the single point measurements take only 0.06 second for each data point after which there is a 10 second interval with no current. It is therefore reasonable to suppose that if there is any heating in the sample, it is

Figure 3-20: Comparison of the numerically averaged and measured average data points for (a) Sample 4 at low temperature and (b) Sample 5 close to $T_c$. 
much greater in case of the averaged measurements compared to the single point measurements.

It is not clear why $I^2R$ heating does not cause a similar shift in temperature at low temperatures. Other than this slight quantitative discrepancy, the two kinds of measurements are in close agreement and it is reasonable to conclude that either one accurately represents the phenomenon.

![Figure 3-21](image)

**Figure 3-21**: Resistance as a function of temperature (single measurement) at different fields for Al electrode. The base resistance of $\sim 620 \, \Omega$ comes from the DR measurement leads ($\sim 420 \, \Omega$) and a normal nanowire ($\sim 200 \, \Omega$).

To check whether dimensionality of the system being measured has a role to play, single point measurements at high excitation current (2.5 $\mu$A) were also done for an Al electrode on one of the devices. The result of the measurement is shown in figure 3-21. No bistability and switching is seen and the resistance drop is continuous even with single measurements. The base resistance of $\sim 620 \, \Omega$ comes from the DR measurement leads ($\sim 420 \, \Omega$) and a normal nanowire ($\sim 200 \, \Omega$). The broad transition is a result of the difference in the sizes of the Al strips making up the electrodes.
3.6 Theoretical Model

Before discussing potential physical mechanisms, we must address the important experimental issue of heating. The first possibility is that the wires are heated by the current and the effect of the magnetic field is to enhance their thermal conductivity by increasing the quasiparticle density. Then the electron temperature of the wire would cool to a lower value. This cooling would then appear as an enhancement of superconductivity. In case of the observation without the magnetic field (eg. figure 3-14(d)) a similar explanation could hold. As the temperature increases, the thermal conductivity of the surroundings of the wire increase and the boundary resistance between the wire and the substrate decreases effectively cooling the wire and reinstating superconductivity. If this were the case, one could in principle translate values of current into electron temperatures by relating the resistive states with high currents at low temperatures to the resistive states just above the critical temperature at low currents. As the former resistive states can be destroyed by a weak magnetic field, one would expect the same thing to happen to the latter. This is clearly not the case. Moreover, in the case of heating, the IV curves of superconducting nanowires are expected to be hysteretic. This possibility has been carefully studied in reference [72] and the nanowires have been shown to be non-hysteretic. Having eliminated heating as an explanation of the phenomenon observed, we move on to possible physical mechanisms of the APE.

Electrical transport measurements discussed above give an experimental picture of the APE. However, an exact theoretical model elucidating the microscopic origin of APE is required to fully understand this novel phenomenon. In the following paragraphs, some theoretical models relevant to understanding the APE will be discussed.
Buchler et al. [20] investigated the conductance and quantum fluctuations in a thin superconducting nanowire of finite length coupled to the environment through appropriate boundary conditions. The coupling between the nanowire and the environment impose a drastic change in the phase-slip dynamics while modifying the wire’s low energy physics. They found that the environment plays a crucial role on the conductance of the finite-size nanowire and modifies the phase diagram of the system at $T = 0$ K. In this case, the disappearance of the superconductor to insulator quantum phase transition and its resurrection due to the wire’s coupling to its environment is characterized through the dimensionless shunt conductance $K = \frac{R_Q}{R_P}$, where $R_Q = 6.5$ k$\Omega$ is the quantum resistance and $R_P$ is the shunt resistance which characterizes coupling of the environment to the nanowire. When $K < 1$ (i.e. $R_Q < R_P$), a nanowire of either finite or infinite length, is in insulating/metallic state due to the proliferation of phase slips. In the case of $K > 1$, a highly conducting shunt relaxes the strain on nanowire leading to a superconducting state. In this case, quasi-long-range order and stiffness of superconducting order parameter survives at $T = 0$ K. In our system, the shunting resistance (represented by the contact resistance between the nanowire and the electrode $\sim 10$ $\Omega$) is always smaller than the quantum resistance which falls under the category of $K > 1$. So, even though this model highlights an important issue regarding the effect of environment on finite length nanowire, the observed APE cannot be explained using this approach.

Martin-Rodero et al. [96,97] developed a self-consistent theory consisting of a narrow superconducting channel coupled to two wider superconducting electrodes. In their model, wires of different lengths ($L$) were considered as superconducting mesoscopic weak-links. Our system resembles the theoretical case of $L \gg \xi_0$. In this limit, the theory predicts the existence of a well-defined core region of length $\xi_0$ at the center of the channel between the electrodes where the superconducting order parameter is nearly zero at $T = 0$ K and the phase shows an abrupt change.
In other words, there would be a phase-slip center at zero bias voltage. This phase slip center would lead to a very low value of critical current and a finite resistance at the core region. How this phase slip center disappears when the electrodes are normal is not addressed in the paper although one can imagine that under significantly different boundary conditions the solutions within the nanowire would change completely. Qualitatively, this calculation does describe the destruction of superconductivity in the superconducting nanowire by the superconducting electrodes. However, this model cannot explain the switching between the normal and the superconducting states. This model would instead predict a constant finite resistance of the nanowire when the electrodes are superconducting.

3.6.1 Vodolazov Model

A more quantitative mechanism using the time independent Ginzburg-Landau equations was proposed by Vodolazov et al. [73]. The paper decouples experiments seeing a negative magnetoresistance [88,89,98] from the experiments seeing the APE. The model is based on the argument that the phase-slips processes in quasi 1D superconducting nanowire are analogous to the thermal fluctuations in a point-like Josephson junction with a finite capacitance. It is known that an increase in the intrinsic dissipation \( W \) in Josephson junctions \( (W = V^2/R) \) suppresses both quantum and thermal fluctuations. The author argued that magnetic field can enhance the critical currents of the phase slips processes in nanowires and intensifies the intrinsic dissipation. Similar to the case of Josephson junctions, it would lead to a suppression of rate of fluctuations and a decrease in the fluctuated resistance. Time-dependent Ginzburg-Landau (TDGL) equation was used to describe the dynamics of absolute value of order parameter, \( |\Delta| \) and the phase gradient of the order parameter, \( \nabla \phi \), in the phase slip center. These dynamics are used to estimate the critical
currents, $I_{c1}$ and $I_{c2}$. The current $I_{c2}$ corresponds to the critical current measured on sweeping the current up starting from the superconducting state of the nanowire. It corresponds to the onset current of the phase slips. On sweeping the current down from the normal towards the superconducting state, the phase slips do not stop occurring at $I_{c2}$ and go on until a lower current $I_{c1}$. This corresponds to the retrapping current of the Josephson Junction. For short nanowires $L < \Lambda_Q$ the hysteresis disappears and the two critical currents are the same. This applies to the crystalline 2 µm and 6 µm long ZnNWs for which the $\Lambda_Q$ is calculated to be $\sim$ 22 µm. For the longer ZnNWs, the granular ZnNWs and the AlNWs however, the wires are far from this limit. Moreover, the critical current that we are measuring in our experiments is $I_{c2}$ since the current is always swept up for our measurements. Using the TDGL equation in 1D (width of the wire $< \xi$) with the appropriate boundary conditions the following expression is obtained for $I_{c1}$:

$$\frac{I_{c1}(H, L)}{I_{c1}(H = 0, L = \infty)} = \frac{-Q_0/Q_c + \cosh \left(\frac{L}{2\Lambda_Q}\right)}{\sinh \left(\frac{L}{2\Lambda_Q}\right)}$$

(45)

Where, $L$ is the length of the nanowire, $H$ is the applied field, $Q_0$ is the charge imbalance at the end of the nanowire and $Q_c$ is the charge imbalance in the phase slip center. When the electrodes are superconducting, $Q_0$ is 0. As a field is applied that makes the electrodes normal, the NS boundary moves closer to the end of the nanowire and $Q_0$ reaches a maximal value (with sign opposite to $Q_c$ when the boundary touches the end of the nanowire. This leads to maximum value of $I_{c1}$ for the field that makes the electrodes normal. The quantitative calculations for the enhancement of $I_{c2}$ are not provided and the following argument is used. Because the normal current exists at a finite distance from the NS boundaries inside the superconductor, the current $I_{c2}$
is enhanced too for wires with \( L \gg \Lambda_0 \). Indeed, when the normal current penetrates far into the sample it decreases the superconducting component of the current because \( I_s + I_n = I \). Hence, we need a larger applied current \( I \) to satisfy the condition \( I_{c2} = I_s \). Although the argument is sound, it is qualitative in nature. The quantitative predictions made are for \( I_{c1} \) and are not applicable to most of our results. Another problem is that the presence of a magnetic field is implied to be necessary to see this effect. Subsequent experiments have proved that this is not the case (figures 3-9 (b), 3-10, 3-14(d), 3-17 (a) are just a few examples of the APE without an applied field). The essential point of the theory however, is the changing of the boundary conditions and it is possible that it can be reformulated without a magnetic field. In spite of these two shortcomings, the theory explains a salient qualitative feature (enhancement of \( I_c \)) of the APE. Let us proceed to match some of the quantitative predictions of the theory with experiment.

The mechanism of Vodolazov uses the fact that the diameters of the wires are smaller than the superconducting coherence length to model them as a 1D system. The coherence length for the crystalline AlNWs in these experiments can be estimated using the value of \( \rho l \) (where \( l \) is the mean free path) as \( 9 \times 10^{-16} \, \Omega \, \text{m}^2 \) [91,92], the dirty limit coherence length \( \xi(0) = 0.855(\xi_0 l)^{0.5} \) and 1600 nm as the value for \( \xi_0 \). \( \xi(0) \) is estimated to be \( \sim 75 \, \text{nm} \). The fact that the APE is seen in 80 nm diameter nanowires but not in 200 nm diameter nanowires then is supported by the theory. In granular AlNWs, the calculated coherence lengths are listed in table 3-1. Although all the nanowires are close to fulfilling the condition \( d < \xi \), the APE is not seen for some of them. In fact, for the granular NWs it seems that the APE is only present in the nanowires with the smaller \( \xi \). Either the calculation of \( \xi \) for these systems or the condition \( d < \xi \) needs to be modified for these nanowires. The model also predicts a weakening or absence of the APE in nanowires with length \( L > \Lambda_0 \) (the charge imbalance length). In the transport data shown in figure 3-7, the APE is seen in 50 \( \mu \text{m} \) long ANWs. The charge imbalance length for this sample is calculated to be \( \sim 19 \, \mu \text{m} \).
In comparison, the charge imbalance length of the crystalline ZnNWs was calculated to be 22 µm, and this was used to explain the relatively weak APE in 30 µm long Zn NWs. In a separate case, ΛQ in Sn nanowires used in [29] was estimated to be 750 nm. Since, lengths of the Sn nanowires were in the range 6-30 µm, it is not surprising that APE was not seen in those nanowires. In case of granular nanowires, in reference [72], the strength of the APE measured by ΔIc was compared for 1, 2, 4 and 10 µm long wires. The effect was found to be strongest for the 4 µm long wire and almost undetectable in the 10 µm long nanowire. The authors concluded that the APE was strongest when the wire was of intermediate length as suggested by Vodolazov’s model. In our experiment on the other hand the APE was also seen in a 20 µm long AlNW (sample 4, figure 3-14) and the strength of the APE ~ 1 µA was of the same order as that for the 5 µm long nanowire (sample 2). This may seem surprising at first, but, we must remember that the absolute value of the length is not important only the ration L/ΛQ is. From table 3-1 we can see that this ratio is ~ 0.5 for sample 2 and ~ 2 for sample 4. The APE should therefore be weaker in sample 4. However, the d/ξ ratio for sample 2 is larger than that for sample 4 which may make the APE stronger in sample 4. Overall, since more than one parameter controlling the strength of APE is varying from sample to sample for the granular nanowires, it is difficult to obtain a straightforward interpretation. The only general trend that is seen for most of the samples is that the APE is strongest when the estimated L/ΛQ is ~ 0.6 – 0.7.

### 3.6.2 Fu Model

After the original APE experiments described in section 3.1, a theoretical model applicable to this system was given by Fu et al. [74] generalizing the resistively shunted Josephson junction to include superconducting nanowires. Details of how this mapping is done
are given in section 1.3.2. Through a duality transformation, connection between quantum phase slips and BKT vortices (instantons) in 1+1 dimensions is established. At $T = 0$ an isolated superconducting wire of finite length is equivalent to a classical two-dimensional electrostatic problem where bulk charges (vortices) interact with two metallic boundaries each representing the (imaginary-time) world line of the end points of the quantum wire. Because of screening, vortices separated sufficiently far apart in the imaginary-time direction always unbind, and the wire is normal even at $T = 0$. With shunt resistance $R$, the screening is incomplete. For $0 < R < h/4e^2$, and with $1/C = 0$, the vortices remain bound and the quantum wire is superconducting at $T = 0$. For the experimental setup in case of NW arrays, the contact resistance between the nanowire and the electrodes provides the shunting resistance and the PCM or AAM membranes provide the capacitance. For the single nanowire measurements, the Si/Si$_3$N$_4$ substrate provides the capacitance and the contact resistance with the electrodes provides the shunting resistance. In converting the experimental setup to the RCSJ model the nanowire connected to the two bulk superconducting electrodes gets converted to a nanowire in parallel with a resistor (equal to the two contact resistances) and in parallel with a capacitor. When the electrodes are normal, the contact resistance is non-zero thus providing a finite resistance in parallel with the nanowire. If there is a phase slip in the nanowire in this configuration, a finite voltage is induced in the nanowire and hence across the resistor in parallel with it. A finite voltage in across a non-zero resistor would require a current to flow through the resistor and is energetically unfavourable. Thus the occurrence of phase slips in the nanowire is suppressed therefore stabilizing the superconductivity. When the electrodes are superconducting, the contact resistance becomes zero and in effect there is no shunting resistor. Therefore, there is no extra energy cost to phase slips and they become more likely making the wire resistive. This model seems to cover the qualitative behavior of the APE quite adequately. However, the important parameters in these experiments
are the ‘characteristic’ diameter and the length of the nanowires that define the presence or absence of APE. It is difficult to obtain quantitative predictions for these quantities from this model. Moreover, the model needs to be further augmented to explain the bistability and switchings. The model does suggest, that the APE induced resistive state might be a good platform to study quantum phase slips. A qualitatively similar picture is also made in reference [20].

