ABSTRACT

PERFORATED SUPERCONDUCTING NIOBIUM NITRIDE FILMS FORMED ON ANODIC ALUMINUM OXIDE MEMBRANES

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Introducing an array of holes into a superconducting film can dramatically change its properties. For example, the holes can serve as pinning centers against the motion of magnetic vortices, thus increasing the current carrying capability of the film without dissipation. The film can also become a superconducting wire network which behaves completely different from a continuous film when the spacing between the neighboring holes decreases to the order of superconducting coherence length.

Traditionally, the holes are fabricated through lithography (photo- and electron-lithography) techniques which require expensive equipment and are not efficient for making a large area of hole array. Recently, our group developed a new approach to fabricate superconducting films containing arrays of holes by utilizing anodic aluminum oxide (AAO) membranes, a new generation of porous membranes as substrates. By coating niobium (Nb) on AAO membranes, superconducting Nb films containing arrays of nanoscale holes were achieved and novel properties were observed.

The purpose of this thesis work is to explore the possible application of AAO membranes as substrates to fabricate superconducting films which require elevated
to form. Niobium nitride (NbN) was chosen to be the test system. AAO membranes were fabricated by anodizing aluminum foils in an oxalic acid solution and imaged with scanning electron microscopy (SEM). NbN films were coated by sputtering Nb in a nitrogen atmosphere. The influence of the substrate temperature was investigated and superconducting NbN films were obtained at a substrate temperature above 400° C. X-ray diffraction was conducted to identify the phase of the NbN films. Four-probe resistive measurements were used to characterize the transport properties of the NbN films with holes and minima were observed in the field dependence of the resistance at matching fields where the magnitude of the magnetic flux through each unit cell is an integer number of the flux quantum. Possible origins for this matching effect are discussed based on hole-induced suppression of the critical temperature (Little-Parks effect), commensurate flux pinning enhancement, and the Josephson effect.
PERFORATED SUPERCONDUCTING NIOBIUM NITRIDE FILMS FORMED ON ANODIC ALUMINUM OXIDE MEMBRANES

BY

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CHAPTER 1

INTRODUCTION

Superconducting nanoporous Nb thin films deposited on anodic aluminum oxide (AAO) substrates have been the topic of great interest in recent years. The most interesting work is the effect of a periodic pinning array with pinning site sizes on the order of length scales comparable to the superconducting coherence length and the penetration depth. Rich varieties of phenomena in vortex dynamics exist in these films and have been seen in many previous experiments [1-8]. By introducing artificial nanoscaled pinning centers embedded into the films, one can try to understand theoretically and experimentally the interactions between vortices and material imperfections, vortex-vortex interactions, periodic oscillations in the critical temperature $T_c$ vs. field strength, and many other aspects of superconductivity in multiply connected geometries [1-13]. In addition, these nanostructures have the ability to enhance the critical current at matching fields by tailoring the array of nanoscale holes to desired conditions. The enhancements of the critical current is closely related to the optimization of the size and geometric distribution of pinning centers, whether they are anti-dots or artificially added imperfections of a different material. In this study we tested the structural stability of an AAO template in high
temperature sputtering. We found that AAO templates are stable in high temperature environments. This allowed us to sputter new compounds onto nanoporous AAO templates, to investigate the nature of superconductivity in new nanoporous systems. The compound we’re interested in sputtering onto the AAO template is niobium nitride (NbN). For these two elements to bond, a high temperature environment is required. Thus, it is challenging to sputter without deformation to or damage inflicted on the periodicity of the substrate. In regards to the superconducting nature of these nanoporous structures, we wanted to determine the mechanism responsible for oscillations in the magnetoresistance as well as enhancements of the critical current density and pronounced matching effects over specific temperature ranges.

Theoretical simulations and experiments in periodic pinning arrays including holes and magnetic dot arrays have found numerous commensurability effects in which the pinning strength is enhanced at applied fields where the number of vortices is equal to an integer or rational fraction of the number of pinning sites [14-21]. The periodic pinning depends mainly upon the characteristics of the pinning centers such as the pinning size, distance between pinning centers, material and doped defects properties, etc. To understand possible mechanisms for the observed matching at integer and non-integer fields of nanoporous superconducting films we turn to transport measurements. A review of literature shows that many transport measurements related to induced dips in R(H) or peaks in $I_c(H)$ were done at temperatures very near zero-field critical temperature $T_{c0}$ [10-14]. However, it is not clear whether the matching effect seen in superconducting films with periodic arrays
of nanoscaled holes originates from hole-induced pinning enhancement at integer flux quanta matching fields, hole-induced Tc suppression at non-integer flux quanta fields, or the Josephson effect in which Cooper-pairs tunnel with reduced resistance at matching fields when the holes capture integer flux quanta [11, 16]. In our experiment we sputtered NbN onto a nanoporous AAO substrate. Using a two-step anodization process, AAO-containing arrays of periodically spaced nanoscale holes were fabricated. Here the resistance minima we observed in the R(H) curves occur at integer flux quantum matching fields. These observations seem to support additional suppression of the superconducting critical temperature Tc by magnetic field at noninteger flux quantum values arising from either Josephson Junction effect or fluxoid quantization effect (Little-Parks effect), instead of the flux pinning enhancement.
Types of Superconductors and Vortices

Superconductors undergo a phase transition at the critical temperature $T_c$ at which a material loses finite resistance. Below $T_c$ a material will allow supercurrent to flow freely without resistance through the crystal lattice. Superconducting materials such as mercury, lead, niobium, and many others each have a unique $T_c$. When a magnetic field is applied to a type-I superconducting material at a fixed temperature $T$ and allowed to increase in value, the superconductor will transition from being superconducting until the field reaches a value $H_c$ at which the superconducting state is destroyed and the material will then act as a normal conductor would. In general, for a material to exhibit total zero resistance superconductivity, the critical temperature $T_c$ must not be exceeded.

Applying a magnetic field to a type-II superconductor at a temperature below $T_c$ the first phase transition occurs at the lower critical field, known as $H_{c1}$. Below $H_{c1}$ the superconducting material expels all applied magnetic field from an opposing magnetic field created by circulating supercurrent or screening current, and the material is in a perfect superconducting state with no electrical resistance and zero magnetic field in its
interior due to the screening currents. The material exhibits perfect diamagnetism from the screening currents that produce a flux density inside the material to cancel out the flux density from the applied field. This is known as the Meissner effect [22], in which the applied magnetic field penetrates the material in a layer called the penetration depth \( \lambda \), which is typically on the order of thousands of angstroms and decays exponentially inside the material. The equation below describes the penetration depth where \( m \) is the mass of an electron, \( c \) is the speed of light, \( e \) is the charge of one electron, and \( n_s \) is the density of the Cooper pairs.

\[
\lambda = \left( \frac{mc^2}{4\pi n_s e^2} \right)^{1/2}
\]  

Using the penetration depth one can find the distribution of the magnetic field penetrating in a superconductor, as given by the equation below where \( B_0 \) is the applied field outside the superconductor, \( x \) is the distance from the surface of the superconducting material and \( \lambda \) is the penetration depth.

\[
B = B_0 \exp\left(-\frac{x}{\lambda}\right)
\]  

The current density \( J \) inside a superconductor also falls exponentially off the deeper inside the material given by equation below, where \( J_c \) is the critical current: i.e. the maximum current a superconducting material can be allowed before the Cooper pairs become normal electrons and superconductivity is lost.

\[
J(x) = J_c \exp\left(-\frac{x}{\lambda}\right)
\]  

By inspection of equation (2-1), when the density of Cooper pairs \( (n_s) \) rises, the penetration depth becomes small. Equations (2-2) and (2-3) thus indicate that the
magnetic field and current density must always penetrate a superconductor in the Meissner state on a very small order of nanometers.

