SUPERCONDUCTIVITY AND VORTEX DYNAMICS IN
NANOSTRUCTURES OF TWO-DIMENSIONAL CRYSTALS OF
NIOBIUM DISELENIDE

A Dissertation in
Physics
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2016
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Abstract

The confinement offered by superconducting nanostructures enables the study of the motion of individual Abrikosov vortices in reduced dimensions. At the present time, most superconducting nanostructures are fabricated from deposited films of metals, which are often polycrystalline or amorphous. The realization of a single-crystal nanostructure would provide the opportunity to explore the effects of the electronic band structure. Consider crystalline superconducting nanostructures of NbSe$_2$. Questions such as the how the charge density wave order influences vortex pinning and the logarithmic vortex-vortex interaction, as well as how the crystal thickness dependence of the electronic band structure affects intrinsic vortex properties motivated our efforts to develop techniques to fabricate and measure superconducting nanostructures of 2D crystal NbSe$_2$. Additionally, nanoscale transport devices are relevant to potential future superconducting electronics.

In this dissertation, we begin by presenting a novel technique for the preparation of single-crystal nanostructures prepared from mechanically exfoliated few-layer crystals of NbSe$_2$ using a process combining electron beam lithography and reactive plasma etching. Our technique allows for the preparation of ultra-thin, single-crystal superconducting nanostructures with a desired geometry for the study of vortex dynamics in extremely confined systems. A primary advantage of transport devices is the ability to directly manipulate individual vortices through the use of an applied current and other parameters.

We first present magnetoresistance measurements on NbSe$_2$ nanowires and show features related to vortex crossing, trapping, and pinning. The vortex crossing rate is found to vary non-monotonically with the applied field, which results in non-monotonic magnetoresistance variations in agreement with theoretical calculations in the London approximation. Above the lower critical field, $H_{c1}$, the crossing rate is also influenced by vortices trapped by sample boundaries or pinning centers, leading to sample-specific magnetoresistance patterns. We show that the local
pinning potential can be modified by intentionally introducing surface adsorbates, making the magnetoresistance pattern a “magneto fingerprint” of the sample-specific configuration of vortex pinning centers in a superconducting nanowire.

Building upon our work on NbSe$_2$ nanowires, we next focus on NbSe$_2$ nanoloops. The doubly-connected topology of nanoloops presents a unique opportunity for the manipulation of Abrikosov vortices; numerical calculations in the London limit suggest that an Abrikosov vortex can be trapped in a nanoloop above a critical magnetic field and generate a phase shift in the magnetoresistance oscillations. We measure magnetoresistance oscillations resulting from vortex crossing events in NbSe$_2$ nanoloops and demonstrate experimentally that the crossing of vortices can be directed at a pair of constrictions in the loop, leading to more pronounced magnetoresistance oscillations than those in a uniform loop. We also observe for the first time a phase shift in the magnetoresistance oscillations resulting from vortex trapping in the nanoloop, and we manipulate the trapped vortex with an applied transport current.

Results obtained in our NbSe$_2$ devices provide a starting point for the manipulation of individual Abrikosov vortices, allowing further exploration of the fundamental properties of this topological object that will lead to a deeper understanding of the motion, including the quantum motion, of vortices. Longstanding, unresolved issues such as the Aharonov-Casher quantum interference of Abrikosov vortices may be solved.
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Acknowledgments

Obviously, no dissertation exists but for the patient guidance of one’s advisor. In this respect, I am grateful to Prof. Ying Liu for providing an environment in which I could develop into a proper experimentalist, writer, and communicator. I have also appreciated numerous discussions and debates with my friend and colleague, Xinxin Cai, regarding the finer points of vortex dynamics in nanoloops; I am likewise appreciative of senior colleagues Dr. Neal Staley and Dr. Conor Puls for introducing me to the frustrations of device physics.

I am eternally indebted to a long list of Godly men who have labored beside me and provided wise counsel throughout my tenure at Penn State. D.S., L.S., and D.M. were there from the beginning, and helped me maintain an accurate perspective throughout the trials of Ph.D. research; C.C. and J.S. were instrumental in keeping me humble at the end.