3.6.3 Pekker-Tinkham Model

Superconducting nanowires can be thought of as overdamped Josephson junctions [21,22,24]. In overdamped Josephson junctions, a phase slip fluctuation does induce a resistance, but by itself is not sufficient to switch the junction to the normal state. However, the resistance coming from the phase-slip fluctuations is associated with Joule heating. If this heating is not overcome sufficiently rapidly, e.g. by conductive cooling, then it has the effect of reducing the depairing current, ultimately to below the applied current, thus causing switching the normal state. A theoretical model of the stochastic dynamics that leads to the switching of current-biased nanowires from the superconductive to the resistive state has been developed in detail in reference [22] for the case of MoGe nanowires suspended above a trench. However, it is also relevant to our experimental system in which bistability and switching is seen. The only difference from reference [22] will be the addition of a heat dissipation term through the Si$_3$N$_4$ substrate on which the nanowire is patterned. In the model, the heat generated due to individual phase slip events in the wire is balanced against the cooling rate at which the heat is dissipated away from the leads that are held at a constant temperature and the heat dissipated away through the substrate. The phase slip is assumed to occur in a central segment far away from the
electrodes and a Langevin type equation for the time evolution of the temperature of the central segment is obtained. Ignoring the discrete nature of the phase slips this equation can be written as:

\[
\frac{dT}{dt} = -\alpha(T, T_b)(T - T_b) + \eta(T, I)\Gamma(T, I)
\]  

Here, \(T_b\) is the temperature of the bath, \(\alpha\) is the cooling rate, \(\eta\) is the heat ‘pulse’ provided by a single phase slip event and \(\Gamma\) is the rate of occurrence of phase slip events. This equation can be thought of as the equation for motion of a particle whose position is represented by \(T(t)\) in a potential \(U(T)\): 

\[
\frac{d^2T}{dt^2} = -\frac{\partial U}{\partial T}.
\]  

If the potential \(U(T)\) is plotted as a function of temperature at different excitation currents, it is seen to develop two minima at higher currents. The first minimum corresponds to the superconducting state with the temperature = \(T_b\) while the second minimum corresponds to the resistive state with temperature = \(T_{rs}\). This is the basis of the bistability. A local maximum at a temperature \(T_{sp}\) separates the two minima. If a single or multiple phase slips cause the temperature to rise beyond \(T_{sp}\), then the system chooses the minima at \(T_{rs}\).

Having understood the origin of the bistability, the second important thing to understand is the number of phase slips needed to switch from one minima to the other. For this, a mean first passage time \(\tau(T \rightarrow T^*)\) is defined which is the time taken for the system to reach a temperature \(T^* > T_{sp}\) starting from temperature \(T\). The mean switching time then would be \(\tau(T_b \rightarrow T^*) = \tau_s\).

A differential equation governing \(\tau(T)\) is found. The map of the number \(N(T_b, I)\) of phase slips needed to reach temperature \(T^*\) over the I-T\(_b\) plane was presented in Fig. 3 of reference [99] and is reproduced here in figure 3-22. This map was found to contain two important points. First the typical value of \(N(T_b, I)\) was only ten or fewer. Second, there is a region in the I-T\(_b\) plane in
which the occurrence of just one phase slip is sufficient to cause the nanowire to switch from the superconductive to the resistive state. The mean switching time in bistable current-biased systems can be measured directly by performing waiting-time experiments or it can be extracted from switching-current statistics. An important observation is that in the single slip to switch regime, the total rate of phase slip $\Gamma$ (including thermal and quantum phase slips) and the switching time $\tau_s$ will be related by $\tau_s = \Gamma^{-1}$.

![Figure 3-22](image)

**Figure 3-22:** Map showing number of phase slips required for system to switch from superconducting to resistive state as function of temperature and excitation current. The contour lines show the mean switching rates (solid) and the phase-slip rate (dashed). The depairing critical current (dashed-dotted line) is plotted for reference.

This theoretical model taken in conjunction with the Fu model to explain the appearance of resistance at low temperature fits the qualitative features of our experiment. The model was used by the creators to fit the experimental data of MoGe nanowires [100]. A good quantitative agreement with experimentally measured quantities in the low-temperature regime was not found.
However, the model is enabled to make quantitative predictions for stochastic switching from superconducting to normal state in superconducting nanowires and can be used to estimate if the picture we are forming for modeling our experimental system is reasonable. Some quantitative comparisons to the model are done in the next section.

### 3.6.4 Comprehensive Model and Fit to Experiment

There are two parts to understanding our experimental data. The first is to understand the APE and the second to understand the switching. The Fu Model explains the APE and fits the qualitative features of the experiment very well. The diameter dependence of the effect is a built in feature of this model since the analysis only holds for 1D nanowires. One feature it does not address explicitly is the length dependence of the APE. This aspect can be easily understood by looking at a phenomenological description of the process of stabilization of phase slips. The quantum phase slips are stabilized by a ‘dissipative’ environment. In the case of superconducting nanowires, normal electrodes represent the dissipative environment. The source of these normal electrons are the normal electrodes. Since, the normal electrons survive an average distance $\sim \Lambda_Q$ in the superconducting nanowire, the stabilization effect of the normal electrodes should be upto $\Lambda_Q$ away from the contact to the nanowire. It is therefore reasonable that this effect is dominant in nanowires with length $\sim \Lambda_Q$ as is found to be the case.

Another interesting point that comes to light in view of the Fu Model is that close to T$_c$, the electrodes are normal. In this region bistability and switching is observed. These switchings are likely to be mediated by thermal phase slips that cannot be dissipated in spite of the resistive environment. The switchings disappear as we go to temperatures lower than T$_c$. In this regime, the probability of the thermal phase slips is very low. Quantum phase slips can still occur but are
eliminated due to the coupling with the dissipative environment as explained in the model. At temperatures below the $T_c$ of the electrode however the dissipative environment becomes superconducting and quantum phase slips are no longer suppressed. Therefore the switchings that we see at low temperature are unambiguously caused by quantum phase slips.

Having understood the basic phenomenon, we can now move on to the statistics of the phase slip process. The formulae for calculation of thermal and quantum phase slip rates along with current dependent correction factors are discussed in section 1.2.2. Using $L = 20 \mu$m, $R_N = 1558 \Omega$, $\xi(0) = 100 \text{nm}$, $I = 3.2 \mu$A and $T_c$ (at 0 excitation) = 1.55 K we calculate the rate of $\Gamma_{\text{TAPS}}$ at different temperatures. At a temperature of $\sim 1.2$ K, this yields about 1 thermally activated phase slip every 10 seconds (corresponding to $\Gamma_\text{+} = 0.09 \text{per second and } \Gamma_\text{,}$ is negligible in this current biased case). To find $\Gamma_{\text{QPS}}$, the same formulae are used except $T$ is replaced by $T_{\text{eff}} = T_\ast + T_1 T$ in finding the phase slip rate $\Gamma_\text{,}$ and the attempt frequency $\Omega_\text{.}$ Here $T_\ast$ and $T_1$ are fitting parameters. To obtain these fitting parameters in the reference [22], the switching statistics have been used. We use an alternative technique following reference [23]. We know from our measurements that the rate of quantum phase slips has to be less than 1 per $1/30^{th}$ of a second since our single measurement lasts for $1/30^{th}$ of a second and we find the system staying in the superconducting state for that time. Using this value for $\Gamma$ in the formula

$$\Gamma(I) = \frac{I}{\tau_{\text{shift}}} \exp \left( -\frac{0.83\pi R_g I_{\text{co}} \left(1 - \frac{I}{I_{\text{co}}}\right)^{5/4}}{92 T_c} \right)$$

we can find the minimum value of $I_{\text{co}}$ (all the symbols and derivations for this formula are explained in section 1.2.2). This value is found out to be 5.6 $\mu$A whereas the measured value of $I_c$ for this particular sample is 5.2 $\mu$A. There are no free fitting parameters used to obtain this value. It must be pointed out that the measured value of $I_c$ is expected to be suppressed below the expected value $I_{\text{co}}$ by the 4/5 power of $(k_B T/\Delta F)$, with a
logarithmic factor depending on sweep rate so this lower number is close enough to the calculated value to show us that it is not unreasonable to expect this rate of quantum phase slips.

The fact that we do not see any switching of the system from the superconducting to the normal state while we are measuring is explained by the low probability of the phase slip with the excitation current we are using. However, the fact that the wire is in the normal state for ~ 50% of the measurements is surprising and inexplicable with this phase slip rate. Therefore, it is reasonable to think that the phase slip probability is enhanced while the current is being ramped up. That is, the phase slip probability depends not only on the value of I but also on dI/dt. This has been suggested in references [8,22,23] and is well known for Josephson Junctions. The explicit form of the dependence is expected to be logarithmic. If we think of it macroscopically, during the measurement, when the current has a steady value I << I_c for that particular sweep, the superconducting state is measured. When the current has a steady state value I >> I_c for a particular sweep the normal state is measured. During the current ramp, the value of I_c is logarithmically suppressed with dI/dT increasing the chances for the I >> I_c state to occur.

Finally, let us calculate the heat generated by a single phase slip to see if it is reasonable to suppose that we are in the single slip-to-switch regime predicted in reference [22]. We can set up a heat flow equation analogous to 46. The heating caused by a single phase slip is given by I^2R where R is the estimated resistance of a single phase slip center (since we know the normal current from a phase slip center survives for a distance Λ_Q) and I is the normal current in the phase slip center. The heat is dissipated away via (i) electronic heat conduction through the nanowire to the electrodes and (ii) phonon heat conduction through the substrate. The phonon heat conduction through the electrodes can be neglected because the cross sectional area of the nanowire (A_w ∼ 6 x 10^{-15} m^2) is much smaller than the area of contact of the nanowire with the substrate (A_c ∼ 6 x 10^{-13} m^2). In reference [22] the specific heat and the thermal conductivity of
the MoGe nanowires are not known and are used as a fitting parameters in the experiment. In case of Al however, the specific heat has been measured for bulk Al in the superconducting state [101] and it has been shown elsewhere that the heat capacity signature of superconducting nanowires is not significantly different from bulk [102]. We therefore feel justified in using the bulk specific heat of superconducting Al (0.02 mJ/(mole-K)). Detailed values of electronic and phonon thermal conductivities of AlNWs have been obtained by Li et al [103]. Therefore we do not need to use fitting parameters for the heat flow equation. The following equation is obtained for the final temperature \( T_f \) of the nanowire, after a single phase slip at bath temperature \( T_b \):

\[
T_f^3 - T_f^2 T_b + \frac{(C_v + \kappa A_w)}{\sigma A_t} (T_f - T_b) - \frac{l^2 R_n}{\sigma A_t} = 0
\]

(47)

where \( C_v \) is the specific heat, \( \kappa \) is the electronic heat capacity (we use the normal state value which gives us an underestimate of \( T_f \)) and \( \sigma T^3 \) is the Kapitza boundary conductance at temperature T. Using \( \kappa = 5 \times 10^{-3} \frac{W}{mK} \) and \( \sigma = 300 \frac{W}{m^2K^3} \) [103] we obtain a minimum value of \( T_f = 4.5 \) K for sample 3. At temperatures greater than this, the nanowire is normal. Similar values are obtained for the other samples. Therefore, given the measurement parameters, a single phase slip generates enough heat to make the nanowire switch from the superconducting to the normal state. We have therefore shown that a single QPS can cause the switch thereby mapping on each macroscopic quantum tunneling event to an easily measurable switch in the resistance state of the nanowire.
3.7 Conclusions and Outlook

Aluminum nanowires have been a favorite candidate for studying superconductivity for a number of reasons including their long coherence length and robustness on exposure to atmosphere. However, most studies in the past have focused on granular AlNWs. Here, we have developed a method to grow single crystal AlNWs and have studied them along with granular nanowires to prove that the effects we are seeing are not caused by defects and grain boundaries. Single-crystal Al nanowires have been prepared for the first time by template based electrodeposition at room temperature. XRD, HRTEM and SAED show that the deposited ANWs are single crystal with [110] as the preferred growth direction, homogenous diameters and surrounding oxidation layer. The availability of ANWs of controllable diameters, which are surrounded by a stable, insulating oxide layer opens some exciting avenues for individual nanowire measurements on single-crystal wires, including measurements to study quantum phase slip phenomena.

The anti-proximity effect, first observed in Zn nanowires has been confirmed in crystalline AlNW arrays establishing the universality of the phenomenon. From the studies on crystalline AlNWs the diameter dependence of the APE has been confirmed since the phenomenon is seen in 80 nm diameter NWs but not in 200 nm diameter NWs. Systematic four probe transport measurements on single nanowires of different diameters have been performed. These measurements show that the superconducting properties of the nanowires are in agreement with expectations with $T_c$ and $H_c$ enhanced from the corresponding bulk values as the diameter decreases. In these measurements the APE has also been seen in the absence of magnetic fields, clearly establishing that it is a function of the bulk measuring electrodes and ruling out the interpretation of the APE as a magnetoresistance effect. 6-electrode measurements on single
AlNWs with a combination of superconducting and normal electrodes have also been performed to confirm this.