Above $H_{c1}$ type-II superconductors will enter a mixed state in which the material will have superconducting and non-superconducting regions. In the mixed state, magnetic vortices enter the material in arrays of quantized flux. This mixed state breaks down at an upper critical field known as $H_{c2}$, and at fields with strength above $H_{c2}$ superconductivity is destroyed. This is a unique feature of type-II superconductors having two critical fields $H_{c1}$ and $H_{c2}$, unlike type-I superconductors, which only have one critical field $H_c$ above which superconductivity breaks down and the material becomes a normal conductor.

Another important parameter of superconducting materials is the superconducting coherence length $\xi$. It is a temperature- and material-dependant quantity and the coherence length may be regarded as the shortest length in which the order parameter can vary without breaking the paired electrons (Cooper pairs). This allows Cooper pairs to move great distances through the superconducting material unhindered. The superconducting coherence length is given by the equation below for a material at temperatures below $T_c$, where $\xi_0$ is the zero-temperature coherence length of a given material.

$$\xi(T) = \xi_0(1 - T/T_c)^{1/2} \quad (\text{for } T<T_c)$$  \hspace{1cm} (2-4)

Another important quantity in superconductivity is the order parameter that was introduced by Vitaly Lazarevich Ginzburg and Lev Landau (GL), in which the behavior of the Cooper pairs can be described by an “effective wave function” $\Psi(r)$,
in which $|\Psi(r)|^2 = n_s$ where $n_s$ is the density of the Cooper pairs in a
superconducting material. GL theory was introduced to deal with situations where $n_s$
varies in space and with applied fields strong enough to alter $n_s$.

The idea behind GL theory is that if $\Psi$ is small and doesn’t vary too fast in
space, the free energy density can be expanded in powers of $|\Psi(r)|^2$ and
$|\nabla \Psi(r)|^2$. In addition, the theory is most applicable to temperatures near the
second-order phase transition, as well as spatial variations of $\Psi$ and the vector
potential $A$, which are not too rapid. The free energy in full form considering applied
fields and gradients is given by

$$f = f_{no} + \alpha |\Psi(r)|^2 + (\beta/2)|\Psi(r)|^4 + \text{term involving gradients} + \frac{\hbar^2}{8\pi}\left(\frac{2-5}{2m^*}\right)$$  \hspace{1cm} (2-5)

Derivation of this equation shall not be dealt with here. The importance of
this equation is that given the proper boundary conditions and physical situation,
superconductors can be classified into two different classes, i.e. type-I and type-II
superconductors dictated by the superconducting coherence length and penetration
depth. The difference between type-I and type-II superconductors can be seen as a
ratio of the penetration depth to the superconducting coherence length. This is known
as the Ginzburg-Landau parameter $\kappa = \lambda/\xi$, which can be derived from the GL
equation (2-5). For type-I superconductors, $\kappa<1/\sqrt{2}$ and $\kappa>1/\sqrt{2}$ for type-II
superconductors. When $\kappa>1/\sqrt{2}$, $H_{c2}>H_c$ is the condition in which the vortex phase
in type-II superconductors is present. When $\kappa<1/\sqrt{2}$, $H_{c2}<H_c$ is the condition in
which the material is in the Meissner state. This can be visualized by looking at what
is known as the surface energy, i.e. the energy between the normal and
superconducting phases, which feeds the Gibbs free energy by an additional contribution which is proportional to the total area of the boundary between the normal and superconducting phase. We consider the Gibbs free energy because one wants to compare the difference in the magnetic contribution to the free energy of the superconducting and normal phase when a material is subject to an applied field. When the surface energy is positive (type-I) the free energy is minimized. If the free energy is negative (type-II) it will be energetically favorable for the material to split up into normal and superconducting regions. To conceptually see this for type-I superconductors, refer to Figures 2-1 to 2-6. In these diagrams it is seen that for type-I superconductors $\xi > \lambda$.

Type-I energy contributes to the free energy as follows.

![Figure 2-1. Coherence length and penetration depth for Type-I superconductors at boundary of normal and superconducting regions [22].](image-url)
Figure 2-2. Contributions to the free energy from the applied field and from the persistence current created by the Cooper pairs, for Type-I superconductors. Here $f$ is the free energy density [22].

Figure 2-3. Total free energy for type-I superconductor, origin of positive energy [22].
For type-II superconductors the surface energy is negative i.e. $\xi<\lambda$.

Figure 2-4. Penetration depth and coherence length for type-II superconductors at normal and superconducting boundary [22].

Figure 2-5. Contributions to the free energy from the applied field and from the persistence current created by the Cooper pairs, for type-II superconductors. Here $f$ is the free energy density [22].
Once the magnetic field is increased beyond $H_{c1}$, the material enters a mixed state in which the applied magnetic field penetrates the sample in an array of quantized flux tubes called Abrikosov vortices. Each tube of flux has $\Phi_0 = \frac{h}{2e} \approx 2.0678 \times 10^{-15}$ Wb of flux. Supercurrent swirls around a non-superconducting core while the core captures a quantum of flux. At the core of a vortex the superconducting order parameter $|\Psi(r)|^2$, which gives the density of the supercurrent, goes to zero because the magnetic field is strong enough to destroy the superconductivity in the region: i.e. the Cooper pairs are unpaired by the strength of the applied magnetic field.

As we move away from the core the order parameter increases and reaches a constant value at the distance on the order of the superconducting coherence length. In other words, the superconducting condensate gradually rises to a constant value at a distance $\xi$ from the center of the core. This can be visually seen in Figures 2-7 and 2-8.
Once the field value reaches the second critical field $H_{c2}$ superconductivity is destroyed and the material acts as a normal conductor. In Figure 2-9 one can see the generalized phase transition for a type II superconductor.

Using equations 2-8 and 2-9 one can estimate the magnetic field for the case where $R<<\lambda$, and for $R>>\lambda$, where $R$ is the distance from vortex core and $\Phi_0$ is a single flux quantum. These equations are used to describe the nature of vortex close to the core and far away from the core. Both equations relate directly to Figure 2-8.