Finally, I must express my deepest appreciation to my growing family. My wife, Rachel, has been a constant source of support in all areas of life. Thank you for your willingness to take this risk with me, and for handling virtually every detail in our lives unrelated to NbSe$_2$ nanostructures. To my children – thank you for tolerating the often long and odd hours. And thank you for your constant innocence, joy, and enthusiasm, which has contributed immeasurably to my outlook over the years. As you grow, I pray you continue to mark time with Nerf gun battles, Attack-apillars flops, and tackling games, and not the customary months and years we adults employ.
But beyond this, my son, be warned: the writing of many books is endless, and excessive devotion to books is wearying to the body.

Ecclesiastes 12:12 (New American Standard Bible)
Chapter 1

Introduction

Superconductors are not merely materials which exhibit a zero resistivity state; they constitute a remarkable phase of matter. As with any phase featuring long-range order, dimensionality plays an important role in the physics of the superconducting state. The intriguing phenomena of the phase transition in dimensionally confined systems has been the subject of condensed matter physics research over many decades. A true long-range order in the two-dimensional (2D) limit is prohibited at any finite temperature. A quasi-long-range, or topological long-range, order is achieved in a 2D superconductor through a Berezinskii-Kosterlitz-Thouless (BKT) transition involving the binding of vortex-antivortex pairs interacting logarithmically [1–3]. Below $T_{c}^{BKT}$, vortex-antivortex pairs can be generated by thermal excitation. Above $T_{c}^{BKT}$, the pairs unbind, and the quasi-long-range order is lost. Interestingly, in the absence of superconducting order, electron localization is expected to result in an insulating ground state at zero temperature [4]. Therefore, in 2D, a superconducting-insulating quantum phase transition exists, confirmed experimentally in deposited amorphous films [5] and tunable by disorder, film thickness, and magnetic field [6,7].

Additional confinement such as 1D nanowires [8] and 0D particles [9], and the strong influence of both thermal and quantum fluctuations in such confined geometries, have led to discoveries of novel physical phenomena. Advancing nanofabrication techniques have allowed for increasingly complex confined 2D geometries which help reveal the rich physics of superconductivity in low dimensions [10,11]. The BKT vortex-antivortex unbinding transition is modified in the case of a finite
system size, which imposes a cutoff length on the vortex interaction. Much theoretical [12–16] and experimental effort has been devoted to elucidating the nature of static [17–26] and dynamic [27–31] vortices in confined geometries, but previous work lacks in several notable ways. Most systems employed are polycrystalline, and thus grain boundaries and inhomogeneities may affect the motion of vortices. Furthermore, the type-II superconducting nanostructures studied experimentally have not been designed with the goal of manipulating vortex motion in mind. The manipulation of individual vortices within nanoscale transport devices will enable experiments quantifying intrinsic properties such as the effective vortex mass [32–35] and the magnitude of various forces exerted upon vortices [36]. Significantly, the fundamental issue of whether a vortex can move as a macroscopic quantum particle remains an open question [37]. Superconducting nanostructures of 2D crystals in which individual vortices can be isolated and manipulated are a promising avenue for addressing the issue [38–41]. Specifically, 2D crystal nanostructures should feature the lowest achievable dissipation associated with vortex motion, which will maximize the length scale over which a vortex remains coherent.

The aim of this dissertation is to explore superconductivity in confined systems – specifically, 2D crystal nanostructures of NbSe$_2$ – with the intention of manipulating the motion of Abrikosov vortices. We started by selecting a suitable superconducting 2D crystal material system, followed by developing a process in which nanostructures (nanowires, nanoloops, etc.) are fabricated from the 2D crystal [42]. We performed low-temperature transport measurements to characterize and manipulate the vortex dynamics in such structures [43,44]. This sets the stage for future work which can provide insight into the influence of vortex dynamics, both classical and quantum, on the superconducting phase in confined 2D crystal superconductors.
Chapter 2

Vortices in type-II superconductors

In this chapter, we review briefly two phenomenological formalisms of superconductivity – the London and Ginzburg-Landau (GL) theories. In the context of these formalisms, we develop a basic understanding of Abrikosov vortices. We then specifically apply these theories to the case of a superconducting wire and a superconducting loop.