The APE is also studied in granular AlNWs of varying diameters and length. These measurements shed light on each of the three aspects of the APE observed in earlier experiments viz. dependence on material of electrode, length dependence and diameter dependence.

In averaged resistance measurements of granular AlNWs as a function of temperature, field and applied current, the APE is clearly established to be excitation current dependent in agreement with the results of ZnNW arrays with Pb electrodes [71]. Understanding this current dependence calls for reinterpretation of the result in which the strength of the APE was thought to be dependent on the material of the electrode. In fact, the difference in the extent of suppression of the superconductivity may have been caused by the differences in the measurement current densities. For 6 µm long ZnNWs with Sn electrodes [3], the current density used for the measurement was $3.9 \times 10^7$ A/m$^2$ while for 6 µm long ZnNWs with In electrodes, the current density used for the measurement was $2.6 \times 10^7$ A/m$^2$. This is clearly one explanation for the weaker effect seen in the ZnNWs with the In electrodes. The current density for which the APE was not seen in the ZnNWs with Pb electrodes was $1.6 \times 10^7$ A/m$^2$. It was seen for $4 \times 10^8$ A/m$^2$.

For comparison, in the granular AlNW measurements, the APE is not seen in the low excitation measurements at $1.6 \times 10^7$ A/m$^2$ and seen in measurements at $5.1 \times 10^8$ A/m$^2$. The expected length dependence of the APE is confirmed and samples with the same length relative to the charge imbalance length are found to have approximately the same strength of APE as measured by the change in $I_c$ when the electrodes go from superconducting to normal. The diameter dependence of the APE is found to be different from what would be expected with the relationship that the APE is observable in nanowires with $d << \xi$. The APE is found to be present in nanowires with the smallest $\xi$ calculated using the BCS dirty limit which is valid for nanowires. These nanowires are
also the ones with the smallest grain sizes and the highest resistivities. Similar observations were also found for granular ZnNWs [72]. This apparent incongruity might be due to one of two possible reasons. The first is that in the case of granular nanowires grain size $< \xi$ becomes the relevant condition rather than $d < \xi$. The second is that due to the strain on the nanosized grains, the electron-phonon coupling and therefore the $\xi$ are different from what has been calculated. The first of these interpretations seems likely.

Most of the transport measurements on nanowires average the resistance obtained from several measurements (in this study most commonly 50) to reduce the noise. This yields smooth superconducting transitions and a finite resistance in the APE state. In this study additional measurements were performed on the granular AlNWs to enable extraction of data representing single resistance measurement. A phase diagram as a function of field, temperature and excitation current was obtained. Two regions were found in which the system was in a bistable state with switchings between the superconducting state and the normal state. One of these regions was close to $T_c$ and the other was at low temperatures. In the region close to $T_c$, the switching is mediated by thermal phase slips and in the low temperature regime, the switching is mediated by quantum phase slips.

In the region close to $T_c$, at low currents, the bistability and switchings were absent. The superconducting transition was continuous even with single measurements and fitted well to the LAMH theory [18,19]. Switching currents in superconducting Al nanowires have been studied carefully in reference [104]. Above an excitation current of $\sim 0.8 \mu\text{A}$ however, the transition region became bistable and switchings were observed in a small temperature regime around $T_c$ ($\sim 0.1\text{K}$). The width of the temperature regime for which the switchings were observed became broader with increasing excitation current (decreasing $T_c$). This is in agreement with expectations.
as the rate of phase slips goes as \( \exp \left( -\frac{\Delta F(U_c-I)^{5/4}}{k_BT} \right) \). The exponent becomes linearly larger with \( T \) but smaller with increasing \( I \) with the exponent 5/4. The net result of using higher currents is therefore an increase in the rate of thermal phase slips and hence a broadening of the bistable region. At low currents, the bistability is not observed for two reasons: a single phase slip in conjunction with the \( I^2R \) heating is not sufficient to cause the nanowire to become completely normal and the \( \Delta F \) is very small close to \( T_c \) (\( I=0 \)) giving a high probability of phase slip. This brings us closer to the traditional understanding of the rounded transition in reduced dimensionality systems where continuous phase slips give some finite value of resistance below \( T_c \).

At low temperatures, quantum phase slips cause bistability and switchings in the nanowire. The probability of quantum phase slips in the nanowire is very low. However, the measurement process which corresponds to the application of a large current bias along with a rapid current gradient (\( dI/dt \)) can enhance this probability. The process of phase slips however is still stochastic. If a single quantum phase slip occurs while the current is being ramped, the \( I^2R \) heating causes the entire nanowire to turn normal. If the quantum phase slip does not occur during the ramping, the wire stays in the superconducting state since the probability of a phase slip occurring with \( dI/dt = 0 \) is very low. Calculations of the expected critical current using the expected quantum phase slip rate agree with experiments.

These results are significant for a number of reasons. The first is that resistance measurements on nanowires to detect quantum phase slips have been inconclusive to date. These experiments offer a clean region in which quantum phase slips can be seen. Moreover, in these current biased nanowires each switching corresponds to a single quantum phase slip event. Probing individual phase-slip events via the nanowire switching thus offers a way of unearthing
and exploring the physics of nanoscale quantum tunneling of the one-dimensional collective quantum field associated with the superconducting order parameter. Thirdly, in superconducting qubits, it is assumed that the wires connecting Josephson junctions are ideal, i.e., that phase changes occur in the superconducting wave function only as a result of deliberate steps in the computing cycle. This assumption was thought to be justified as the nanowires are relatively thick [23]. These experiments show that in a large regime of measurement currents, thermal and quantum phase slips in the nanowire are significant. Lastly, these experiments help us unravel and understand the counterintuitive anti-proximity effect at a microscopic level.
Effects of Electrodes on Ferromagnetic Nanowires: The Long Range Proximity Effect

In a singlet (s-wave) superconductor, the spins of the electrons making a Cooper pair are antiparallel (the spin part of the wavefunction is given by \(|\uparrow \downarrow \rangle - | \downarrow \uparrow \rangle\) (see section 1.1.1). The spins of electrons in a ferromagnet, on the other hand, are aligned parallel to each other. This incompatible spin order between singlet superconductors and ferromagnets makes for new and interesting physics when the two are placed in contact with each other. When a superconductor is placed in contact with a normal metal, the Cooper pairs in the superconductor tunnel into the normal metal up to some distance. This makes the normal metal partially superconducting. This is known as the superconducting proximity effect (for details see section 1.3.2). The distance to which Cooper pairs survive in the non-superconducting material is the range of the proximity effect. This range, for a bulk normal metal can be ~ 1\(\mu\)m. For a bulk ferromagnet however, the incompatible spin order ensures that the singlet cooper pair cannot survive beyond a few nanometers.

A historical background of studies of the proximity effect in ferromagnetic systems is given in section 4.1. The details of the synthesis and characterization of Co and Ni nanowires used in our experiments are given in section 4.2. In section 4.3, the experiments done by us to study the proximity effect due to an s-wave superconductor on a ferromagnetic nanowire are described. A very long-range proximity effect, 2 orders of magnitude larger than that seen in bulk ferromagnets has been found (as described in section 4.3.1). In addition, a very large resistance peak close to the transition temperature (\(T_c\)) is found (section 4.3.2). Some light is shed on these phenomena by the control experiments done to understand their origins (section 4.3.3) and some additional interesting features like magnetoresistance oscillations and conductance peaks are
observed. Theoretical models explaining some of the observations are given in section 4.4 and conclusions and potential future experiments are outlined in section 4.5.

### 4.1 Historical Background

The superconducting proximity effect in ferromagnets has been widely studied as it offers, in addition to the interesting physics, the possibility of coupling the coherence effects of superconductors with the spin polarization of ferromagnets. However, as explained in the introduction to this section, the range of the proximity effect in a ferromagnet is expected to be only a few nanometers. This expectation has been confirmed in macroscopic (Fe, Ni)–In junctions [105] and submicrometre Ni–Al structures [106] where the spatial range of the proximity effect was found to be limited to $\sim 1$ nm.

In mesoscopic ferromagnet-superconductor (FS) hybrid structures, for the last decade several indications of a surprisingly long-range proximity effect have been found. In granular evaporated Co films 100 nm wide close to Al islands, coherence effects $\sim 180$ nm in range were calculated using Thouless energy calculations. The actual resistance drop in the wires was $< 1\%$ of the normal state resistance [106]. A recent experiment detected super-current in half-metallic ferromagnet CrO$_2$ thin film sandwiched between two singlet superconducting electrodes (Nb/NbTi) separated by 1 $\mu$m [107]. The authors attributed the effect to the superconductivity being spin triplet (spin wavefunction given by one of $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$ or $|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$ which do not preclude parallel spins) rather than spin singlet in nature. This claim was supported by experiments performed on Co films in proximity to superconducting Nb. In these experiments the range of proximity effect was found to depend on the presence of a weakly ferromagnetic CuNi or PdNi layer between the Co and the Nb [108]. It was speculated that the CuNi/PdNi layer provide an area of non-collinear magnetization. When the Cooper pairs from the singlet
superconductor go through this ‘spin active’ area, their correlations can change to triplet superconductivity. Further evidence for this triplet superconductivity in SF interfaces was found in [109]. The researchers constructed an interferometer from Ho, which is a conical ferromagnet (a conical ferromagnet is one whose total magnetic moment makes a helix along some axis). Interference effects indicating coherent electron transport were found with the interferometer arms upto 120 nm long. A review of some of some other interesting ferromagnet/superconductor interface effects is given in [110].

In ferromagnetic films, the long-range proximity effect seems to be well explained by the presence of triplet superconducting order generated by spin active interfaces. In all the experiments on ferromagnetic films, the samples were granular. The effects of grain boundaries on decoherence have often been discussed. Experiments on crystalline ferromagnets would enable one to get rid of these effects. Moreover, it would be interesting to check if these long-range proximity effects seen in ferromagnetic films persist in quasi 1d nanowires made of hard ferromagnets like Co and Ni. These objectives were achieved by experiments performed on ordinary, hard ferromagnetic crystalline nanowires in standard 4-probe measurements. The long-range proximity effect was observed in these systems [69]. The rest of this chapter focuses on these experiments.

4.2 Cobalt and Nickel Nanowires: Synthesis and Characterization

The Co and Ni nanowires (CoNW and NiNW) were synthesized using template-based electrodeposition into the pores of an AAM membrane (diameters 40 nm, 80 nm) and track-etched PCM (diameter 60 nm) respectively. The electrolyte for the Ni electrodeposition was an aqueous solution of 100 g/L NiSO₄, 30 g/L NiCl₂ and 40 g/L H₃BO₃ [111]. The pH of the solution was adjusted to 2.5 by adding drops of 1 molar H₂SO₄. For Co the electrolyte was made by
adding 200 g/L CoSO₄, 40 g/L H₃BO₃ with pH = 1.0 adjusted using 1molar H₂SO₄ [112]. The PCM membranes had Cr/Au/Ag (10nm/50nm/100nm) evaporated on them that acted as the cathode in the electrodeposition. A Pt anode was used along with a Ag/AgCl reference electrode. The CoNWs were electrodeposited at a potential of $V = -1.45 \text{ V vs. Ag/AgCl}$ while the NiNWs were electrodeposited at a potential of $V = -0.9 \text{ V vs. Ag/AgCl}$. The electrodeposition of Ni was tested at a range of potentials from -0.4 V to -4 V vs. Ag/AgCl. The crystallinity of the Ni NW is controllable by the applied potential [113]. 100 % Single crystalline Ni NW were not obtained at any of the potentials. With the applied potential of -0.9 V, more than 95% of the Ni NWs were found to be polycrystalline in a statistical study done using the TEM. This value of the potential was used to synthesize the nanowires used for measurement so that it was known with 0.95 confidence that the sample being measured was polycrystalline.

Figure 4-1: High resolution Transmission Electron Micrograph of a 40 nm diameter Co nanowire grown in an AAM membrane. The atomic planes can be seen to be lined up and an oxidation layer ~ 3 nm on the surface. The inset shows an electron diffraction pattern from the sample. Indexing of the pattern allows us to conclude that the wire is a single crystal with a hexagonal close packed structure with [0001] as the preferred growth direction.

XRD spectroscopy shows that the CoNWs are single crystalline while the NiNWs are polycrystalline. Figure 4-1 shows a high resolution TEM image of a single Co NW released from an AAM membrane. For obtaining this image the nanowire was prepared as described in section
2.2.2 after the membrane was dissolved in the organic solvent CH\textsubscript{2}Cl\textsubscript{2}. The image shows a 3-4 nm thick oxide layer on the surface of the nanowire. The crystal planes are well aligned confirming the single-crystal nature of the wire. The inset of the figure shows an electron diffraction pattern from the CoNW. The pattern is indexed to show that the nanowire is crystalline with a hexagonal close packed structure and the preferred growth direction of the nanowire is [1000]. There is upto 5% variation in the nanowire diameter due to inhomogeneity in the PCM pores.

Figure 4-2: (a) An X-Ray diffraction pattern from a 60 nm diameter Ni NW array embedded in a PCM. The peaks correspond to the (111), (200) and (220) planes and indicate that the wires are polycrystalline (b) Transmission Electron Micrograph of a 60 nm diameter Ni nanowire grown in a PCM membrane. The grain boundaries can be seen in the image. (c) Electron diffraction pattern from the sample. The ring pattern shows that each wire is polycrystalline.

The XRD spectrum of an array of NiNW embedded in a PCM is shown in figure 4-2(a). The pattern indicates that either each wire has multiple regions with different preferred growth directions or different wires have different growth direction. TEM has to be performed to see which of the two is true. The TEM shown in figure 4-2(b) shows the grain boundaries present in each wire. The electron diffraction pattern in figure 4-2(c) shows rings that indicate that the wire is polycrystalline ([64], chapter 18).