In the vortex core, the magnetic field takes the behavior of the $\ln(\lambda/R)$ function, and far away from the core the magnetic field exponentially decreases.

$$B \sim (\Phi_0/2\pi\lambda^2)\ln(\lambda/R) \quad R<<\lambda$$  (2-8)

$$B \sim (\Phi_0/2\pi\lambda^2)(\pi\lambda/2R)^{1/2}\exp(-R/\lambda) \quad R>>\lambda$$  (2-9)
Figure 2-9. Phase diagram for type-II superconducting material.
Vortex Motion in Thin Films

Vortices present in the mixed state will repel each other. The circulating current from one vortex will be in the opposite direction of the circulating current in a neighboring vortex; see Figure 3-1.

\[ F_{1,2} = J_2 X B \]

\[ F_{2,1} = J_1 X B \]

Figure 3-1. Forces two neighboring vortices exert on each other in a type-II mixed state. \( F_{1,2} \) is the force felt on vortex 1 from supercurrent circulating in vortex 2 and \( F_{2,1} \) is the force vortex 2 experiences from circulating supercurrent in vortex 1.

To conceptually see the effect of passing current on vortices in the type-II mixed state, consider a thin continuous superconducting film without the presence of defects. When passing a current through the film while its in the mixed state and applying a magnetic field perpendicular to its surface, the current will feel a sideways volume force \( J \times B \), where \( J \) is the applied current and \( B \) is the local field.
The vortices feel a volume force in reaction to the current volume force of $\mathbf{J} \times \mathbf{B}$. This force causes the vortices to move at some velocity across the film where they will disappear at the opposite edge, while new vortices will reappear on the other edge so that a steady flow of vortices across the film is maintained, as indicated in Figure 3-2.

![Figure 3-2. Volume force the transport current exerts on vortices in a thin film in a perpendicular magnetic field [21].](image)

The motion of the vortex lattice induces an electric field that is opposite to that of the transport current. While the transport current moves through a region of magnetic field with some velocity $v$ an electric field is created via $\mathbf{E} = v \times \mathbf{B}$ such that in the rest frame of the transport current there is an electric field $\mathbf{E}$ with direction $(\mathbf{J} \times \mathbf{B}) \times \mathbf{B}$. So the flux lattice induces an electric field that will act to oppose the transport current (this is shown in Figure 3-3), the vector relations among the magnetic field, current density and the velocity $v \sim \mathbf{J} \times \mathbf{B}$ [21].
Figure 3-3. Vector relations between magnetic field, current density and vortex velocity [21].

**Pinning of Vortex Lattice**

Much research has been invested in finding ways to pin the vortex lattice from movement via the introduction of defects, imperfections, irradiation damage, anti-dots, magnetic dots, precipitates, interstitial atoms, grain boundaries, etc. as talked about in Chapter 1. When the vortex lattice moves across a sample with these added features they can be attracted to these imperfections. With the proper geometry and engineering the vortex lattice may become snagged on these imperfections and become unable to move. In such cases the flux-flow resistance [22] caused by the moving vortex lattice vanishes and the transport current, once established, persists to flow as in a Type-I superconductor.
Though vortices are trapped by the defects which act as pinning centers, there exists a limit to how great a force the pinning centers can hold the vortex lattice from movement. If the Lorentz force becomes too large, the vortex lattice will walk off the pinning centers and begin to move across the sample. The largest current density at which a type-II superconductor maintains without flux-flow resistance is called the critical current density $J_c$. The goal of introducing pinning sites into thin films is to enhance the value of the critical current carried by the film.

Conceptually the critical current can be found if one knows the volumetric Lorentz force on the flux line lattice and the pinning force from defects present in the film. The forced motion of vortices moving through the electron gas, normal electrons and Cooper pairs causes energy dissipation which causes the material to have resistance. To prevent the material from energy loss a pinning force $F_p$ must be introduced to limit the motion of vortex lattice. When the volume force $|F| \leq F_p$ the vortex lattice will be pinned by defects present in the film. In the case where $|F| > F_p$ the vortex lattice become unpinned and will move. However, when $|F| = F_p$ the corresponding current density is defined as the critical current density in which when can say,

$$F_p = J_c B$$  \hspace{1cm} (3-1)

$$J_c = F_p / B$$  \hspace{1cm} (3-2)

One can calculate the pinning force based on this definition, however determining $J_c$ or $F_p$ is not always obvious theoretically.
Flux-Flow Resistivity

Considering a superconductor that is pin-free, vortices under the Lorentz force $\Phi_0 J$ move in the presence of a viscous drag $\eta v$ exerted by the surrounding medium i.e defects, electron gas, normal electrons,

$$\Phi_0 J = \eta v \tag{3-3}$$

where $\Phi_0$ is the flux quantum, $v$ is the velocity, $J$ is the current density, and $\eta$ is the viscous drag coefficient. Multiplying this equation by the magnetic field $B$ gives the electric field $E$

$$E = Bv = (B/\eta)\Phi_0 J = \rho_{ff} J \tag{3-4}$$

Thus we can calculate the flux flow resistivity [24]

$$\rho_{ff} = (1/\eta)B\Phi_0 \tag{3-5}$$

The most widely accepted theory of flux-flow resistance was created by Bardeen and Stephen [24]. They treated the vortex core of radius $\xi$ in the normal state. Using the fact that when the vortex is set into motion an electric field is generated in its surroundings including the vortex core. The induced resistive currents present inside the vortex core contributes an energy loss

$$W = \rho_{ff} J^2 \tag{3-6}$$

Thus the motion of the vortices themselves causes flux-flow resistance. Their useful result is,

$$\rho_{ff} = \rho_n (B/B_{c2}) \tag{3-7}$$
Where $\rho_n$ is the normal state resistivity, $B$ is the applied field, and $B_{c2}$ is the upper critical field. This formula is simple and reveals the nature of a few simple aspects of a type-II superconductor. Namely, when $B = B_{c2}$ the normal state resistivity is recovered. When $B=0$ the flux flow resistivity goes to zero $\rho_{ff}=0$, and the superconductor will be in the Meissner state. The term $B/B_{c2}$ can be regarded as the fraction of material occupied by the vortex cores.
Matching Effects and Pinning Enhancement

Traditionally in the mixed state of a type-II superconducting thin film an external magnetic field applied to a sample penetrates in the sample in the form of quantized bundles of flux, known as flux or vortex lines. These vortices arrange themselves in a triangular pattern on the film as shown below in Figure 3-4.

Figure 3-4. Motion of vortices from left to right in a pure type-II material in a perpendicular magnetic field. Due to the Lorentz force vortices move perpendicular to the applied current.
Thus, when a current is applied to a type-II superconductor in the mixed state, the magnetic vortices feel a force that pushes them perpendicular to the current flow. If this force exceeds the pinning force, vortices start to move. This movement dissipates energy and produces resistance within the material, which lowers the critical current. Much research has been performed to limit the motion of these vortices, i.e. to enhance the critical current.

Previous research using regular arrays of anti-dots as well as other types of artificial pinning centers (magnetic dots and introduced impurities) have shown matching anomalies (i.e. maxima in the critical current at integer magnetic fields). Enhancements of the critical current in these samples occur when the number of vortices coincides with the number of pinning centers. Pinning is the phenomenon in which defects and nano-pores arranged on a thin film act to limit the motion of superconducting vortices traveling in the film. At matching fields the defects and holes literally pin down the vortices at the defect sites, as well as pin vortices at interstitial sites through the caging effect.