2.1 London theory of superconductivity

The London theory, originally proposed by brothers Fritz and Heinz London, postulates two equations governing the electrodynamics of a superconducting system [45]:

\[
\vec{E} = \frac{\partial}{\partial t} \left( \Lambda \vec{J}_s \right) \tag{2.1}
\]

\[
\vec{B} = -c \nabla \times \left( \Lambda \vec{J}_s \right) \tag{2.2}
\]

where \( J_s \) is the super current density, and

\[
\Lambda \equiv \frac{4\pi \lambda^2}{c^2} = \frac{m}{n_s e^2}, \tag{2.3}
\]

where \( n_s \) is the density of superconducting electrons, and \( m \) and \( e \) are the mass and charge of an electron, respectively. Eq. 2.1 clearly describes perfect conductivity in that the presence of an electric field produces an accelerating super current.
However, taken alone, it mathematically allows a solution wherein an external magnetic field can be “frozen in” when cooling a superconductor through $T_c$ [45], in what is essentially a limiting case of Lenz’s Law. This solution is in direct contradiction to experiments by Meissner and Oschenfeld, who observed perfect diamagnetism in superconductors even when cooled through $T_c$ in the presence of an external field [46], leading the London brothers to postulate Eq. 2.2, which describes the screening of an external magnetic field over a characteristic length scale of $\lambda$.

The screening can be seen by substituting Maxwell’s equation, $\nabla \times \vec{B} = 4\pi \vec{J}/c$, into Eq. 2.2:

\[
\vec{B} = -c\Lambda \nabla \times (\frac{c}{4\pi} \nabla \times \vec{B}) \tag{2.4}
\]
\[
= -\lambda^2 \left[ \nabla \left( \nabla \cdot \vec{B} \right) - \nabla^2 \vec{B} \right] \tag{2.5}
\]
\[
\nabla^2 \vec{B} = \frac{1}{\lambda^2} \vec{B} \tag{2.6}
\]

A more compact method of writing Eqs. 2.1 and 2.2 is given by

\[
\vec{J}_s = n_s e \langle \vec{v}_s \rangle = -\frac{\vec{A}}{\Lambda c} \tag{2.7}
\]

Eq. 2.1 is recovered by differentiating Eq. 2.7 with respect to time, and Eq. 2.2 is recovered by taking the curl of Eq. 2.7. However, Eq. 2.7 cannot be gauge invariant, lending some insight into the conditions required for the phenomenological London theory to be applicable. The necessary choice of gauge (known as the London gauge) is given by requiring $\nabla \cdot \vec{A} = 0$, $\vec{A} \cdot \hat{n} = 0$ on the sample surface, and $\vec{A} \to 0$ deep inside the material [45,47].

The major strengths of the London theory are its simplicity (containing only a single phenomenological parameter, $\lambda$, which can be experimentally measured) and its applicability over a wide range of temperatures below $T_c$ by accounting for the temperature dependence of $\lambda$. It is formally restricted to situations where $|\vec{B}|$ is small and approximately uniform so as to be treated as perturbation that does not significantly modify $n_s$ [47]. However, simple modifications can be made to Eq. 2.2 to allow for situations in which the magnetic field is not necessarily uniform, but in which deviations from the bulk value are spatially confined. In particular, for the case of an isolated Abrikosov vortex located at position $\vec{r}$ and carrying a flux $\phi_0$...
oriented in the z-direction, the modified London equation

$$\vec{B} = -c\nabla \times (\Lambda \vec{J}_s) + \phi_0 \delta(\vec{r}) \hat{z}$$  \hspace{1cm} (2.8)$$

is valid everywhere outside the vortex core.

### 2.2 Ginzburg-Landau theory of superconductivity

Ginzburg and Landau [48] proposed a general approach to describing superconductivity, in which the Gibbs free energy of the system is expanded in even powers of an order parameter [49]:

$$f = f_n + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m^*} \left| \left( \frac{\hbar}{i} \nabla - \frac{e^*}{c} \vec{A} \right) \psi \right|^2 + \frac{H^2}{8\pi},$$  \hspace{1cm} (2.9)$$

with a crucial assumption that $\psi$ be complex-valued, such that

$$\psi(\vec{r}) = |\psi(\vec{r})|e^{i\varphi(\vec{r})}.  \hspace{1cm} (2.10)$$

Here, $f_n$ is the free energy in the normal state, $\alpha$ and $\beta$ are phenomenological coefficients, $e^*$ and $m^*$ are the effective charge and mass, respectively, of the superconducting charge carrier, $H$ is the local magnetic field, and $\psi$ is the order parameter governing the continuous phase transition, with $|\psi|^2 \propto n_s$. In the superconducting state, $|\psi| > 0$. It turns out that $e^* = 2e$ [50,51], with its origin of electron pairing emerging in the microscopic Bardeen-Cooper-Schrieffer (BCS) theory [52]. The coefficients $\alpha$ and $\beta$ are phenomenological parameters which can be expressed in terms of physical properties as