Magnetic force microscopy measurements were performed on the nanowires at room temperature and the wires were found to be ferromagnetic.
The nanowires were released from the membrane by dissolving the PCM in CH$_2$Cl$_2$ and the AAM membranes in 1M NaOH solution. The suspension obtained was cleaned and dispersed on a Si/Si$_3$N$_4$ substrate and contacted by a FIB system with superconducting tungsten (W) electrodes as described in section 2.3.2. An SEM image of the final sample can be seen in the inset of figure 4-3(a).

Granular NiNWs were made using e-beam lithography followed by e-beam assisted evaporation of Ni. The details of the technique are described in section 2.1.2. These nanowires were contacted using an FIB system with superconducting W electrodes.

A description of how the samples are connected to electronic transport measurement circuitry and placed in the refrigerator is given in a section titled ‘wiring the sample’ within 2.3.2 (a).

### 4.3 Four Probe Transport Measurements

The samples were cooled to low temperatures and their resistance as a function of temperature (T) and applied field (H) was measured.

#### 4.3.1 The Long Range Proximity Effect

The R vs. T measurements on an individual 40 nm diameter, 0.6 µm long (length L is defined as the distance between voltage electrodes) CoNW are shown figure 4-3(a) (the inset shows the measurement geometry). The vertical scale is normalized to the resistance at T = 6 K and the excitation current is 50 nA. The Co nanowire shows an onset of superconductivity near 4.2 K, slightly lower than that of the W electrode strip. Zero resistance, defined as a resistance smaller than the instrumental resolution (0.2Ω for 50 nA excitation current), is found below T =
3.5 K. Measurements with an excitation current of 1 µA also show zero resistance below T = 3.5 K with a resolution of 0.01Ω. The fact that a nanowire 600 nm long turns completely superconducting indicates that the spatial extent of the proximity-effect-induced superconductivity in the Co nanowire is at least 300 nm.

![Graph](image)

Figure 4-3: (a) Resistance as a function of temperature for a 600 nm long, 40 nm diameter Co NW contacted with superconducting W electrodes. The inset shows a scanning electron micrograph of the sample. There is a superconducting transition at ~ 4K and the wire becomes completely superconducting at 3.5 K (b) Scanning electron micrograph of W strips of the same dimensions as those used as electrodes. The inner strips are ~ 500 nm apart.

Two concerns that need to be addressed before such an interpretation can be unequivocally accepted is the spreading of the W electrodes and the leakage of current between the W electrodes. A careful study of the spreading of the FIB deposited W electrode was performed using EDX [70]. The electron beam was swept along a Ni nanowire with a W electrode deposited on it and the chemical composition was determined at points on either side of the electrode. The spreading of the W electrode was found to be at most 400 nm (200 nm on either side of the electrode defined by the FIB). Moreover, the entire extent of the spread may not be electrically conducting, making the impact on transport measurements smaller than 200 nm. The fact that the 600 nm long nanowire is superconducting therefore cannot be attributed to the
superconducting W electrodes being shorted. Even if the entire spread of the W electrode is conducting, the range of the proximity effect is at least ~ 100 nm which is still 2 orders of magnitude larger than the expected value of ~ 1 nm. To address the other issue of the leakage current between the two W electrodes, W strips of the same dimensions as the electrodes used on the sample were made on a Si/Si$_3$N$_4$ substrate as shown in figure 4-3(b). The strips are < 500 nm apart. The measured resistance at 1.8 K was greater than $10^5$ Ω indicating an absence of leakage current between the electrodes. It can be concluded that the supercurrent does pass through the nanowire and a proximity effect ~ 100s of nm does exist in the ferromagnetic CoNWs.

Figure 4-4 shows the R vs. T as a function of H for two CoNWs 40 nm in diameter (panel (a)) and 80 nm in diameter (panel (b)) contacted with 4 superconducting W electrodes (similar to the geometry in the inset of figure 4-3(a)). The applied field is perpendicular to the wire axis unless otherwise specified. The distance between the voltage electrodes, L = 1.5 µm for both the wires. Although neither of the wires go completely superconducting, both exhibit a large resistance drop when the temperature is lowered below the $T_c$ of the W electrode. In the 80 nm
diameter nanowire, the resistance shows a large drop to 50% of its normal state value at low temperature. From the magnitude of the drop, we estimate the range of the proximity effect in this wire to be ~ 325 nm. With the application of a magnetic field, the \( T_c \) shifts to lower temperatures as expected. The resistance drop in the 40 nm diameter CoNW is larger and the resistance drops to 11% of the normal state value at the \( T_c \) of the W electrodes. This suggests that the range of the proximity effect increases with decreasing diameter of the nanowire. To confirm the ferromagnetic nature of the nanowire \( R \) vs. \( H \) above the \( T_c \) was measured (figure 4-5). A negative magnetoresistance was observed as the magnetic field was scanned in both directions. Since magnetic field is perpendicular to the wire, there is a clear anisotropic magnetoresistance (AMR) contribution indicated by the negative magnetoresistance. AMR % can be determined by the following equation:

\[
\text{AMR}\% = \frac{R_{\text{max}} - R_{\text{min}}}{R_{\text{min}}} \times 100 \tag{48}
\]

For the CoNW it is found to be ~ 0.8%. The ferromagnetism of electrochemically grown CoNW has also been seen by other groups in traditional magnetization measurements [114].

The expected singlet coherence length (section 1.3.2) in Co nanowires is given by

\[
\xi_s = \sqrt{\frac{\hbar D}{k_B T_{\text{Curie}}}}, \quad \text{where } T_{\text{Curie}} \text{ is the Curie temperature and } D = (1/3)v_F l \text{ is the electron diffusion constant (here, } v_F \text{ is the Co Fermi velocity } \sim 10^8 \text{ cm s}^{-1} \text{ and } l \text{ is the mean freepath). The experimentally measured resistivities yield a singlet coherence length of 3.3 nm for the sample shown in figure 4-4(b), which is much smaller than the observed coherence length of 500 nm. This mismatch in the coherence length of singlet superconductivity with the observed range of the proximity effect makes the suggestion of triplet superconductivity in this system plausible.
It has also been suggested [43] that the transport in these nanowires may be ballistic which could lead to undamped singlet proximity effect. The estimated mean free path $l$ however, can be calculated from the measured resistivity to be $\sim 2$ nm. This would put the wire in the diffusive limit and rule out ballistic transport.

![Image](image_url)

Figure 4-5: Magnetoresistance behavior of an 80 nm diameter CoNW with $L = 1.5$ $\mu$m at 5.8 K. The image is reproduced from Wang et al., Nat. Phys. 6, 389 (2010)

In the experiments on proximity-induced superconductivity in ferromagnets described in section 4.1, the subject of grain boundaries and how they affect the range of the proximity effect was very relevant. To explore whether the presence of grain boundaries will change the range of proximity effect in ferromagnetic nanowires, the experiment was repeated for polycrystalline NiNWs.

Figure 4-6(a) shows the R vs. T at different H for a 60 nm diameter, 3 $\mu$m long NiNW. The resistance of the wire begins to drop at the $T_c$ of W (4.8 K). The residual resistance at 1.9 K (97.8 $\Omega$) is 52% of the normal state resistance at 6 K (187.7 $\Omega$). This implies the range of the proximity effect $\sim 700$ nm which is comparable to that found in the CoNW. The R vs. H at different temperatures is shown in figure 4-6(b). Interestingly, in the Ni nanowire we observe a small bump (negative magnetoresistance) near zero field at 3.5 K and 4.0 K. As discussed before,
this (AMR) is a signature of ferromagnetism and indicates that at least a portion of the Ni wire, which has shown an ‘incomplete’ superconducting drop, is still ferromagnetic. Since the polycrystallinity of the NiNW is only known with 95% confidence, these measurements were repeated for several NiNW. A similar range of the proximity effect was found for all the samples. From this we can begin to conclude that the long-range proximity effect is unaffected by the presence of grain boundaries. To further confirm this assertion, experiments measuring the range of the proximity effect were performed on a granular NiNW made using EBL followed by thermal evaporation as described in section 2.1.2. The nanowire was contacted with FIB assisted superconducting W electrodes.

The R vs. T at different field for the evaporated (granular) NiNW with superconducting W electrodes is shown in figure 4-7(a). The inset shows an SEM image of the sample. The nanowire is 250 nm wide, 35 nm thick and 3.5 µm long. At low temperature, the resistance drops to 65% of its normal state value. From this, the range of the proximity effect can be estimated to be ~ 600 nm. Unlike most of the electrochemically grown nanowires in which the resistance

Figure 4-6: (a) Resistance as a function of temperature at different applied fields for a 3 µm long, 60 nm diameter NiNW contacted with superconducting W electrodes. (b) Resistance as a function of field at different temperatures for the same NiNW. The image is reproduced from Wang et al., Nat. Phys. 6, 389 (2010)
shows a downward trend even at low temperature, for this sample, the resistance at low temperature seems to saturate.

The $R$ vs. $H$ characteristics at different $T$ are shown in figure 4-7(b). The $H_c$ is close to the $H_c$ of the W electrodes and AMR is not observed below the $T_c$. From both the $R$ vs. $T$ and $R$ vs. $H$ curves, the superconducting transition seems to occur in two steps. The $R$ vs. $T$ at 0 Oe field has a ‘foot’ from 3.3 K to 4 K and the $R$ vs. $H$ at the lowest temperature has a foot from 8000 Oe to 40000 Oe. The reason for the transition being in two steps is not known.

From these experiments, we can conclude that a long-range proximity effect exists in ferromagnetic nanowires contacted with superconducting electrodes. The range of the proximity effect is 2 orders of magnitude larger than that predicted by theory and measured in bulk ferromagnet/superconductor hybrid structures. The conflicting spin order of singlet superconductors and ferromagnets make it likely that the induced superconductivity in the ferromagnet is not singlet in nature. This indicates a strong possibility that the superconductivity in this system also may be triplet in nature. It has been suggested that the region between the W electrodes and the CoNW is damaged by the FIB process and may thus be largely inhomogeneous.
and act as a seeding ground for triplet pairing. Another explanation may be that the surface of the CoNW and NiNW are not ferromagnetic and the superconducting proximity effect is only on the non-ferromagnetic surface of the nanowires. A possible candidate for the non-ferromagnetic surface is the oxide layer on the nanowire surface. The proximity effect cannot be in the surface oxide layer since it is known to be insulating. It also is unlikely to be in the layer between the oxide and the metal since the nature of this layer changes very much from crystalline to granular nanowires while the proximity effect remains unchanged. A third possibility is that of an underdamped singlet Josephson supercurrent being set up between the two W electrodes. This possibility requires ballistic transport in the nanowires and is therefore unlikely. Moreover, we have conducted further experiments to rule out this possibility. These experiments are discussed in more detail in section 4.3.3.

4.3.2 The Peak Effect

Other than the extremely long-range proximity effect, another striking feature visible in figures 4-4(a) and (b) and 4-6(a) is the very large resistance peak (~ 25% of the normal-state resistance) found near the temperature of the superconducting resistance drop. A satisfactory explanation of this peak is yet to be found. Some qualitative properties of this peak are found to be the same from sample to sample while some are found to lack this universality. We will discuss both in the following paragraphs.

The ‘critical peak’ is preceded by a small dip on the high-temperature side of the peak. This pattern is seen almost in all the samples although the 80 nm CoNW in figure 4-4(a) seems to be an exception to this. Measurements in both warming up and cooling down scans show an absence of hysteretic behavior. Both the peak and the superconducting drop are stable on cycling the sample to room temperature. Resistance (R) as a function of the magnetic field (H) at
different temperatures for the 60 nm NiNW is shown in figure 4-6(b). At 3.5 K, the magnetoresistance peaks are symmetric under the change in the direction of the magnetic field. With increasing temperature, the two peaks move towards zero field and merge into a single peak at 4.6 K. At 5.5 K a peak can still be seen at zero field. This temperature however, is above the $T_c$ of the sample and the peak seen here is unrelated to the critical peak and corresponds to the AMR peak for the sample. Finally, the magnitude of the peak is inversely proportional to the magnitude of the superconducting drop. For samples that become completely superconducting, the peak is absent (figure 4-3(a)). Other than these features which remain unchanged from sample to sample, there are a few properties of the peak that are qualitatively different for some samples.

In all the samples discussed so far, the size of the critical peak decreases with increasing field. In a few samples, however, the peak size has been seen to increase with increasing field or even decrease and then increase with increasing field. An example of the latter is shown in figure 4-8 which shows the $R$ vs. $T$ at different $H$ for a 60 nm diameter NiNW contacted with 4 superconducting W electrodes. The wire is 2.5 µm long. The critical peak decreases in magnitude till a field of 1 T and then begins to increase in magnitude.

![Figure 4-8: Resistance as a function of temperature at different applied fields for a 2.5 µm long, 60 nm diameter NiNW contacted with superconducting W electrodes.](image)
For nanowires measured in an array configuration by squeezing between superconducting electrodes, the peak was not seen at all [70]. This makes it clear that the origin of the peak lies in the nature of the interface between the nanowire and the electrode. However, for some samples contacted using FIB, the peak was not present. At first the data suggested that samples that turned completely superconducting (like the one in figure 4-3(a)) did not show the critical peak. But, later other samples, like the evaporated CoNWs contacted with FIB deposited W shown in figure 4-7 that did not go completely superconducting also did not show the critical peak. A 60 nm diameter 2.5 μm long NiNW sample for which the peak was absent in perpendicular field (figure 4-9(a)) was rotated so that the field was parallel to the wire axis and the R vs. T as a function of H was measured again. The critical peak reappeared in this configuration (figure 4-9(b)). These deviations from the patterns mentioned earlier in the peak behavior might be because the peak is a very sensitive function of the nature of the interface between the nanowire and the superconducting electrode. Using the FIB technique, the nature of the interface cannot be carefully controlled.