However, in our cases we don’t have a continuous medium in which vortices move freely in the mixed state as described above. Thus, pinning may be present in our sample at matching fields, or the integer fields at which the vortices will be locked into nano-pores in NbN films. Thus, unlike a pure defect free superconducting thin film, matching of the vortex structure onto the nano-porous template may arise from the interaction with our tailored array of pinning centers present in the film, i.e. nano-pores.
The first matching field, \( H_1 \), is defined as the field where each pinning center captures one vortex. Here vortices are thought to be strongly pinned. As a result an increase in the critical current or a decrease in the resistance is observed (see Figure 3-5).

Figure 3-5. Configuration of the first matching field \( H_1 \) when each anti-dot or defect captures one flux quantum.

The second matching field is the field value at which two vortices are captured at each anti-dot or defect and is denoted as \( H_2 \). The general formula is \( H_m = mH_1 \) where \( m \) is an integer (see Figure 3-6).

Figure 3-6. Second matching field \( H_2 \) in which each anti-dot captures two vortices.
According to V. V. Metlushko [7], the maximum possible magnetic fluxoid trapped by an individual anti-dot varies with the superconducting coherence length based on the formula

$$\Phi_s = n_s \Phi_0 = \Phi_0 D/4\xi(T)$$  \hspace{1cm} (3-8)

where $D$ is the anti-dot diameter, $\Phi_0$ is the single flux quantum, and $\xi(T)$ is the temperature-dependent coherence length (i.e. the larger the anti-dot and smaller the coherence length the more flux quanta an anti-dot can encompass). Accordingly, each anti-dot will have a saturation number noted above as $n_s$. In addition, once the saturation number of each anti-dot has been reached, additional vortices will be repelled into interstitial sites and remain there at higher matching fields. These interstitial vortices are in general weakly pinned and are much more mobile than the vortices pinned by the anti-dots. Thus, the motion of the interstitial vortices causes a drop in the critical current.

However, the interstitial vortices can be stable if they are symmetrically caged by the balance in forces between the already present vortices. Another important fact to note is that the matching effect weakens and is eventually destroyed as the angle subtended between the sample and field. When the field is perpendicular to the sample the greatest matching effects are seen as oscillations in the $R$ vs. $H$ data. The matching fields in general are given by the formula $H_m(\alpha) = H_m(0)/\cos(\alpha)$, where $\alpha$ is the angle between the field and thin film surface.
Figure 3-7. Schematic assuming that the saturation number of vortices for each anti-dot has been reached, and thus new vortices are repelled into interstitial sites between holes and trapped there by the balance of forces between the vortices.

In previous research, U. Patel et. al. found matching effect in Nb thin films with a periodic triangular hole array [11]. They took an experimental approach to determine whether the matching effect arises from the pinning enhancement or from hole-induced suppression of $T_c$ at non-integer matching fields. They used the baselines of $R$ vs. $H$ curves for both pinning enhancement and the baselines for a wire network to determine what mechanism was involved in the matching they observed (see Figure 3-8).
They obtained data for their films in perpendicular fields (when the film is flat and the magnetic field is perpendicular to the surface of the film) and in parallel fields (when the film surface is parallel to the applied magnetic field). They assumed that at parallel fields their films would behave as a superconducting strip of material because the area of the film exposed to the magnetic field will have the same geometry of that of a thin strip. This implies that if a film containing a hole array behaves like a wire network, $R(H)$ curves in parallel fields can be used to derive the baselines of those in perpendicular fields. Their experiment revealed that their film behaves as a wire network in perpendicular fields with hole-induced $T_c$ suppression (Little-Parks effect). The most important feature in their experiment is that the $R(H)$ curves for parallel field directions touch with the values of $R(H)$ for the perpendicular fields at the matching fields.
Little-Parks Experiment

In 1962 R.D. Parks and W.A. Little observed a quantum periodicity in the transition temperature of a thin superconducting cylinder (1 micron in diameter) made of tin [23]. The critical temperature and thus the electrical resistance oscillate periodically as the magnetic field is gradually increased. The period is found to be the superconducting magnetic flux quantum $\hbar c/2e$, divided by the area of the cross-section of the cylinder.

$$\frac{\Phi_o}{\pi r^2} = 1 \text{ period} \quad (4-1)$$

Thus one period corresponds to an increase of the magnetic flux through the cylinder by one flux quantum $\hbar c/2e$. Fritz London predicted these “fluxoids” as the sum of the external magnetic flux and a term involving the persistent current (supercurrent) would be quantized in units of $\hbar c/e$ in a multiply connected superconductor. The fluxoid is given by

$$\Phi = \oint H \cdot dS + \int_{\partial \Omega} J \cdot dl \quad (4-2)$$
where $S$ is the surface of the superconductor and $P$ is the perimeter bounding the superconductor, in their case a cylinder. $J$ is the supercurrent and $\Lambda$ is the London parameter which is equal to $\Lambda = \frac{m}{n\epsilon^2}$. The first term in equation (4-2) is simply the applied magnetic field while the second term is due to the supercurrent circulating around the cylinder.

The experiment performed by Little and Parks used a thin-walled superconducting cylinder because the penetration depth is much greater than the wall thickness of the superconducting cylinder: i.e. $\lambda \gg t$ where $t$ is the thickness of the cylinder. They expected that the Meissner effect would be vanishingly small in this case so that they had a uniform magnetic field in the cylinder not only in the interior but also existing in the walls and equal to the axial applied magnetic field. They determined that the first term in the fluxoid equation must be determined solely by the applied field and quantum periodicity must arise from the second term describing the supercurrent $J$. In the Little and Parks experiment the total flux given by equation (4-2) always adds to an integer number times one flux quantum: i.e. $\Phi = n\Phi_0$ where $n$ is an integer and $\Phi_0 = \frac{hc}{2e}$. Thus, solving equation (4-2) for the current assuming that the total flux must be given in quantum units,

$$n(\frac{hc}{2e}) = \int_S \mathbf{H} \cdot d\mathbf{S} + \int_P c\Lambda J \cdot d\mathbf{l}$$  \hspace{1cm} (4-3)$$

$$n(\frac{hc}{2e}) = H\pi r^2 + c\Lambda J 2\pi r$$  \hspace{1cm} (4-4)$$

rearranging to solve for the current $J$,

$$J = \frac{(n\frac{hc}{2e} - H\pi r^2)}{c\Lambda 2\pi r}$$  \hspace{1cm} (4-5)$$
Inserting equation (4-5) for the current into the associated kinetic energy and using the fact that

$$J = n_e e v$$  \hspace{1cm} (4-6)

where $n_e$ is the number of electrons, $e$ is the charge of an electron and $v$ is the velocity of the electrons, solving for $v$, $v = J/n_e e$ and plugging into the equation for the kinetic energy

$$ KE = \frac{1}{2} m v^2 $$  \hspace{1cm} (4-7)

$$ KE = \frac{1}{2} n_e m (J/n_e)^2 $$  \hspace{1cm} (4-8)

$$ KE = \frac{1}{2} \frac{m}{n_e e^2} J^2 $$  \hspace{1cm} (4-9)

And recognizing that $\Lambda = m/n_e e^2$, the kinetic energy simply is

$$ KE = \frac{1}{2} \Lambda J^2 $$  \hspace{1cm} (4-10)

Plugging the current density $J$ into this equation, one arrives at the following equation:

$$ KE = \frac{1}{2} \Lambda J^2 = \frac{\hbar^2}{16\pi^2 e^2 \Lambda^2 r^2} (n - (2e/\hbar c)\Phi)^2 $$  \hspace{1cm} (4-11)

This predicted that the associated kinetic energy for a fluxoid is thus periodic in flux and depends upon the velocity of the Cooper pairs which according to their predictions is also periodic and acts to minimize the kinetic energy. The corresponding graph of the kinetic energy of a superconducting pair vs. flux is shown in Figure 4-1. Also included in Figure 4-2 is the variation of the velocity of the Cooper pairs.
Figure 4-1. Kinetic energy of the center of mass motion of an electron pair vs. the magnetic flux [24].