$$\alpha(T) = -\frac{(e^*)^2}{m^*c^2} H_c^2(T) \lambda_{\text{eff}}^2(T)$$  \hspace{1cm} (2.11)$$

and

$$\beta(T) = \frac{4\pi (e^*)^4}{(m^*)^2 c^4} H_c^2(T) \lambda_{\text{eff}}^4(T),$$  \hspace{1cm} (2.12)$$
where $\lambda_{\text{eff}}$ is a characteristic length scale defined below in Eq. 2.23, and $H_c$ is the thermodynamic critical field defined by

$$\frac{H_c^2(T)}{8\pi} = f_n(T) - f_s(T).$$

(2.13)

The final two terms on the right side of Eq. 2.9 account for the presence of gradients and magnetic fields. This is a notable advantage over the London formalism, which is restricted to systems in which $n_s$ is constant in space. Gor’kov showed the GL theory to be a limiting case of the microscopic BCS theory for temperatures very near $T_c$ [53]. In this context, $\psi$ is seen to be proportional to the BCS energy gap, $\Delta_{\text{BCS}}$, which is also in general a complex value. However, it has been shown that the GL theory can be applied substantially below $T_c$.

The kinetic energy term in Eq. 2.9 is

$$E_K = \frac{1}{2m^*} \left( \hbar \nabla \phi - \frac{e^* \vec{A}}{c} \right)^2 |\psi|^2.$$  

(2.14)

Using the London gauge in which $\nabla \phi = 0$,

$$E_K = \frac{(e^*)^2 A^2 |\psi|^2}{2m^*c^2}. $$

(2.15)

We can also arrive at an expression for the kinetic energy of the supercurrent from Eq. 2.7 by using the standard expression for the kinetic energy associated with a current:

$$E_K = \frac{1}{2} m v_s^2 n_s$$

(2.16)

$$= \frac{1}{2} m \left( \frac{e \vec{A}}{mc} \right)^2 n_s$$

(2.17)

$$= \frac{e^2 A^2 n_s}{2mc^2}$$

(2.18)

Eq. 2.18 is seen to be equivalent to Eq. 2.15 in the case that

$$|\psi|^2 \equiv n_s^* = \frac{1}{2} n_s,$$

(2.19)
giving us further insight into the physical significance of the phenomenological $\psi$. The factor of $1/2$ is logical, given that the BCS theory proves the number of superconducting charge carriers is precisely half of the number of normal electrons that pair together in the superconducting condensate.

Standard variational techniques, along with the definition of $\psi$ in Eq. 2.10, lead to the GL differential equations:

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

(2.20)

and

$$\vec{J} = \frac{e^*}{m^*} |\psi|^2 \left( \hbar \nabla \varphi - \frac{e^*}{c} \vec{A} \right) = e^* |\psi|^2 \vec{v}_s,$$

(2.21)

where $\vec{v}_s$ is defined to be the superfluid velocity. This set of coupled, second-order differential equations can be simplified when $|\psi|$ is small, either because $T \approx T_c$ or $H \approx H_c$. Eq. 2.20 can be linearized by dropping the term containing $\beta$ (valid when $|\psi|^2 \ll -\alpha/\beta$).

There are two characteristic length scales in the GL theory of superconductivity. The coherence length, $\xi$, is a measure of how rapidly spatial variations in $\psi$ will decay:

$$\xi(T) = \frac{\hbar}{\sqrt{2m^*|\alpha(T)|}} \propto \frac{\xi(0)}{\sqrt{1 - T/T_c}}.$$  

(2.22)

The penetration depth, $\lambda_{\text{eff}}$, is a measure of how rapidly currents decay:

$$\lambda_{\text{eff}}(T) = \frac{\phi_0}{2\sqrt{2\pi H_c(T)\xi(T)}} \propto \frac{\lambda_{\text{eff}}(0)}{\sqrt{1 - T/T_c}},$$

(2.23)

where $\phi_0 = h c/2e = 2.07 \times 10^{-7} \text{ G} \cdot \text{cm}^2$ is the magnetic flux quantum (in S.I units, $\phi_0 = h/2e = 2.07 \times 10^{-15} \text{ Wb}$). $\lambda_{\text{eff}}$ plays an analogous role to $\lambda$ in the London theory (see Eq. 2.3), but in real materials, $\lambda_{\text{eff}}$ can be quite different from the value derived in the local London theory. In practice, this does not complicate the analysis of such materials, as $\lambda_{\text{eff}}$ can be experimentally measured. For the remainder of this dissertation, we will make no distinction between $\lambda$ and $\lambda_{\text{eff}}$.