Figure 4-9: (a) Resistance as a function of temperature at different applied fields perpendicular to the sample plane for a 2.5 μm long, 60 nm diameter NiNW contacted with superconducting W electrodes. (b) Resistance as a function of temperature at different applied fields parallel to the wire axis for the same NiNW.
This peak does not conform to charge imbalance peaks typically seen in superconducting mesoscopic systems since a very large magnetic field is required to destroy it. Charge imbalance peaks on the other hand are destroyed by very small applied fields [85,86]. Another mechanism used to explain resistance peaks in Fe-In junctions is spin accumulation [115,116]. In that case, however, the absolute peak value \( \Delta R \) was many orders of magnitude smaller \( (10^8 \Omega) \), as was the relative change from the normal-state resistance \( \Delta R/R \sim 0.05\% \). Furthermore, spin accumulation would assume that the induced superconductivity is singlet in nature, which seems inconsistent with the long range proximity effect. A satisfactory explanation of this peak is yet to be found. Since the peak effect seems to depend strongly on the interface, to get more consistent data about the peak, carefully controlled interfaces using an alternative technique like e-beam lithography followed by ion milling and evaporation need to be used.

4.3.3 Control Experiments

(a) Role of Superconducting Electrodes

In all the experiments described so far, the voltage and current electrodes were both made of superconducting W. To explore the precise role of the superconducting electrodes, a 40 nm CoNW sample was prepared with two normal Pt strips as voltage electrodes. The current electrodes were still superconducting W. The scanning electron micrograph (figure 4-10(a), inset) shows that the lengths of the Co wire between the neighbouring inner edges of the W–Pt–Pt–W strips are respectively 0.8, 2.4 and 1.7 µm. The R vs. T measurement in this geometry is shown in figure 4-10(a). Since the nearest W strip in this geometry is at least 800 nm away from the part of the nanowire being measured, the drop in resistance at the \( T_c \) of the W strip confirms the long-range proximity effect. A critical peak is also seen. The magnitude of the critical peak is very
small, of the order of 0.1% of the normal-state resistance. After the initial drop at 4 K, the resistance shows an upturn of 0.03 Ω below 2.4 K and 1.8 K. A similar upturn was reported in Co–Al junctions. This ‘reentrant’ behavior has been attributed to strong electron-electron interaction and ‘thermal effects’ due to energy dependence of diffusivity [110,117–119]. Such an upturn in R may also be present but not seen in all other samples in this study because it could have been swamped by the large drop in R resulting from the much more substantial proximity effect. Subsequent to the measurement with the configuration shown in the inset of figure 4-10(a), external leads to the electrodes were disconnected and the sample was returned to the FIB chamber and an extra W strip between the two voltage electrodes was added (figure 4-10(b)) and the sample was re-measured with the same current and voltage electrodes as those in the previous measurement. The additional W strip was not connected electrically. The resistivity of the sample at 6K changes from 5.3 µΩ-cm to 7.6 µΩ-cm. This might be because of oxidation of the sample in the time it spent in atmosphere although great care was taken to keep it in vacuum conditions for most of the time between the two measurements. Interestingly, the critical peak and the superconducting drop were both found to increase by two orders of magnitude, comparable to the magnitudes seen in the earlier samples with 4 W electrodes. This experiment shows that both the long-range proximity effect and the critical peak require only a superconducting electrode to be in contact with the nanowire; it is not necessary for the superconducting strip to be either a current or a voltage electrode.
Different Geometry: Long Range Proximity and Peak Effect

The long-range proximity effect observed in ferromagnetic films is attributed to triplet superconductivity with a large degree of certainty [108]. However, the mechanism of the long-range proximity effect observed in ferromagnetic nanowires needs to be further explored. One of the possible explanations for the long-range proximity effect was given by Konschelle et al. [43]. For all the experiments described so far, the system consists of a nanowire with at least 2 superconducting strips patterned on it. This system can be modeled as a superconductor-constriction-superconductor (S-c-S) Josephson junction. In the reference, the nanowire was assumed to have ballistic transport. The Eilenberger equation for it was solved and using the boundary condition of the two superconducting electrodes a Josephson supercurrent was calculated. This Josephson supercurrent with singlet correlations was found to be only weakly damped and was held responsible for the long-range proximity effect.

Figure 4-10: (a) Resistance as a function of temperature for a 40 nm diameter CoNW with 2 superconducting W current electrodes and 2 normal Pt voltage electrodes. The inset shows a scanning electron micrograph of the structure. (b) Resistance as a function of temperature for the same sample with an additional superconducting W strip patterned between the voltage electrodes. The inset shows a scanning electron micrograph of the structure. The image is reproduced from Wang et al., Nat. Phys. 6, 389 (2010).
To explore this possibility, an experiment with one superconducting strip on electrochemically grown single crystalline ferromagnetic CoNWs was planned. The setup of the experiment is shown in the inset of figure 4-11(a). The four measurement electrodes were all made of normal Pt and a superconducting W strip was deposited between the two voltage electrodes. The measurement in this geometry is carried out for varying distances between the inner edge of the Pt voltage electrodes and the outer edges of the W strip (d). For some samples this distance was ~ 700 nm making the total length of the nanowire being measured ~ 1.4 µm while for others this distance was ~ 2 µm making the total length of the nanowire being measured 4 µm. The two samples discussed the most in this section are called sample 1 and sample 2. Both these samples are CoNW 70 nm in diameter and for both the distance d between the Pt voltage electrodes and the W strip was 2 µm. The main purpose of this control experiment is to see whether the long-range proximity effect persists in this measurement geometry.

The R vs. T at different H for a 70 nm diameter CoNW with the distance d = 2 µm (Sample 1) is shown in figure 4-11(b). The total length of wire being measured is 4 µm since the
two Pt voltage electrodes are symmetrically placed with respect to the W strip (the W strip is 2 µm away from either of them). What the resistance being measured represents needs to be carefully considered as the W strip itself offers a path parallel to the CoNW to the current for some distance near the center of the nanowire being measured. We estimate the resistances of the two parallel paths. The W path has width ~ 5 µm, thickness ~ 250 nm and length ~ 200 nm (these are the dimensions of the strip). From the resistivity measured on experiments on FIB deposited W strips (4400 µΩ·cm), this yields a resistance of ~ 7 Ω. The CoNW path has diameter 70 nm and length 200 nm. With the resistivity of the CoNW (~ 5 µΩ·cm) we obtain a resistance of ~ 2.5 Ω. Therefore, it can be assumed that in the normal state the entire resistance comes from the CoNW. Below the Tc of Whowever, the W path becomes more suitable for the current. Therefore, in the total resistance drop that we see, we can attribute ~ 10 Ω to the current passing through the W strip. In figure 4-11(b) the resistance drops by 110 Ω to 35% of its normal state value. If 10 Ω of this drop is attributed to the current choosing to pass through the W strip, this suggests that the range of the proximity effect in this geometry is ~ 1.6 µm. This range is quite comparable to that seen in experiments discussed earlier in this chapter with two W electrodes on Co/NiNWs. It can be concluded that the long-range proximity effect is not mediated by singlet coupled underdamped Josephson supercurrents. Also, the peak effect is not present in any of the samples with one W strip. This observation may help in constraining possible theoretical models for the peak effect.
The magnetoresistance behavior of the samples with 4 normal Pt electrodes and 1 superconducting W strip was studied carefully and yielded some interesting results. Figure 4-12(a) shows the magnetoresistance in perpendicular applied field for sample 1 at different temperatures (the R vs. T of the sample was shown in figure 4-11(b)). The $H_c$ for the sample is close to the $H_c$ of the W strip. In the region of transition from the superconducting state to the normal state several resistance plateaus can be seen. These plateaus get smaller and finally disappear as the temperature is increased. The differential magnetoresistance ($dR/dH$) in the region of one of these plateaus is numerically calculated and found to exhibits periodic peaks with a period of $\sim 500$ Oe. A representative plot at temperature = 2.2 K is shown in figure 4-12(b). Figure 12(c) shows the peak position as a function of peak number. It is apparent that the

(c) Different Geometry: Magnetoresistance Oscillations
peaks are periodic as a function of field. The most common explanation for magnetoresistance peaks in proximity induced superconducting systems is vortex motion [120]. Using a single flux quantum and the formula \( H.A = \phi_0 \), where \( \phi_0 \) is a flux quantum, we get an effective area of 40000 nm\(^2\). One possibility is that the oscillations have their origin in the interface of the nanowire and the W strip. If we take into account the spreading of the W strip 200 nm on either side of the electrode defined by the software ([70], page 130), the width of the strip is 600 nm and the diameter of the nanowire is 70 nm. This gives an interface area of 48000 nm\(^2\). Given that the spread of the W electrode is and estimated number and varies slightly from sample to sample, it seems reasonable that the oscillations originate in the interface. The interface maybe an easy region for vortex penetration due to the large inhomogeneity and roughness generated by the FIB process.

The magnetoresistance in parallel field for sample 2 (\( d = 2 \) µm, diameter = 70 nm) is shown in figure 4-13(a). Large magnetoresistance oscillations with a period \( \sim 1.3 \) T at 1.9 K can be seen. The peaks move towards smaller field with increasing temperature. The period is therefore temperature dependent. The period of the oscillations does not change with increasing field. Except for the fact that they are seen deep in the superconducting state instead of close to \( T_c \), the oscillations are reminiscent of Little Parks (LP) oscillations (discussed in section 1.2.1 and seen in Bi nanowires [62]). If these are LP oscillations they might suggest that the superconductivity in the sample exists only in a surface layer that is not ferromagnetic while the interior of the nanowire remains normal.
Using fluxoid quantization, a period of 1.3 T leads to an area of the cylinder of 1538 nm$^2$ corresponding to a cylinder of radius 22 nm. The actual wire radius is 35 nm with an oxide layer ~ 3 nm thick (from TEM images) leading to an effective radius of 29 nm. These radii calculated from LP oscillations and TEM images are close enough to warrant serious investigation into the possibility of superconductivity existing only in a thin surface layer that is non-ferromagnetic. The possibility of superconductivity only existing in the CoO layer has been suggested in [43] but, is unlikely since CoO is an insulator. In addition to the 1.3 T oscillations, oscillations with a period of ~ 500 Oe are also seen in both samples 1 and 2 in parallel field (see figure 4-13(b)). The oscillations reduce in magnitude with increasing field and increasing current. They are strongest in the intermediate temperature regime (between 2 K and 3.5 K) and disappear at both low and high temperatures. These oscillations do not correspond to any obvious area in the parallel field configuration.

Figure 4-13: (a) Resistance as a function of field at different temperatures for sample 2. The distance between the W strip and either of the Pt voltage electrodes for this sample is 2 µm. (b) A closer look at the 1.9 K data from panel (a) to see the oscillations with period 500 Oe (c) The magnetoresistance oscillations with period 500 Oe from sample 1.
Different Geometry: Conductance Peaks

The R vs. I at different T for sample 1 are shown in figure 4-14(a). Peaks in the voltage are seen in the intermediate temperature regime (2.6 K – 3.8 K). To see the peaks more clearly, one of the curves (at 3.0 K) is plotted with a smooth background subtracted in panel (b). If the numerical derivative of the current as a function of voltage is taken and plotted as a function of V (panel (c)), the peaks are seen to be periodic with voltage. The period seems to be dependent on the length of the sample. These peaks are seen in other samples in this geometry as well and are very reminiscent of Shapiro steps in Josephson junctions (chapter 6, [8]). However, Shapiro steps require a microwave source and multiple Andreev reflections (requiring two superconductors) and both of these conditions are not satisfied in this experiment. In view of these factors, a satisfactory explanation of these peaks is yet to be found.
4.4 Conclusions and Outlook

Our systematic study of ferromagnetic CoNWs and NiNWs connected to superconducting W electrodes has demonstrated the spatial extent of the proximity effect to be of the order of 500 nm, similar to that found in paramagnetic gold nanowires. The observation of long-range proximity effect in ferromagnetic nanowires is a surprising phenomenon that defies traditional wisdom and experimental results from bulk samples. Three possible mechanisms have been suggested to explain it [43]: (1) ballistic transport leading to underdamped Josephson supercurrents with singlet correlations, (2) a non-magnetic dead layer on the surface of the nanowire and (3) triplet superconductivity. The first of these assumes ballistic transport in the nanowire and solves the Eilenberger equation in the 1D limit obtaining an underdamped Josephson supercurrent with singlet correlations. The calculated mean free path for the crystalline CoNWs is ~ 5 nm. This puts them in the diffusive regime. Even if we assume that this calculation is incorrect due to resistivity changes in the region under the W electrodes, the long range proximity effect has also been observed in polycrystalline and granular samples. These samples do not have ballistic transport and therefore the possibility of such an explanation being correct is very low. The observation of long-range superconductivity in samples with only 1 superconducting strip (section 4.3) further precludes the possibility of a Josephson supercurrent, as no Josephson junction is present in this geometry. The possibility of a dead layer on the surface of the nanowire through which the singlet superconducting correlations may pass remains a concern. The third and most interesting possibility is that of triplet superconductivity. It has been noted in the literature [110,121] that conversion from singlet to triplet superconductivity requires inhomogeneous magnetic moments. The attachment of the W electrodes by the FIB deposition process involves the bombardment of high-energy ions and heating of the nanowire. This process may very likely produce defects and inhomogeneous magnetic moments in W–Co contact regions which serve as the ‘spin active’ interface leading to triplet correlations. This is an interesting
question worthy of systematic investigations. Two possible routes for exploring this further are being considered. The first one is to make electrodes on CoNW using e-beam lithography followed by evaporation of superconducting electrodes. This eliminates the damaged interface area due to the FIB process and perhaps eliminates the ‘spin active’ region. If the long-range superconductivity disappears in these experiments then the case for triplet correlations becomes stronger. The second route is to construct an interferometer [109] and experimentally determine the Josephson current phase relationship as recommended in reference [43]. A strong suppression of the second harmonic would indicate that the superconducting correlations are singlet in nature. Both these experiments are underway at the present time.