Figure 4-2. Variation in the velocity of the Cooper pairs vs. magnetic flux quanta [24]
As the applied magnetic field increases from zero with \( n=0 \), the kinetic energy of a Cooper pair increases quadratically. At \( \Phi=1/2(hc/2e) \) \( n \) switches from 0 to 1 and a further increase in the applied magnetic field at this point leads to a quadratic decrease in the kinetic energy of a Cooper pair, as shown in Figure 4-2. When \( \Phi=3/2(hc/2e) \) \( n \) switches from 1 to 2 and the kinetic energy of the Cooper pair increases once again to a maximum value. Thus, this prediction shows that there exists a periodicity in flux which arises due to the velocity of Cooper pairs and their kinetic energy in this cylindrical geometry.

In addition, they also predicted that the \( T_c \), which is the temperature where the free energies of the normal and superconducting states are equal, must be a periodic function of the enclosed flux in their tin cylinder. The kinetic energy of the Cooper pairs which is proportional to the change in \( T_c \) i.e. \( -\Delta T_c \), as shown in Figure 4-3.

![Figure 4-3. Schematic of velocity and \( T_c \) suppression with respect to the applied field [26].](image-url)
They equated a formula to describe these oscillations in $T_c$ which is given below along with the $T_c$ and H phase diagram shown in Figure 4-4. Here $r$ is the radius of the cylinder, $m^*$ is the $2m$ (twice the mass of an electron), $\Phi$ is the flux, $n$ is an integer, $c$ is the speed of light, and $h$ is Planck's constant. From direct observation of the formula below one can see the periodic dependence of change in $T_c$ on flux,

$$\Delta T_c = \frac{h^2}{16m^*r}(2e/hc)\Phi + n$$

(4-12)

The corresponding velocity is,

$$v_s = \frac{h}{m^*r}(n - \Phi/\Phi_0)$$

(4-13)

For the flux entering the sample imposed by $H$, the energy of the supercurrent inside the cylinder will be smallest at integer $n$ for which $v_s$ is zero. This choice of $n$ will allow for the system to remain superconducting at the highest possible temperature. Thus the system will remain superconducting at the lowest possible energy level where the periodicity in $v_s$ acts to suppress $T_c$ at half integers' flux values.

Figure 4-4. Predicted oscillations in $H$ vs. $T$ phase diagram put forth by R. D. Parks and W. A. Little [23].
The experimental data observed by Little and Parks is shown in Figure 4-5. The period of the parabolic scallops is $\hbar c/2e$ in the magnetic flux as predicted by their calculations. However, they attribute the quadratic background (which was not predicted by their calculations) in their data to the weakening of the Cooper pairs by the applied magnetic field, i.e., the field at which the Cooper pairs are broken apart. In general, Little and Parks’ experiment was an amazing discovery in showing that induced supercurrent gives rise to a quantum nature of flux expelled in multiply connected geometries such as theirs. Their experiment also gave legitimacy to the Bardeen-Cooper-Schrieffer (BCS-theory) in terms of observing the basic quantum flux unit to be $\hbar c/2e$ rather than $\hbar c/e$.

Figure 4-5. Resistance vs. magnetic field of an indium cylinder at a temperature below $T_c$. The quantum periodicity in the free energy superconducting Cooper pairs is shown, as well as the quadratic background, which was not predicted by their theory [23].
**Josephson Effect**

Brian Josephson predicted that Cooper pairs could tunnel through weak links placed between superconducting media with zero voltage and further predicted that if a voltage were to be applied across the weak link the Cooper pairs would alternate with time across the weak links with a frequency of $2eV/h$, where $h$ is Planck’s constant.

Considering a bulk superconducting material that is separated by a thin insulating region, usually an oxide layer, supercurrent is able to flow through a thin insulating region without an applied voltage. If a potential difference between the insulating regions is present, the supercurrent will oscillate as a function of time. The thickness of the insulating region must be on the order of ~1-2nm to observe this effect. In general, the thickness must be small compared to the superconducting coherence length.

Consider the condensate wave function where $x$ is the direction across the insulating barrier:

$$\Psi(x,t) = (n_s)^{1/2} \exp[i\Phi(x,t)]$$  \hspace{1cm} (4-14)

We then assume a supercurrent $J$ flowing across the insulator in the $x$ direction: the condensate wave function will depend on the insulating barrier thickness.

$$J = (e*/m*)n_s d\Phi/dx$$  \hspace{1cm} (4-15)

The condensate wave function will undergo a phase shift while crossing from region 1 to region 2 in the form

$$\phi = \Phi_1 - \Phi_2$$  \hspace{1cm} (4-16)
thus the charge carriers change quantum states from $\Psi_1(t)$ to $\Psi_2(t)$ while crossing the insulating barrier with a transition amplitude $K$ which contains the material properties of the insulating barrier. This can be described in the following equation:

$$i\frac{d\Psi_1(t)}{dt} = K\Psi_2(t)$$  \hspace{1cm} (4-17)

Similarly, one can also write,

$$i\frac{d\Psi_2(t)}{dt} = K\Psi_1(t) + e^*V \Psi_2(t)$$  \hspace{1cm} (4-18)

where $e^*V$ is the electrostatic energy due to an applied voltage. Taking time derivatives and separating into real and imaginary parts one obtains the equations

$$\frac{dn_{s1}}{dt} = 2K(n_{s1}n_{s2})^{1/2}\sin(\phi)$$  \hspace{1cm} (4-19)

$$\frac{dn_{s2}}{dt} = -2K(n_{s1}n_{s2})^{1/2}\sin(\phi)$$  \hspace{1cm} (4-20)

$$\frac{d\phi}{dt} = e^*V + K[(n_{s1}/n_{s2})^{1/2} - (n_{s2}/n_{s1})^{1/2}]\cos(\phi)$$  \hspace{1cm} (4-21)

The current passing through the insulating barrier is given as the number of carriers tunneling per unit time: i.e.

$$I \sim dn_{s1}/dt.$$  \hspace{1cm} (4-22)

$$I = I_c\sin(\phi)$$  \hspace{1cm} (4-23)

where $I_c \sim K(n_{s1}n_{s2})^{1/2}$. If both superconducting materials are made of the same element then $n_{s1}=n_{s2}$ and $\phi= e^*V$ and we obtain

$$I = I_c\sin(\phi_0 - e^*Vt)$$  \hspace{1cm} (4-24)

where $\phi_0$ is the phase shift without an applied voltage. Thus $I<I_c$ flows through the insulating barrier without an applied voltage granted $\phi_0$ is non-zero. When a voltage is applied, the current will oscillate with a frequency equal to

$$\omega = e^*V/\hbar$$  \hspace{1cm} (4-25)
Josephson current also oscillates as a function of applied magnetic field. If we apply a magnetic field in between the insulating region the field will penetrate in a region $s = t + 2\lambda_H$, where $t$ is the thickness of the insulating region and $\lambda_H$ is the Pippard dirty limit penetration depth which accounts for impurities present in the material.