The ratio of characteristic length scales is denoted by

$$\kappa \equiv \frac{\lambda(T)}{\xi(T)} = \frac{2\sqrt{2\pi H_c(T)\lambda^2(T)}}{\phi_0}.$$  

(2.24)
Abrikosov showed that the critical value of $\kappa = 1/\sqrt{2}$ separates two qualitatively different types of materials [54]. Type-I superconductors ($\kappa < 1/\sqrt{2}$) exhibit perfect diamagnetism and expel external magnetic fields up to the thermodynamic critical field, $H_c$. Type-II superconductors ($\kappa > 1/\sqrt{2}$) favor the formation of a lattice of Abrikosov vortices [55] above a lower critical field,

$$H_{c1} = \frac{\phi_0}{4\pi \lambda^2} \ln \kappa = \frac{H_c}{\sqrt{2\kappa}} \ln \kappa. \quad (2.25)$$

Each vortex is threaded by a single quantum of magnetic flux. Eq. 2.25 is derived in the limit $\kappa \gg 1$, which is a reasonable approximation for the experimental NbSe$_2$ systems that are the focus of this dissertation. The energy gain provided by not requiring the complete expulsion of the external field allows superconductivity to persist to a much higher field in type-II materials. In a bulk type-II material, the upper critical field at which superconductivity is destroyed is given by

$$H_{c2} = \frac{\phi_0}{2\pi \xi^2(T)} = \sqrt{2\kappa} H_c. \quad (2.26)$$

Materials with an upper critical field exceeding the thermodynamic critical field were first observed by Shubnikov, et al. in 1937 [56], but a satisfactory description of the mechanism responsible, namely, flux penetration through Abrikosov vortices, was not provided for another twenty years [55].

We can calculate the maximal current density a thin superconducting wire can sustain by assuming $|\psi|$ does not vary appreciably in space (guaranteed by the “thinness” condition), and then minimizing Eq. 2.9 with respect to $v_s$, which yields

$$|\psi|^2 = \left( \frac{\alpha}{\beta} \right)^2 \left( 1 - \frac{m^* v^2_s}{2|\alpha|} \right). \quad (2.27)$$

Inserting Eq. 2.27 into Eq. 2.21 and solving for the maximal $J$, we obtain a theoretical upper limit for the critical current density,

$$J_c = \frac{cH_c(T)}{3\sqrt{6\pi \lambda(T)}}. \quad (2.28)$$

While this value of $J_c$ was derived for the specific case of a thin wire, it is a general property of superconductors that superconductivity will be destroyed at
Figure 2.1. Schematic of an isolated Abrikosov vortex. The magnitude of order parameter ($|\psi|$) and the magnitude of field ($|\vec{B}|$) are shown. Arrow length indicates $|\vec{J}|$, and arrow color indicates relative phase ($\varphi$). Characteristic length scales $\xi$ and $\lambda$ are noted.

sufficiently large currents. In the BCS theory [52], this critical current is related to the depairing velocity, above which the energy associated with the momentum of the pair at the Fermi surface, $\hbar k_F v_s$, exceeds the gap, $\Delta_{\text{BCS}}$ [57].

### 2.3 Structure of the Abrikosov vortex

Type-II superconductors with $\kappa \geq 1/\sqrt{2}$ feature a mixed state when $H_{c1} < H < H_{c2}$. In this field regime, magnetic flux can penetrate the superconducting material in the form of Abrikosov vortices. As shown in Figure 2.1, the magnitude of $\psi$ is found to decrease from the bulk value to 0 over a distance of $\sim \xi$ from the center of the vortex, and the phase, $\varphi$, winds by $2\pi$ when following a closed contour enclosing the vortex. The vortex is threaded by a single quantum of magnetic flux, $\varphi_0$, sustained by a circulating current persisting to a distance of $\sim \lambda$ from the center of the vortex. Near an isolated vortex, it is convenient to express $\psi$ as