For several of the Co and NiNWs, the resistance shows an unexpected peak immediately before the onset of superconductivity, which cannot be easily explained on the basis of the existing theoretical models. This peak was not seen in non-magnetic Au nanowires. The ‘critical’ resistance peaks observed in our systems are distinct from resistance peaks reported previously in the literature. A resistance peak near the onset of the superconductivity was reported in lithographically fabricated systems of mesoscopic Al wires and strips connected to Al electrodes [86]. In these results, the peak was attributed to a non-equilibrium charge imbalance resulting from the different spatial gradients of the respective electrochemical potentials of the quasi-particles and the Cooper pairs at the normal-metal/superconductor interface. The observed peak was found to be very sensitive to the applied magnetic field, suppressed by a tiny field of approximately 10Oe, far smaller than the critical field of the superconductivity. Moreover, the resistive anomaly depended on the cooling history, disappearing on thermal cycling. In sharp contrast, the resistance peak observed in our Co and NiNWs is robust with respect to thermal cycling and persists even in the presence of a large (several T) magnetic field, indicating that it is distinct from the peak effect reported in references [85,86]. Another possible explanation for the peak is spin accumulation [116,122]. This has been suggested as the origin for the resistance peak
observed in mesoscopic Fe–In junctions. In that case, however, the absolute peak value was small ($\sim 10^{-8} \Omega$), as was the relative change from the normal-state resistance ($\Delta R/R \sim 0.05\%$).

Furthermore, spin-accumulation is caused by a contact resistance that arises from a mismatch between the spin-polarized current in the ferromagnet and the unpolarized current in the singlet superconductor. Taking a simple model where the conductivity of spin-up electrons, $\sigma^\uparrow$, is larger than the conductivity $\sigma^\downarrow$ of spin-down electrons in the ferromagnet, one can define a measure of the ‘transport polarization’ $p = (\sigma^\uparrow - \sigma^\downarrow)/(\sigma^\uparrow + \sigma^\downarrow)$ and the total conductivity $\sigma_T = \sigma^\uparrow + \sigma^\downarrow$.

Theoretical models then show that the resistance of a ferromagnet/normal-metal junction increases once the normal metal turns into a singlet superconductor. The increment in resistance is given by $\Delta R = \frac{p^2}{1-p^2} \frac{l_{sd}}{\sigma_T A}$ where $l_{sd}$ is the spin diffusion length in the ferromagnet and $A$ is the area of the ferromagnet/normal-metal junction. It is apparent that the quantity in the parenthesis is equivalent to the resistance of a segment of the nanowire with length $l_{sd}$. On the basis of the bulk spin polarization of Co ($p \sim 0.42$ [123]) and an estimated value of $l_{sd} \sim 60$ nm in CoNWs [124], the spin-accumulation mechanism would lead to a much smaller resistance peak in the 1.5 µm CoNW ($\Delta R/R \sim 4\%$) than that observed in our experiments ($25\% < \Delta R/R < 100\%$).

Furthermore, the spin-accumulation model assumes that the induced superconductivity is singlet, which may not be true for our experiments as described in the previous paragraph. The critical peak also shows some sample dependent behavior and seems to have its origins in the interface between the superconducting electrodes and the ferromagnetic nanowires. The FIB technique does not allow much control over the nature of the interface therefore samples using an alternative technique like e-beam lithography followed by ion milling and evaporation need to be used. The peak is completely absent in samples with just one superconducting strip and may therefore be related to interference effects from two superconducting electrodes. All these observations can help in constraining possible theoretical explanations of the critical peak.
In control experiments performed with one superconducting strip, magnetoresistance oscillations have been seen. The oscillations in perpendicular field have their origins in vortex motion through the ferromagnet/superconductor interface. The origin of the oscillations in parallel field is not well understood at the present time. Conductance peaks periodic in voltage have also been observed in these systems. The design of experiments to clarify these phenomena is in progress.

Our study underscores the need for a direct probe of the pairing symmetry and magnetic behavior in the nanowires, to demonstrate the coexistence of superconductivity and ferromagnetism. To test the universality of the phenomena reported here, it will be interesting to ascertain if the observed phenomena can be replicated with standard superconducting electrodes other than FIB-deposited W strips, including conventional as well as high-$T_C$ superconductors. The long-range proximity effect in ferromagnets offers the possibility of combination of the zero-resistance supercurrents of superconductors with the spin alignment of ferromagnets. This has tremendous implications for spintronics [125]. Superconducting spintronic devices offer elements of non-locality (if the superconducting coherence length is larger than the nanoscale device), coherence (electrons in a Cooper pair are coherently coupled even if they go in separate electrodes) and entanglement (stemming from coherence), all of which are essential for quantum computing. The availability of triplet supercurrents may also revolutionize the field of spintronics with new spin valves, pumps, switches, transistors and filters.
Effects of Electrodes on Normal Nanowires: The Proximity Effect

The superconducting proximity effect, wherein the superconducting order penetrates a normal metal through a superconductor-normal metal (NS) interface, has been the subject of much experimental and theoretical study (section 1.3.2). Recent developments in synthesis techniques have made possible the exploration of this effect in nanoscale systems [126–128]. The interplay between superconductors and normal metals in the quasi 1d regime is interesting from the point of view of fundamental physics. One may also envision the use of proximity induced superconducting (non-heat generating) interconnects for producing denser and faster chips. The study of proximity-induced superconductivity in normal nanowires was initially planned as a control study for the experiments on proximity induced superconductivity in ferromagnetic nanowires (discussed in chapter 4). These experiments help in interpreting the results of the experiments on ferromagnetic nanowires. In addition, they also reveal some interesting physics of proximity induced superconducting systems.

A summary of the experiments performed in our lab on single crystalline AuNWs is given in section 5.1. Section 5.2 contains detailed descriptions of the synthesis and characterizations of the AuNW. Section 5.3 contains descriptions of results from measurements using lithography to contact AuNW and 5.4 summarizes and outlines other potential experiments in these systems.
5.1 Historical Background

Transport measurements were performed on 70 nm diameter crystalline gold nanowires (AuNW) contacted with superconducting W electrodes (measurement geometry can be seen in top left inset of figure 5-1(a)) [4]. The other inset of figure 5-1(a) is a high resolution TEM image showing that the AuNW used for this study are crystalline. Figure 5-1(a) shows the resistance as a function of temperature for nanowires of three different lengths 1.9 µm, 1.2 µm and 1 µm. The 1 µm and 1.2 µm nanowire become completely superconducting while the 1.9 µm nanowire does not. This was used to estimate the range of the proximity effect to be ~ 600 nm which is of the same order as predictions and that determined by tunneling spectroscopy in bulk systems [37,39,83,126]. The superconducting transition of the 1.2 µm long nanowire occurs in two steps. This can be seen more clearly in panel (b) of figure 5-1 [4]. The lower T_c transition disappears at a field of ~ 30 kOe which is smaller than the critical field of ~ 7 T for the higher T_c transition. The smaller transition is associated with a mini-gap δ in the AuNW that is separate from and smaller than the gap Δ of the superconducting electrodes.

Figure 5-1: (a) Resistance as a function of temperature for AuNW with W electrodes. The lengths of the 3 nanowires are 1.0 µm, 1.2 µm and 1.9 µm. The inset on the top left shows an scanning electron micrograph of the sample and the inset on the bottom right shows a transmission electron micrograph of the AuNW (b) The resistance as a function of temperature at different fields for the 1.2 µm AuNW. The graphs are reproduced from J. Wang et al., PRL 102, 1-4 (2009).
The differential magnetoresistance (numerically calculated from the magnetoresistance) is plotted as a function of applied field (figure 5-2(a), figure 5-2 is taken from references [129]). For both the 1.0 µm and 1.2 µm nanowire, periodic oscillations in differential magnetoresistance with a period of 0.25 T are seen. These oscillations were explained by the sequential generation and moving of vortices across the wires. The gap within the nanowire as a function of length was modeled as shown in figure 5-2(b). By gradually increasing the magnetic field perpendicular to the nanowire, the central part of the nanowire will first be driven normal allowing one vortex carrying one flux quantum $\phi_0$ to enter the nanowire, as shown in figure 5-2(c). Since the cross-sectional area for the first vortex threading the wire is $\sim \pi r^2$, where $r$ is the radius of the wire.
nanowire, the field at which the first vortex enters \( B_p = \frac{\phi_0}{(\pi r^2)} \) is estimated to be 0.5 T. When the field is further increased to \( B_2 = B_p + \Delta B_v \) to allow the second vortex to condense into the nanowire, the additional field \( \Delta B_v \) is equal to \( \frac{\phi_0}{(2\pi r^2)} \) or 0.25 T. In general, the relationship \( B_N = B_p + (N-1)\Delta B_v \) is obtained which is pictorially shown in figure 5-2(c).

Although many electronic and transport properties of hybrid SN structures are now well understood, the situation is less satisfactory when dealing with the magnetic field dependence of those properties. The results in AuNW-W electrode proximity systems shed some light on these properties. Moreover, the idea that in such a system, vortices, instead of proliferating may be introduced one by one by tuning the field opens up a wide range of possible applications. However, this magnetoresistance behavior has only been seen in a very specific morphology of nanowires with very specific sample geometry. Experiments testing the universality of these results are necessary before general conclusions about magnetic field dependent properties of hybrid SN structures can be drawn. This forms the motivation for the experiments described in this section.

5.2 Gold Nanowires: Synthesis and Characterization

The single-crystal AuNW were synthesized using template-based electrodeposition into the pores of a track-etched PCM (diameter 70 nm) (section 2.1.1). For the electrodeposition the instructions in [46] were followed with a few modifications. The back of the PCM was coated with thermally evaporated layers of Cr/Au/Ag of thickness 5nm/35nm/140nm respectively. This evaporated layer acted as the working electrode (cathode). The electrolyte was prepared by adding a small amount of gelatin (about 2 wt %) to a 20-mL commercial Orotemp Au bath (Technic Inc), which was then diluted with water to 40 mL. A platinum wire was used as the counter electrode. For most synthesis, no reference electrode was used and the voltage was
adjusted in a two probe setting till a deposition current of ~ 1 mA was obtained. Sometimes a Ag/AgCl reference electrode was included in which case a voltage of $V = -0.8$ with respect to Ag/AgCl was used for the electrodeposition. A schematic of the setup is shown in figure 2-4. The deposition is carried out at room temperature. The nanowires were harvested by dissolving the PCM in dichloromethane and precipitating from the solvent by means of a centrifuge. The free-standing nanowires were stored as a suspension in isopropanol. TEM specimens were prepared by placing a drop of the nanowire suspension on a lacey carbon coated copper grid. The nanowires were found to be single crystalline with [111] as the preferred growth direction. The high resolution TEM images and the electron diffraction patterns both indicating this are shown in figure 5-3 [46].

Figure 5-3: High resolution transmission electron micrograph of an Au nanowire tip showing the [111] growth direction. (200), (111), and (111) atom surfaces and a twin boundary transverse to the wire axis are indicated. Inset a is the electron diffraction pattern of the tip. Insets b and c are, respectively, a locally enlarged transmission electron micrograph and the electron diffraction pattern of the twin boundary area. (image taken from Tian et al., Nanoletters, 3, 7, pp. 919-923 (2003)).
The granular nanowires were patterned using e-beam lithography (section 2.1.2). To obtain small diameter nanowires a bilayer resist (MMA/MAA EL6, 950 PMMA A3) was used according to the recipe given in section 2.1.2 (b). The nanowire was defined to be 25 nm wide in the L-Edit software and was written with a beam spot size of 15 nm and a dose of 1500 µC/cm². The sample was developed in mixture of MIBK:IPA in a ratio of 1:3 for 1 minute followed by immersing in IPA for 15 seconds. The sample was then washed with deionized water and IPA. A 40 nm thick layer of Au was evaporated with the help of an e-beam at 1 Å/s. The evaporation is done at a slow rate and breaks are taken after every 5 minutes to prevent overheating and melting of the PMMA layer. These precautions have to be taken since the evaporator used in this study is water cooled. Perhaps higher rates can be used for liquid nitrogen cooled evaporators. This recipe yields granular Au nanowires with diameters ranging from 60 – 120 nm. The grain size is ~ 10 nm.

With the alignment process as described in section 2.3.3, electrodes were patterned onto the AuNWs. The exact recipe used for making electrodes was as follows: a lower layer of MMA/MAA EL 11 spun at 2000 rpm for 45 seconds and baked at 150° C for 3 minutes and an upper layer of PMMA A3 spun at 4000 rpm for 45 seconds and baked at 150° C for 3 minutes. A 10 nm Au layer was thermally evaporated to ensure ease of height measurements. Electron beam spot sizes of 100 nm or 200 nm were used with a dose of 400 µC/cm². The pattern was developed in a solution of MIBK:IPA::1:1 followed by IPA for 15 seconds. A 75 nm thick layer of the desired electrodes (Al or Pb) was evaporated on the developed mask. The sample was immersed in acetone at room temperature for liftoff and was washed with isopropanol and water after liftoff.
5.3 Four Probe Transport Measurements

5.3.1 Crystalline AuNW

The mini-gap state is seen in crystalline AuNW contacted with FIB deposited W electrodes. Since we were cautiously aware of the tendency of the FIB deposited W electrodes to spread and also of the Ga ion contamination caused by the process, we were eager to confirm these results with different electrodes. A 70 nm crystalline AuNW was contacted with Al electrodes as described in the previous section. An SEM image of the sample is shown in figure 5-4. Four-probe transport measurements are performed on the AuNW with the two voltage electrodes 1.2 µm apart. This means the effective length being measured is 1.2 µm.