To find the effects of the magnetic field on the supercurrent crossing the insulating barrier we consider a contour path that crosses the insulating region twice. The currents flow along $x$ are canceled and the screening current is negligible if the contour is much larger than $s = t + 2\lambda_H$. Refer to Figure 4-6.

![Figure 4-6. Josephson’s weak link between two superconductors](image)

Using the equation below where $dl$ is the path of integration, $A(r)$ is the vector potential, $\delta \Phi$ is the phase shift across the insulating barrier,

$$c\int dl \cdot A(r) = \frac{\delta \Phi}{e^*}$$  \hspace{1cm} (4-25)

The left-hand side of this equation is just the elementary flux $d\Phi = B \cdot sd\gamma$ while the right-hand side is the phase shift across the region,

$$d\Phi = [\phi(y+dy) - \phi(y)]/e^*$$  \hspace{1cm} (4-26)
This reveals that the field presence affects the Josephson current density $j = j_c \sin \varphi(y)$ such that the current density isn’t uniform in the insulating region. Because,

$$\varphi(y) = e^*Bsy + \varphi_o$$

(4-27)

thus the total current through the contact is [22],

$$I = j_c L \int dy \sin(e^*Bsy + \varphi_o) = I_c (\sin \varphi_o)[\sin(\pi \Phi_B/\Phi_0)/\pi \Phi_B/\Phi_0]$$

(4-28)

where the function $dy \sin(e^*Bsy + \varphi_o)$ is integrated from $-s/2$ to $s/2$, i.e., the insulating gap.

Current in a Josephson junction in the presence of a magnetic field oscillates as a function of the applied magnetic flux which is shown graphically below; notice the quantum interference pattern made from quantum flux dependence of $I_c$ in Figure 4-7.

![Figure 4-7. Magnetic field dependence of the Josephson current [22].](image)

M. Tinkham, David W. Abraham, and C.J. Lobb have found periodic variation of resistance of large arrays of Josephson junctions made of Pb-Cu-Pb,
normal to an applied magnetic field, with resistance minima for integral numbers of
flux quantum per unit cell of the array [15]. They showed that the resistance
modulation is attributed to a periodic, field-dependent $T_c$. More importantly, they
observed sharp resistance dips at integer flux values and secondary dips at the half
integer values in resistance. This is similar to the Little-Parks effect in the aspect of
resistance minima at integer fields and different due to the appearance of secondary
dips at half matching fields in addition to Cooper-pairs tunneling through junctions
at matching fields (see Figure 4-8).

Figure 4-8. Magnetic field dependence of the resistance observed at
various temperatures within the resistive transition of a two
dimensional array of superconductor-normal metal-superconductor
junctions (Pb-Cu-Pb) [15].
Production of anodic aluminum oxide (AAO) in our experiment was carried out through a 2-step anodization process which will be described in the following paragraphs. We begin with a single strip of high purity polished Al (99.9%) with dimensions of roughly 2x2 cm². To minimize dust and contaminates on the surface we must first clean our Al square in a bath of acetone with ultrasonic vibrations pulsing through the bath, provided by a Branson 2510 ultrasonic vibration source. We then clean off the Al strip with DI water. Then the Al is connected to the positive terminal (anode). We then immerse the Al strip and a Pt strip which serves as the cathode into a beaker of 0.3 M oxalic acid. The beaker rests in a Neslab RTE 10 thermo base at 3 degrees Celsius. The voltage applied between the Al and Pt strips is 40V, and the system is left to evolve for 24 hrs in which an initial oxide layer is formed on the surface of the Al strip by the electric field generated between the two strips. This is known as the 1\textsuperscript{st} anodization. The setup is depicted in Figure 5-1.
The purpose of the first anodization is to prepare the Al strip for a 2\textsuperscript{nd} anodization in which continuous and uniform nano-pores are grown. Nano-pores are grown during the 1\textsuperscript{st} anodization, but these pores vary in diameter and don’t have the periodic arrangement we desire. The pores after the first anodization resemble that of Figure 5-2.

After the first anodization the Al/Al-oxide barrier will have a periodic uniform structure of nano-dimples at the pore base, which is what we desire to have for the 2\textsuperscript{nd} anodization. Now we must strip off the grown Al-oxide layer and re-anodize the Al foil for 12 hrs. The strip-off procedure requires placing our sample in a bath of chromic acid for 24 hours, at roughly 65 degrees Celsius. By doing this the
chromic acid etches away the non-uniform Al-oxide pore structure and leaves us an Al foil with fine surface structure as depicted in Figure 5-3.

![Figure 5-3. Desired template of Al for purpose of the second anodization.](image)

After the chromic acid has depleted the non-uniform Al-oxide layer, we are left with a uniform continuous template in which a uniform Al-oxide barrier will be grown. The 2\textsuperscript{nd} anodization parameters are exactly the same as those used in the first step with exception of the length of time left, which is now 12 hrs. The anodization time of an Al strip is determined by the desired thickness of the nano-porous oxide layer. Thus, the longer Al is anodized, the thicker the oxide layer will be. If left long enough the entire Al will be converted into Al-oxide. After the 2\textsuperscript{nd} anodization is complete one will obtain a uniform template of AAO, which is represented in Figure 5-4.

![Figure 5-4. Desired template after second anodization.](image)
Under the conditions described above, the resulting anodic alumina is a self-organized material containing a high density of periodically spaced uniform cylindrical pores with spacing of roughly 100 nm. In addition, the pore diameter is tunable from 5nm to hundreds nm, with a pore density from $10^{12}$ to $10^9$ cm$^{-2}$.

According to models based on formation of anodic alumina the diameter of the pore is given by

$$W = 2TV + P$$ (5-1)

where $W$ is the cell size, $T$ is the wall thickness in angstroms per volt, $V$ is the forming voltage, and $P$ is the pore diameter [25].

![Figure 5-5 Schematic side and top view of anodic alumina and corresponding cell size $W$ and pore diameter $P$ [25].](image)

**SEM Imaging**

Imaging of AAO was performed using a scanning electron microscope (SEM). Probing materials with electrons has proved of great significance for imaging due to the short wavelength electrons can achieve, making it possible to reveal small
features down to 1-5nm or less. The wavelength can be varied with the applied voltage used to accelerate the electrons.