$$\psi(r, \theta) = \psi_\infty f(r)e^{i\theta}, \quad (2.29)$$

where $\psi_\infty$ is the magnitude of $\psi$ deep inside the bulk superconductor, $f$ is a function we wish to determine, and we have chosen our origin to coincide with the axis of the vortex. In principle, a phase winding of any integer multiple of $2\pi$ is allowed, but it can be shown [47] that the vortex energy depends quadratically on the threading flux, making multi-quanta vortices energetically unfavorable in the bulk. Inserting
Eq. 2.29 into Eq. 2.21 yields for the current

\[ \vec{J} = \frac{e^* \hbar}{m^* \psi_\infty^2} f^2 \left( \frac{1}{r} - \frac{2\pi A(r)}{\phi_0} \right) \hat{\theta}, \]  

(2.30)

where

\[ A(r) = \frac{1}{r} \int_0^r r'h(r')dr' \]  

(2.31)

is the vector potential [57]. By considering the asymptotic forms when \( r \to 0 \) and \( r \to \infty \), it can be shown that \( f \) can be approximated as

\[ f \approx \tanh \left( \frac{\nu r}{\xi} \right), \]  

(2.32)

where \( \nu \) is a constant of order unity [57]. Because Eq. 2.32 increases from 0 to 1 over the distance \( \xi \), in materials where \( \kappa \gg 1 \), it is convenient to approximate \( f \) as constant outside a “normal core” of radius \( \xi \), in which case we would expect the London equations to hold true everywhere except with \( \sim \xi \) of the vortex position. And indeed, if we take the curl of Eq. 2.30, we find

\[ \frac{4\pi \lambda^2}{c} \nabla \times \vec{J} = -\vec{B} + \phi_0 \delta(\vec{r}) \hat{z}, \]  

(2.33)

which looks like the London Equation 2.2 with the expected modification of the delta function term describing the additional flux carried by the Abrikosov vortex. The solution to Eq. 2.33 is

\[ \vec{B}(r) = \frac{\phi_0}{2\pi \lambda^2} K_0 \left( \frac{r}{\lambda} \right) \hat{z}, \]  

(2.34)

where \( K_0 \) is a Hankel function [58]. We are most interested in the behavior of \( \vec{B} \) in the limiting cases:

\[ \vec{B}(r) \approx \frac{\phi_0}{2\pi \lambda^2} \sqrt{\frac{\pi \lambda}{2r}} e^{-r/\lambda} \hat{z} \quad r \to \infty \]  

(2.35)

\[ \vec{B}(r) \approx \frac{\phi_0}{2\pi \lambda^2} \left[ \ln \left( \frac{\lambda}{r} \right) + 0.12 \right] \hat{z} \quad \xi \ll r \ll \lambda \]  

(2.36)

We see that the field associated with the Abrikosov vortex drops of exponentially on the order of \( \lambda \). Strictly speaking, Eq. 2.34 diverges as \( r \to 0 \), but within the
normal core, $|\psi| \rightarrow 0$, which rounds off the divergence, as seen in Figure 2.1.

In the full microscopic BCS theory of superconductivity, an energy gap,

$$2\Delta_{\text{BCS}} = 3.528k_BT_c,$$

appears in the quasiparticle density of states below $T_c$ [52]. This gap is the energy required to break a Cooper pair into individual quasiparticles, and is proportional to $\psi$ in the GL theory [53]. Consequently, in the core of the vortex, the superconducting gap drops to 0.

## 2.4 Abrikosov vortex statics and dynamics

### 2.4.1 Vortex lattice in bulk systems

In bulk systems with minimal pinning, the logarithmic vortex-vortex interaction dominates, and vortices assemble into a periodic lattice (see Figure 2.2). A triangular lattice results in the lowest energy state for an isotropic material [59], but the underlying symmetries in some material systems favor a square lattice [60]. The existence of strong pinning centers can disrupt the lattice, causing vortices to instead cluster near the specific pinning centers [61].
2.4.2 Vortex configuration in nanoscale systems

In a mesoscopic superconducting system in which the effect of geometric confinement of Abrikosov vortices is significant, the newly-imposed boundary conditions dominate the vortex-vortex interactions, and vortices will arrange in patterns that preserve the geometric symmetry of the system [21], even in the absence of pinning centers. This can result in anti-vortices [20] and giant multi-flux-quantum vortices [18,19,23], both of which are energetically prohibited in bulk systems. By sufficiently reducing sample dimensions, individual vortices can be isolated at reasonable experimental fields [63].