Figure 5-4: A scanning electron micrograph of a crystalline AuNW contacted with evaporated Al electrodes using e-beam lithography.
The R vs. T at different H is shown in figure 5-5(a). The Al electrodes are 300 nm wide, 50 µm long and 75 nm thick. For these dimensions, the electrode $T_c$ and $H_c$ should be close to the bulk values. The data suggests that the $T_c$ is 1.2 K (bulk value 1.1 K) and the $H_c$ is ~ 500 Oe (bulk value ~ 350 Oe) which are indeed close to bulk values. The resistivity of the AuNW is ~ 66 µΩ-cm which is close to the value in the earlier experiments on AuNW described in section 5.1 (51 µΩ-cm). The slight discrepancy can be explained by the fact that the estimated length of the AuNW is not very accurate in the earlier experiment. The exact extent of the spread of the W electrodes is not known and this may have led to an overestimation of the length of the nanowire being measured. The resistance begins to drop at 1.2 K and with further reduction in temperature, reaches its minimum value at 1.0 K (22% of the normal state value). From this drop, the extent of the proximity effect can be estimated to be ~ 470 nm which is in agreement with that found with W electrodes [4] and also from tunneling measurements on normal nanowires in contact with a superconductor [39,126]. At zero field, the transition does not show two steps as seen in the AuNW with the W electrodes. On the application of a field, however, two distinct steps in the superconducting transition can be clearly seen. The lower of these steps is associated with the

Figure 5-5: (a) Resistance as a function of temperature at different fields for a 70 nm diameter crystalline AuNW with 4 superconducting Al electrodes (a scanning electron micrograph of the sample is shown in figure 5-4). (b) Resistance as a function of field at different temperatures for the same sample.
mini-gap state as will be seen more clearly in the $R$ vs. $H$ measurements. At low temperatures there is an upturn in resistance. Similar ‘re-entrance’ of metallic conductance in a proximity induced superconductor has been seen in Cu loop contacted with Al electrodes [128] and also in our experiments on CoNW (figure 4-10). This upturn has also been theoretically predicted [119,127]. In reference [127], the effect has been attributed to the size of the superconductor becoming smaller than the thermal coherence length of the electrons below a certain temperature. The maximum conductance is calculated to occur at $\sim 5E_c$ where $E_c$ is the Thouless energy. $E_c$ for our sample can be calculated using the formula $E_c = \frac{hD}{L^2}$, where $D$ is the diffusion length and $L$ is the length of the sample. The diffusion length is given by $D = \frac{1}{3}v_F l$ where $v_F$ is the Fermi velocity and $l$ is the mean free path. For Au, $v_F = 1.4 \times 10^8$ cm/sec and $l = 1.3$ nm (pages 10 and 52 [130]). For the sample length $L = 1.2$ µm, this yields an $E_c = 3$ mK. The minimum resistance point in our data is at 1K which is more than 300E$_c$. An alternative explanation for this has to be found. It should also be noted that this upturn was not observed in the AuNW contacted with W electrodes. The mini-gap state can be seen more clearly in the $R$ vs. $H$ at different $T$ shown in figure 5-5(b). At 0.1 K the $H_c$ of the smaller gap $\delta$ is $\sim 400$ Oe while that of the larger gap $\Delta$ is $\sim 500$ Oe. The numerically calculated $dR/dH$ as a function of temperature is shown in figure 5-6.

The behavior of the peaks is identical to the behavior of the innermost peak for the 1.2 µm long sample (figure 5-2(a)). At low temperatures the peak is small. The size of the peak increases and it moves towards lower field with increasing temperature and finally disappears above the $T_c$. This peak is related to the mini-gap phase and is different in nature from the other peaks. The magnetic field at which the first vortex is expected to penetrate and the differential magnetoresistance oscillations corresponding to vortices are supposed to commence is $\sim 0.5$ T
(calculated as described in section 5.1 using reference [129]). Since the $H_c$ is ~ 0.05 T, these effects cannot be seen in this sample.

Other electrodes with higher $H_c$ need to be used or the sample geometry needs to be changed in order to see these effects. There are experimental constraints limiting the possible superconducting electrodes. The $H_c$ of the electrode must be high, it must have a low melting point, it must not form an alloy with the nanowire and it must not contaminate the evaporation chamber. We relax one of these constraints and choose Pb (Pb contaminates the evaporation chamber) as are superconducting electrode for the next set of experiments. The $H_c$ of Pb is ~ 5000 Oe. However, this is still not high enough to see the vortex propagation in the 70 nm diameter AuNW. So, we also change the geometry of the sample and synthesize it using e-beam lithography and evaporation as described in section 5.2.

Figure 5-6: Numerically calculated $dR/dH$ for a crystalline Au nanowire with 4 superconducting Al electrodes.
5.3.1 Granular AuNW

The geometry of the measurement of the granular AuNW contacted with superconducting Pb electrodes can be seen in figure 5-7(a). The AuNW is 120 nm wide, 40 nm thick and ~ 4 µm long. The R vs. T at different fields is shown in figure 5-7(b). The resistance drops to 92% of its normal state value starting at a $T_c$ of 5 K. The magnitude of the drop allows us to calculate the range of the proximity effect as ~ 130 nm. There is no evidence of the mini-gap state in the R vs. T. Figure 5-7(c) shows the R vs. H at different temperatures in perpendicular field. There is a well-defined superconducting drop at an $H_c$ of ~ 4000 Oe. An additional mini-resistance valley is found in a
narrow low magnetic field region. A magnified view of the evolution of this mini-resistance valley in nanowire as a function of temperature is shown in figure 5-7(d) (the curves are offset for clarity). At 2.0 K and 2.4 K, the resistance jumps at 400 Oe and then drops back to the superconducting state at 480 Oe. At 2.8 K, the magnetic field-symmetric resistance fluctuations become more clearly developed and the baseline of the fluctuating resistance at fields above the mini-valley region is seen to be smoothly increasing with field. Between 3.2 and 3.8 K, the resistance fluctuations evolve to the low field mini-resistance valley. With increasing temperature the mini-resistance valley continues to shrink both in width and depth, disappearing at T = 4.5 K. This behavior is identical to the mini-gap behavior seen in crystalline AuNW [4]. The crystallinity of the nanowire is therefore not necessary for the existence of the mini-gap state. A surprising detail to be noted here is that the field for the appearance of the mini-gap peak for the AuNW contacted with the Pb electrode (400 Oe) is very close to the AuNW contacted with the Al electrode (450 Oe), in spite of the fact that the Hc's of the larger superconducting transition for the two systems are very different (see figures 5-6 and 5-7(d)).

Attempts were made to see the introduction of vortices one by one in the nanowire with increasing field. The expected field for the first vortex to enter is (H.A = φ₀) ~ 1700 Oe and the period of the magnetoresistance oscillations is expected to be ~ 850 Oe (calculation explained in section 5.1). The area of the vortex is constrained by the area of the nanowire. The vortex is therefore assumed to have a radius equal to half the width of the nanowire (60 nm). However, no periodic oscillations in the differential magnetoresistance were seen in this case. The reason for this is perhaps the granularity of the wire. There are a large number of pinning sites available for the vortices and therefore the regular introduction of vortices starting from the center of the nanowire does not occur.
In magnetic field parallel to the axis of the wire, magnetoresistance oscillations are seen in the R vs. H at different temperatures (figure 5-8). The period of the oscillations is ~ 600 Oe and is independent of the temperature. The amplitude of the oscillations decreases with increasing field and with increasing temperature. The oscillations are present all the way up to the critical temperature and critical field. The observed MR oscillations cannot be explained using standard scenarios. The Shubnikov-de Haas effect is ruled out since the oscillations are not periodic in 1/H. Assuming fluxoid quantization, the observed oscillation period implies a characteristic geometrical area $A = \frac{\Phi_0}{\Delta H} = 3.3 \times 10^4 \text{nm}^2$. This is far larger than any relevant geometrical regions in our devices. The fluxoid quantization is ruled out since the period does not correspond to any obvious area of the sample. A satisfactory explanation of these oscillations remains to be found.

5.4 Conclusions and Outlook

In summary, we have confirmed that the proximity effect in AuNWs is ~ 100s of nm long regardless of sample morphology. The ‘mini-gap’ state is a new superconducting state that opens new avenues for exploration of the physics of nanoscale superconductors. Earlier experiments
had seen this state in crystalline AuNW with FIB deposited W electrodes. We have now demonstrated that the mini-gap state is a robust state that does not depend on the morphology of the nanowire, the nature of the contact or the nature of the electrode. The field at which the mini-gap peak appears in the AuNW contacted with Al and Pb (450 Oe and 400 Oe respectively) is significantly different from the field at which it appears for AuNW contacted with W electrodes (3500 Oe). Moreover, this field is not varying monotonically with the $H_c$ of the larger superconducting transition (larger $H_c$ for Al: 500 Oe, for Pb: 4000 Oe, for W: 8T). The details of the physical mechanism behind the mini-gap peak are not yet known. The results of the experiments reported here will help to constrain future theories explaining the phenomenon.

The differential magnetoresistance oscillations seen in the crystalline AuNW with W electrodes offered a possibility of manoeuvring vortices one by one in the proximity induced superconducting system. Such oscillations were not seen in granular nanowires synthesized using e-beam lithography followed by evaporation. It may be necessary for the sample to be clean and a single crystal so that no defects or grain boundaries pinning the vortices exist. We may also need to reconsider the model used for explaining the oscillations before planning future experiments. A shortcoming of this model is that it requires the gap to vary monotonically along the length of the nanowire (figure 5-2(b)). Other theoretical models [81], tunneling measurements [39] and our transport measurements showing two $H_c$s and $T_c$s corresponding to the mini-gap state indicate that this is not the case. The gap actually has a smaller but, constant value inside the nanowire. Experimentally, attempting to see the differential magnetoresistance oscillations in a crystalline AuNW contacted with a superconductor different from W but, with a sufficiently high $H_c$ may hold the key to unraveling this phenomenon.
Conclusions, Outstanding Questions and Future Experiments

Intrinsic and proximity induced superconductivity has been studied in a wide variety of metallic one dimensional nanowires. Many novel phenomena, contrary to expectations based on measurements made on bulk superconductors, have been seen. Three main classes of structures have been studied: superconducting nanowires with superconducting and normal electrodes, ferromagnetic nanowires with superconducting electrodes and normal nanowires with superconducting electrodes.

A technique to synthesize single crystal superconducting aluminum nanowires has been developed. Granular aluminum nanowires have also been synthesized using traditional e-beam lithography followed by evaporation. Electronic transport properties of these aluminum nanowires have been measured using superconducting indium, tungsten and aluminum and normal platinum electrodes in a variety of measurement geometries. The anti-proximity effect first seen in zinc nanowires has been confirmed in these systems. Moreover uncertainties about whether the observed phenomena is merely a negative magnetoresistance have been put to rest in measurements in which the APE has been seen in the absence of magnetic fields, clearly establishing that it is a function of the bulk measuring electrodes. The three salient features of the effect noticed in earlier experiments viz. the dependence on the length and diameter of the nanowire and the material of the electrode have been studied. The constraint on the diameter of the nanowire ($d < \text{superconducting coherence length}$) to see the anti-proximity effect is the same in crystalline aluminum nanowires as in earlier experiments. In granular nanowires, even in samples with diameters comparable to the coherence length the anti-proximity effect is sometimes not seen. The effect is only seen in the samples with the smallest grain sizes.
Therefore, it is concluded that in granular samples, the relevant condition is that the grain size should be smaller than the coherence length. The length dependence of the effect has been studied by measuring samples of varying length. It is found that the strength of the effect is approximately the same for wires with the same charge imbalance length to length ratio. Measurements at different current densities show that the extent of suppression of superconductivity - earlier interpreted as consequence of material of the bulk electrode may in fact be a current density difference effect. In addition measurements of a single resistance reading found switching from the superconducting to the normal state close to $T_c$ of the wire and at low temperatures in the APE regime. Theoretical models enable us to conclude that the switching at low temperature is triggered by individual quantum phase slips. These results indicate that the low temperature APE regime offers a clean platform for the observation of individual quantum phase slips, a goal eluded in numerous experiments. Probing individual phase-slip events via the nanowire switching offers a way of unearthing and exploring the physics of nanoscale quantum tunneling of the one-dimensional collective quantum field associated with the superconducting order parameter. Lastly, these experiments help us unravel and understand the counterintuitive anti-proximity effect at a microscopic level.

A very long-range proximity effect, two orders of magnitude larger than bulk, was observed for electrodeposited and evaporated nickel and cobalt nanowires in electrical contact with superconducting W electrodes. Three possible mechanisms were suggested to explain this counterintuitive phenomenon. The first two of these (singlet Josephson supercurrents and non-magnetic metallic dead layer) have been explored. Experiments on evaporated nickel nanowires with 4 superconducting electrodes and cobalt nanowires with a single superconducting strip eliminate these two possibilities. The third possibility of triplet correlations within the ferromagnet seems to hold promise. Experiments in Andreev interferometer geometry are underway in an attempt to see interference effects. In addition to the long-range proximity effect,
a large resistance peak near the transition temperature is seen for some of the samples. The magnitude of the peak and its response to magnetic field rules out the possibility of it being a charge imbalance or spin accumulation peak. There are some suggestions that the peak may be a current dependent effect. A theoretical model explaining this peak has not yet been found and further experiments at different bias currents may help in constraining possible theories.

The mini-gap state, first seen in crystalline gold nanowires contacted using a focused ion beam system has been reproduced granular gold nanowires and also in crystalline gold nanowire with evaporated aluminum electrodes. We have demonstrated that the mini-gap state is a robust state that does not depend on the morphology of the nanowire, the nature of the contact or the nature of the electrode. The magnetoresistance oscillations seen in the original experiments were not seen in the experiments on granular nanowires suggesting that the crystallinity of the sample may be an important parameter. Future experiments will be aimed at observing the magnetoresistance oscillations in a crystalline gold nanowire contacted with a technique different from focused ion beam.