When a material is struck by the incident electron beams, it emits visible light, Bremsstrahlung x-rays, characteristic x-rays, Auger electrons, back-scattered electrons, transmitted electrons, diffracted electrons, and secondary electrons. All of the previously listed types of radiation can be utilized to find information about the material. For example, the characteristic x-rays may be captured and analyzed to find the spatial distribution of elements present in a material, which gives insight about the phase of the material. SEM imaging utilizes secondary electrons emitted from the sample surface. When the incident electron beam is applied to the surface of a material, a fraction of these electrons will undergo inelastic collisions with the nucleuses present in the material. Upon collision, outer shell electrons are ejected from the nucleus at much lower energies than that of the incident electron beam. Secondary electrons thus having a much lower energy don’t travel far from the sample surface, and must be drawn into a photoscintillator via an attractive potential near the surface of the sample. Once inside the scintillating material, photons are emitted and collected to form an image of the sample surface. Figures 5-6 and 5-7 show the image we retrieved from SEM.
Fig 5-6. SEM image of AAO showing the grid of nano holes produced by anodization.

Figure 5-7. Magnified image of AAO. Nano pores diameter ~50nm and center to center distance of ~100nm
The deposition of NbN compound onto our AAO substrates was done by using a AJA ATC2400 DC magnetron sputtering system. We have used a reactive sputtering process by introducing nitrogen into the sputtering chamber, to create a nitric film of niobium (NbN).

The system consists of a vacuum chamber containing our synthesized nanoporous AAO template (substrate), the target material of Nb, a permanent magnet located under the target material, and voltage source applied between substrate and target.

Initially the chamber is pumped down to $10^{-7}$Torr, then is filled with Ar and N to the desired level (~ a few mTorr). Once the appropriate gas atmosphere is achieved, the voltage between the target (negatively charged) and the substrate (grounded) is turned on. The discharged Ar atoms will have a net positive charge and become Ar ions. These ions are then immediately accelerated toward the negatively charged Nb target. Upon striking by the Ar ions the Nb atoms are broken off from the target and are deposited on the AAO substrate.

The permanent magnets in this system will act to trap these secondary electrons (as well as free electrons) in the helical paths circulating around the field lines. The magnets act to greatly enhance the ionization probability of the inert Ar gas, thus leading to a higher number of Ar ions for bombardment, which increases the sputtering rate: i.e., without the magnets the sputtering rate is much lower. In
addition, it prevents the free electrons from bombarding the substrate surface, which may cause damage.

Sputtering parameters for the atmosphere inside the chamber were 24sccm Ar + 6sccm N$_2$ pumped into the sputtering chamber held at 3.5 mTorr at a temperature of 500°C with 150W(471mA, 318V) power source. This yields a deposition rate of 1.7Å/s for a 50nm thickness achieved in 4 minutes and 54 seconds.

After the deposition process, further SEM imaging was performed on the AAO and the images are presented in Figures 5-8 and 5-9.

![Figure 5-8. NbN sputtered on AAO substrate.](image)
From Figure 5-9 we can obtain a lattice constant for our triangular array with a lattice constant of roughly $a=100-110$nm. We will use this later for calculation of the matching fields.
CHAPTER 6

XRD

X-rays have a wavelength on the order of a few angstroms (1 Angstrom = 0.1 nm) and are widely used to analyze the crystal phases and structure of materials. When an x-ray beam enters the crystal, a portion of it will be reflected by the first layer. The rest will continue through to the second layer. By the definition of constructive interference, the separately reflected waves will remain in phase if the difference in the path length of each wave is equal to an integer multiple of the wavelength. Below is Bragg’s Law for diffraction where \( n \) is an integer, \( d \) is the distance between atomic planes, and \( \theta \) is the angle at which maximum constructive interference occurs, known as the Bragg angle. See Figure 6-1

\[
2d \sin \theta = n \lambda
\]

Figure 6-1. Schematic of x-ray diffraction off two parallel atomic planes. Notice that the deflected beams from both planes will coherently interfere in this picture. The interference is constructive when the phase shift is a multiple to \( 2\pi \) [26]
Each material has signature angles $\theta$ at which maxima in constructive interference will occur. These maxima appear as intensity peaks when detected upon reflection. The angles at which these maxima occur reveal what material or materials are present in a sample of interest as well as the crystal structure. By using the appropriate known x-ray wavelength and finding the Bragg angles experimentally we have two of the known variables for Bragg's law: this allows us to obtain the spacing of atomic planes within a material, which gives insight into the crystal structure.

Realization of the phase of our NbN film is important mainly because it provides us the knowledge that we successfully have achieved a thin film where niobium and nitrogen have bonded together and formed an atomic structure with one another. Presented in Figure 6-2 is the XRD data of our sputtered film.

![Figure 6-2. Raw XRD data obtain from NbN film after sputtering.](image)
From Figure 6-3 obtained by U. Patel [27] we can see peaks at $\theta \approx 72^\circ$, $61^\circ$-$62^\circ$ and $41^\circ$-$43^\circ$, which is roughly where our XRD shows peaks of intensity. However, our XRD was performed on a thin film of NbN, which could have a preferred orientation, while in Figure 6-3 is powder diffraction XRD. This is why they see more peaks due to the fact that the crystals in the material are oriented in many directions. We cannot say with absolute certainty the exact phase of our crystal structure or composition. On the other hand we can say we have obtained some phase of NbN$_x$ because peaks locate at some constructive interference angles of the powder diffraction XRD.

Figure 6-3. Powder XRD data obtained from NbN ribbons by U. Patel showing the different phases of NbN they have achieved [27].
Resistive measurements were carried out using a Physical Property Measurement System (PPMS) manufactured by Quantum Design, Inc. The system uses the standard four-probe DC measurement setup. If a material is measured with only two wires, the resistance of the contact points of the wires is also included in the total resistance. Typically the contact resistance is much smaller than the resistance of the sample and in general is negligible. However, when measuring a very small sample resistance under variable temperature conditions, the contact resistance can completely obscure changes in the resistance of the sample. This is why when measuring resistance in superconductors one must need to use the four-point method.

A schematic of a four-probe measurement setup is shown in Figure 7-1 below.

![Figure 7-1. Schematic of a four-probe measurement system.](image)
In this schematic, four probes have been attached to the sample. A constant current is applied to flow into the sample through probes labeled 1 and 4. If a resistance exists in the sample due to the current flow, then there will be a drop of potential due to the current applied along the sample. For example, the potential difference between probes 2 and 3 can be measured by a voltmeter. The resistance of the sample between probes 2 and 3 is the ratio of the voltage registering on the digital voltmeter to the value of the output current of the current source. The high impedance of the digital voltmeter minimizes the current flow through the portion of the circuit comprising the voltmeter. Since there is no potential drop across the contact resistance associated with probes 2 and 3, only the resistance associated with the superconductor between probes 2 and 3 is measured.

The probes used in our sample are connected by 25-μm thick gold wires with indium pressed on the probe contacts. The applied DC current is 50μA. Each data point is composed of three measurements averaged to reduce noise. Our sample is held on a rotator that has a range from -10° to 370° with a resolution of 0.053°. The magnetic field is always applied in the vertical direction to the current and ranges from 0 up to 9 Tesla. A thermometer is placed on the rotator for temperature control. The temperature is stabilized within ±2mK when measurements were taken. See Figure 7-2.
Figure 7-2. Schematic of sample inside PPMS. Magnetic field applied in vertical direction with the applied current in horizontal direction. Rotational direction of sample is shown.
Resistance Data and Discussion

Figure 7-3. Temperature dependence of the resistance of a NbN film in various applied fields in steps of 500(G) up to 40,000(G).