Our experiments show that the presence of bulk superconducting/normal metal affects 1D nanowires very differently from traditional expectations. The effect of these changing ‘boundary conditions’ on mesoscopic superconductors has been theoretically studied for several decades but the difficulties inherent to fabricating and studying such systems has constrained experimental explorations. These experimental results therefore shed light on a little known aspect of superconductivity in nanoscale systems viz. the large role of environmental factors.
This section includes some of the scanning and transmission electron micrographs, X-ray diffraction patterns and electron diffraction patterns which are not part of the main text but, may be useful for gaining further insight into the experimental procedure and results.

Figure A-1: (a) Transmission electron micrograph of Al nanowires. The nanowires are upto 20 μm long (not seen in this figure). (b) More magnified micrograph of the Al nanowires. It can be seen that the wire diameter is 50 nm and a 7 nm oxidation layer is on the surface. This oxidation layer is stable with time – if the same set of nanowires is checked again in the transmission electron microscope a month later, the oxidation layer is still 7 nm thick.
Figure A-2: (a) Transmission electron micrograph of Cd nanowires. The nanowires are up to 5 µm long. They are grown in commercial polycarbonate membranes using 0.1 M CdSO₄.8H₂O, 0.5 M H₃BO₃ aqueous solution at -0.72 V with respect to a Ag/AgCl reference electrode and a Pt anode. (b) X-ray diffraction pattern from an array of Cd nanowires embedded in a polycarbonate membrane. (c) More magnified micrograph of the Cd nanowires. It can be seen that the wire diameter is ~ 85 nm and there is a thin oxidation layer on the surface. It can also be seen that the wires are granular. (d) Electron diffraction pattern from the nanowire shown in panel (c). The ring structure shows that the nanowires are polycrystalline.
Figure A-3: (a) Transmission electron micrograph of Co nanowires. The nanowires are 40 nm in diameter and crystalline. The stacking faults can be seen as horizontal lines in the top nanowire. (b) Electron diffraction pattern from the top nanowire. The pattern shows that the nanowires are single crystalline.

Figure A-4: (a) Transmission electron micrograph of Bi$_2$Te$_3$ nanowires. The nanowires are ~110 nm in diameter and crystalline with a 14 nm thick oxide layer on the surface. (b) Electron diffraction pattern from nanowire shown in panel (a) shows that the nanowires are single crystalline.
Figure A-5: Sometimes what appears to be a single nanowire when seen with the scanning electron microscope in the focused ion beam tool, turns out to be two nanowires stuck together when examined more closely with the field effect scanning electron microscope. Two examples of this occurring.

Figure A-6: (a) Scanning electron micrograph of an evaporated Ni nanowire defined using e-beam lithography with focused ion beam assisted W electrodes patterned on it. The nanowire is 250 nm wide and 35 nm thick. The transport data from a similarly synthesized sample is shown in figure 4-7 in the main text. (b) A closer view of the wire with two W electrodes. The spreading of the focused ion beam assisted W electrodes can be clearly seen.
Figure A-7: An evaporated Al nanowire – 100 nm wide and 50 nm thick defined using e-beam lithography. The four brighter contacts (1, 2, 3 and 6 counting from the top) are Au and the two darker contacts (4 and 5) are Al. The purpose of the sample was to check the critical current of the nanowire between the Au electrodes and between the W electrodes basically repeating the experiment done using focused ion beam shown in figure 3-10 with evaporated electrodes. The sample however, was not conducting and poor contact between the Au electrodes and the Al nanowire is suspected to be the possible cause for this.

Figure A-8: An evaporated Au nanowire 60 nm wide and 35 nm thick defined using e-beam lithography. The four electrodes are made of evaporated Al also defined using e-beam lithography. The purpose of the sample was to measure proximity induced superconductivity in the Au nanowire repeating the experiment reported in figures 5-7 and 5-8 with a Al electrode instead of a Pb one. However, the contact resistance was very high and the transport for this sample was not measured. It is believed that the contact resistance can be reduced by evaporating Pd before evaporating Al on the Au nanowire.
Figure A-9: (a) An example of the kind of picture one needs to take with the optical microscope in order to do alignment for the e-beam lithography tool. The golden dots visible in the picture are pre-patterned gold markers made using optical lithography. Each dot is \( \sim 1 \, \mu m \) in size. The position of the gold markers in the picture relative to the larger square alignment markers on the substrate needs to be known exactly. The larger square markers and the numbering on the substrate also done using optical lithography followed by gold evaporation is shown in panel (b). The little dots in this picture are the same gold markers that are visible in panel (a).
Appendix B  Transport Measurements

This section includes some of the transport measurement data which are not part of the main text but, may be useful for gaining further insight into the experimental results.

Figure B-1: (a) R vs. T for a 35 nm diameter, 3 µm long Al nanowire with 4 focused ion beam deposited normal Pt electrodes (see inset). The non-metallic behavior from room temperature was quite common in electrodeposited Al nanowires with focused ion beam assisted electrodes. The reason for this behavior is not known. (b) Resistance as a function of temperature for the same sample at low temperatures. The Al superconducting drop is seen at a $T_c$ of ~ 2K which is enhanced from bulk. One strange feature of this sample was that at low currents, the measured resistance was negative. Perhaps there was a barrier at one of the Al-Pt interfaces which caused this. Because of this anomaly, this sample was not used to draw any conclusions. (c) The R vs. H behavior for this sample, the $H_c$ is ~ 1.5 T (also enhanced from bulk). (d) The V vs. I at different temperatures. The strange behavior at low temperatures and currents can be seen again.
Figure B-2: (a) Scanning electron micrograph of a 70 nm diameter Al nanowire contacted with superconducting W and normal Pt electrodes. (b), (c) R vs. T and R vs. H for the part of the nanowire, 4.7 µm long, between the Pt voltage electrodes. The peak at the critical temperature might be a charge imbalance peak also reported elsewhere (Santhanam et al., PRL 66, 2254–2257 (1991)). (e), (f) R vs T and R vs. H for the part of the nanowire, 1.3 µm long, between the W voltage electrodes. The T_c and H_c are higher than the part between the Pt electrodes showing the standard proximity effect. The peaks in the R vs. H are not understood. (d) Comparison of the I_c between the superconducting electrodes and the normal electrodes. In this sample the I_c between the normal electrodes is lower (opposite of fig. 3-10) but that does not prove that there is no anti-proximity effect since the segment between the normal electrodes is ~ 4 times longer than that between the superconducting electrodes and I_c is known to decrease with length. At the time of making this sample I did not understand the importance of making both segments equal in length.
Figure B-3: (a) Scanning electron micrograph of a 70 nm diameter, ~ 2 µm long, Al nanowire contacted and measured first with just 4 normal Pt electrodes. Then the sample was taken back to the focused ion beam system and a W strip was patterned in the middle of it as shown and the transport was measured again. (b), (c) R vs. T and R vs. H for the nanowire with just the Pt electrodes (e), (f) R vs T and R vs. H for the nanowire after the patterning with the W strip. Both the Tc and Hc have increased from before as has the total resistance. The oscillations in the R vs. H are not understood. (d) Comparison of the Ic with and without the W strip. The Ic with the W strip is significantly lower. However, this can be attributed to the damage caused to the nanowire in the process of depositing the W strip and is therefore not very conclusive.
Figure B-4: (a) R vs. T behavior of a 80 nm diameter Al nanowire array embedded in an alumina membrane and squeezed between superconducting In electrodes. The upturn at low temperatures may be a continuation of the general upward trend of the resistance with reducing temperature contributed by the Al-In interface. (b) R vs. I as a function of applied field. The $I_c$ increases with applied field, showing a maximum between 200 and 350 Oe ($H_c$ of In ~ 300Oe) before decreasing again at 1000 Oe. This shows that the anti-proximity effect is present in this nanowire array just like the system shown in figure 3-7.
Figure B-5: (a) R vs. T behavior of a 9 µm long, 125 nm wide, 50 nm thick Al nanowire made using e-beam lithography followed by evaporation. The electrodes are also made of evaporated Al. This is sample 8 listed in table 3-1 (b) R vs. T at low temperature. The $T_c \sim 1.24$. (c) R vs. H showing an $H_c \sim 1000$ Oe. (d) V vs. I at different applied field showing no enhancement of $I_c$ with applied field hence no anti-proximity effect.
Figure B-6: (a) R vs. T behavior of a 9.1 µm long, 90 nm wide, 50 nm thick Al nanowire made using e-beam lithography followed by evaporation. The electrodes are also made of evaporated Al. This is sample 9 listed in table 3-I. The $T_c \sim 1.23$. (b) R vs. H at low temperature showing an $H_c \sim 1200$ Oe. (c) R vs. I at different applied field showing no enhancement of $I_c$ with applied field hence no anti-proximity effect. (d) R vs. T at high current close to $I_c$ to show that no anti-proximity effect is seen in the R vs. T either in contrast to figure 3-11(c).
Figure B-7: (a) R vs. T behavior of a 5 µm long, 97 nm wide, 50 nm thick Al nanowire made using e-beam lithography followed by evaporation. The electrodes are also made of evaporated Al. This is sample 7 listed in table 3-1 (b) R vs. T at low temperature. The $T_c \sim 1.06$. (c) R vs. H showing an $H_c \sim 1200$ Oe. The extra dip at low field is from the interface region close to the electrodes. (d) V vs. I at different applied field showing no enhancement of $I_c$ with applied field hence no anti-proximity effect.
Figure B-8: (a) R vs. T behavior of a 19.66 µm long, 130 nm wide, 50 nm thick Al nanowire made using e-beam lithography followed by evaporation. The electrodes are also made of evaporated Al. This is sample 10 listed in table 3-1 (b) R vs. T at low temperature. The T_c ~ 1.2. (c) R vs. H showing an H_c ~ 1200 Oe. (d) V vs. I at different applied field showing no enhancement of I_c with applied field hence no anti-proximity effect. It is interesting that the transition seems to be in two distinct steps.
Figure B-9: (a) R vs. T behavior of a 1.5 µm long, 128 nm wide, 50 nm thick Al nanowire made using e-beam lithography followed by evaporation. The electrodes are also made of evaporated Al. This is sample 6 listed in table 3-1 (b) R vs. T at low temperature. The $T_c \sim 1.2$. (c) R vs. H showing an $H_c \sim 1200$ Oe. The extra dip at low field is from the interface region close to the electrodes. The fact that the second transition (at low T and low H) is so pronounced in the shortest sample supports the fact that this transition comes from the region of the nanowire close to the bulk Al electrodes as a result of the ‘reversed’ proximity effect of the lower $T_c$ lower $H_c$ electrodes. (d) V vs. I at different applied field showing no enhancement of $I_c$ with applied field hence no anti-proximity effect.
Figure B-10: (a), (d) R vs. T behavior of a 2.5 µm long, 60 nm diameter electrochemically grown Ni nanowire with superconducting W electrodes made using focused ion beam method in parallel and perpendicular applied fields respectively. The height of the critical peak is smaller in perpendicular field. (b), (e) R vs. H for the same sample in parallel and perpendicular fields respectively. The Hc is higher (as expected) for the parallel field case. (c) The dependence of the critical peak on applied current at an applied field of 0 Oe. The peak gets smaller on increasing current and disappears at 4 µA. (f) In this sample, R vs. T oscillations are seen above the critical temperature at 0 Oe field. The reason behind these oscillations is not known and they are not seen in other samples therefore, they were not pursued further. Part of this data is also shown in figure 4-8. Also, note that this sample is identical to the sample shown in figure 4-9 in the main text as far as we can tell from scanning electron micrographs, but, their transport behavior, especially the behavior of the critical peak are quite different.
Figure B-11: (a), (b) R vs. H behavior in perpendicular and parallel field respectively for a 60 nm diameter, 2.5 µm long Ni nanowire contacted with superconducting W electrodes. This is the same sample as that shown in figure 4-9 in the main text.

Figure B-12: A 50 nm diameter electrochemically grown Bi$_2$Te$_3$ nanowire was contacted using evaporated Al electrodes defined using e-beam lithography. Because of insufficient milling before evaporating the Al electrodes, tunneling contacts instead of ohmic contacts were obtained. On checking on a probe station, the above current-voltage characteristics were obtained. The tunneling voltage is too high for this sample to be measured on the PPMS system. In eventual samples, in which longer milling was done, the voltage decreased somewhat but, the contact was never really ohmic. Perhaps evaporating a Pd layer for adhesion before evaporating Al might help in improving the contact with the electrode.
Figure B-13: This is the R vs. T data from a 4 probe measurement of a 75 nm thick sputtered Nb film. The four contacting electrodes are In dots squeezed onto the film. Surprisingly the film is not superconducting and there is an upturn in resistance at the $T_c$ of the In dots. This may have been caused by contamination in the sputtering chamber. Later experiments revealed that always doing an empty run of Nb sputtering before actually sputtering onto the sample leads to a consistently superconducting Nb film.

Figure B-14: This is the rate at which the native alumina layer on an aluminum surface is ion milled in the evaporator (Lesker 18) in the cleanroom. The instrument uses an Ar ion mill at 20 kV and 3 A. The blue line is a fit that can be used for extrapolation.
References


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Meenakshi Singh was born and raised in Lucknow, India. She received her Bachelor of Science degree in Physics, Mathematics and Statistics from the University of Lucknow, India in 2004 and completed her Master’s degree in Physics from the Indian Institute of Technology, Kanpur, India in 2006. She came for her doctoral studies to the Pennsylvania State University in 2006 where she joined the research group of Professor Moses H. W. Chan. She will graduate with a doctorate in Physics in 2012. After graduation, Meenakshi Singh will pursue post-doctoral research.