In Figure 7-3 we can deduce the superconducting transition to be in the range of 11-12.4K at the zero field curve. We will use temperatures ranging between 11.0K and 12.4K to perform magnetoresistance measurements. In Figures 7-4 and 7-5, matching is observed in the magnetoresistance data obtained in the transition temperature range as presented by Figure 7-3.
Figure 7-4. Resistance vs. magnetic field for the temperature range from 11.0K-12.4K in steps of 0.1K except for the top three curves which are in steps of 0.2K from 12.0K.
Figure 7-5. Magnified view of Figure 7-4 showing dips in the resistance at matching fields.

The most pronounced oscillations are observed in the R vs. H values in between 11.6K and 11.7K. The resistive dips appear at $H_n = n*H_1$ for a value of $H_1=2200$ G, i.e. $H_n = n*2200$ G as shown in Figure 7-5. Considering the amount of field present in our triangular lattice with spacing of ~100nm between neighboring holes, we can calculate where the first matching field should appear using $\Phi_0 = H*A$ [30], where $A$ is the area of the unit cell in the triangular lattice. Our first matching field should appear at a field value where each hole captures one flux quantum.

$$H = \frac{\Phi_0}{A} = \frac{0.5*(\sqrt{3})a^2}{0.5*(\sqrt{3})a^2} = 2380$$ G. Our data is only 7.56% from the theoretical value, which is expected due
to our film not being absolutely uniform everywhere, plus the fact that grain boundaries are present in between the sections of NbN and separation between nano-holes is not exactly the same length.

Next we will explore the angular dependence of the magnetoresistance at 11.7K.

Figure 7-6. Magnetoresistance at angles from 90°-0°D at 11.7K. Curves have been separated at 5 Ω increments to show the smoothing of resistance curves.
As seen in Figures 7-6 and 7-7, the oscillations in the resistance start to smooth out as the angle between the NbN film and field decreases. As seen in previous research [10,11], this behavior can be attributed to the perpendicular component of the magnetic flux threading each hole, being the contributing factor. Notice that the 0° curve shows oscillations that derive from the baseline of the 90°, data which indicates hole-induced $T_c$ suppression. Thus, as the angle between the film and magnetic field is subtended away from zero, the contribution from the field
is weakened by the relation \( H_m(\alpha) = H_m(0)/\cos(\alpha) \). Thus, the smaller the contribution from the magnetic field perpendicular to the surface of our film, the weaker the magnetic field contribution to the interaction with circulating Cooper pairs in and around the holes in the film. This results in larger oscillation periods and smaller oscillations amplitude at increasing angles. Once the angle reaches 90° the film is parallel to the applied field and appears as a thin superconducting strip in which oscillations are not seen.

Next we look at the H vs. \( T_c \) phase diagram in which oscillations in the \( T_c \) can be observed as shown in Figures 7-8 and 7-9.

![Figure 7-8. \( T_c \) vs. \( H_c \) at 10% resistivity for angles 0° and 90°.](image)
Figure 7-9. Expanded view of Figure 7-8, revealing a closer view of oscillations in the $T_c$.

Much like in the Little-Parks experiment in which they observed oscillations in the $T_c$, our sample also reveals the same behavior. The 0° data at matching fields take on values of $T_c$ close to the values of $T_c$ in the 90° data. However, the Little-Parks experiment used thin cylinders. In our experiment we have nano-holes surrounded by NbN junctions, thus the data we have obtained would be favoring the Josephson Junction effect similar to that reported by Tinkham et al. for a two-dimensional array of superconductor-normal metal-superconductor (Pb-Cu-Pb) junctions [15]. In fact, the SEM images in Figure 6-2 in Chapter 6 show a small
separation on the order of less than 5 nm between clumps of NbN. This implies that the phenomenon we see is most likely due to the Josephson effect. In our case at matching fields (where the holes contain integer flux quanta) the Cooper-pairs are allowed to tunnel through sections of NbN across the weak links separating the sections with a reduced resistance.

![Figure 7-10. 2D linear fit of H vs. T from Figure 7-7.](image)

From Figure 7-10 one can see that the upper critical field $H_{c2}$ is non-linear near $T_c$ and at temperatures above ~ 11.32K become linear. As shown by U. Welp
et. al. this can be understood in terms of 1D superconductivity that occurs when the coherence length $\xi$ becomes larger than the width of the NbN sections between holes [11]. In our case the width between holes is not entirely uniform but in the range of $\sim$55-75 nm. We shall use the 2D linear fit, which occurs in the range where the data follows a linear trend, and in the region the coherence length $\xi$ is smaller than the width of the NbN between the holes. 1D and 2D fits to the data can be used to obtain the zero-temperature coherence length. Using the 2D expression for a thin film in parallel fields, in this case can be approximated by the bulk value expression $H_{c2}(T) = \Phi_0/(2\pi\xi(T)^2)$ where $\xi(T) = \xi(0)(1-T/T_c)^{-1/2}$ is the Ginzburg-Landau coherence length [29]. The linear fit reveals that our material has a zero temperature coherence length of $\xi(0)\sim 3.27$nm, which is consistent with previous values obtained in NbN, which are generally in the range of 3-5nm [27, 30]. Given that we cannot explicitly define the absolute Nb/N compositional ratios from our XRD analysis, the consistence of the zero-temperature coherence length in our samples with those of pure NbN indicates that niobium and nitrogen have bonded in our high temperature environment as we desired and that the Nb/N ratio in our material does not deviate significantly from 1:1.
The purpose of this study was to fabricate porous anodic aluminum oxide (AAO) membranes, use them as substrates to fabricate superconducting niobium nitride films containing arrays of nano-scale holes, and to study the physical properties of the synthesized films. The focus of this thesis work is to demonstrate the possible application of AAO membranes as substrates to fabricate superconducting films which require elevated substrate temperatures to form. AAO membranes were fabricated by anodizing aluminum foils in 0.3M oxalic acid solution at 40 V. Scanning electron microscopy imaging shows ordered arrays of nano-channels with diameter of ~ 50 nm and spacing ~ 100 nm. DC magnetron sputtering was employed to deposit NbN films by sputtering Nb in a nitrogen atmosphere with argon gas as the working gas. Superconducting NbN films with critical temperature up to ~ 11.7 Kelvin were obtained at a substrate temperature above 400 C. X-ray diffraction revealed that we had formed some phase of NbNₓ; however, we couldn’t identify the exact phase or composition percentages. Four-probe resistive measurements were carried out on these NbNₓ films with arrays of holes. Minima were found in the field dependence of the resistance at matching fields.
where the magnitude of the magnetic flux through each unit cell is an integer number of the flux quantum. By comparing the field dependences of the critical temperatures and magnetoresistance at parallel and perpendicular magnetic fields, we concluded that the resistance minima in magnetoresistance originate from Josephson Junction arrays of sections of NbNₓ in which resistance dips occur at integer fields when the anti-dots capture integer flux quanta. I hope my work will stimulate the application of AAO membranes as substrates to fabricate other perforate films which require high substrate temperature, for example, high temperature superconductor films.
REFERENCES


26 www.eserc.stonybrook.edu/ProjectJava/Bragg.