2.4.3 Vortex dynamics

A vortex will feel a net transverse force in response to a non-zero current distribution:

\[ \vec{f} = \vec{J} \times \frac{\phi_0}{c} \hat{z}, \]  

(2.38)

where the magnetic flux associated with the vortex is taken to be in the \( \hat{z} \) direction. This immediately implies that, in the absence of any additional pinning or boundary forces, vortices can only be in static equilibrium when located in a symmetric array, since each vortex itself has a corresponding non-zero circulating \( \vec{J} \) [64]. Even a symmetric array, however, will feel a net force in response to an external transport current. The motion of the array induces an electric field [57]

\[ \vec{E} = n \phi_0 \hat{z} \times \frac{\vec{v}}{c} = \vec{B} \times \frac{\vec{v}}{c}, \]  

(2.39)

which acts as a dissipative resistance in the presence of the external current. Eq. 2.39 can be derived by applying the Lorentz transformation for electromagnetic fields associated with changing reference frames from a frame moving with the vortex lattice to a frame stationary in the laboratory.

A moving vortex is also subject to a damping force [65,66]. To account for the energy dissipated by this damping force, a simple model was proposed by Bardeen and Stephen assuming a fully normal core of radius \( \xi \). In this approximation, Bardeen and Stephen showed that the electric field generated by the moving vortex drives the external transport current through the normal core, producing dissipation.
of energy [65]. In this case, a simple result for the effective “flux-flow resistivity,” $\rho_f$, can be calculated:

$$\rho_f \approx \rho_n \frac{B}{H_c^2}. \quad (2.40)$$

Here, $\rho_n$ is the resistivity in the normal state. This relationship was experimentally verified in low-pinning systems [67].

When inhomogeneities exist in a superconductor, vortices are preferentially pinned at locations where the order parameter is artificially suppressed [61]. Vortex motion will only commence above a critical “depinning current,” $\vec{J}_p$, given by

$$\vec{f}_p = \vec{J}_p \times \frac{\phi_0}{c} \hat{z}, \quad (2.41)$$

where $\vec{f}_p$ is the pinning force, which is in general an unknown quantity prior to experimental measurements.

Other forces influencing vortex motion such as the Magnus force and forces associated with a thermal gradient [68] will not be considered in this dissertation.

### 2.5 Phase slips in superconducting wires

The resistive transition in a quasi-1D wire is governed by the Langer-Ambegaokar-McCumber-Halperin (LAMH) theory of phase slips [69,70]. The qualitative picture is that a finite voltage difference between two ends of a superconducting wire will produce a steady increase in the phase difference between the two ends ($\Delta \varphi$) at a rate given by the Josephson relation [71]

$$\frac{d (\Delta \varphi)}{dt} = \frac{2eV}{\hbar}. \quad (2.42)$$

The voltage drop will produce an accelerating supercurrent, unless some process exists by which the increasing phase can relax, thereby maintaining a steady state. This process is known as a phase slip, wherein the magnitude of $\psi$ is momentarily suppressed at a particular point along the length of the wire, which allows for an abrupt “unwinding” of the order parameter phase by $2\pi$ [72]. This phase slip event is spatially confined to where the amplitude of the order parameter is reduced to zero.
The energy barrier that must be surmounted for a phase slip event to occur was calculated to be [69]
\[
\Delta F_0 = \frac{8\sqrt{2}}{3} \frac{H_c^2}{8\pi} A \xi,
\]  
(2.43)
where \( A \) is the cross-sectional area of the wire. This barrier is on the same order as the condensation energy in a volume of \( A \xi \), and can be qualitatively understood as the energy required to drive a length, \( \xi \), of the wire into the normal state (recall that \( \xi \) dictates the length over which \( \psi \) can vary without undue energy cost). The presence of a current, \( I \), breaks the symmetry between the \( \pm 2\pi \) phase slips, making one direction preferable. The difference in energy barrier between the two phase slip directions is given by [73]
\[
\delta F = \Delta F_+ - \Delta F_- = \frac{\hbar I}{2e}.
\]  
(2.44)
The energy barrier can be represented by considering \( \varphi \) as a particle within a standard "tilted washboard" potential [57], such as is shown schematically in Figure 2.3a.

The rate of phase slips is then given by the net rate of thermal activation of
the system over the energy barrier,
\[
\frac{d(\Delta \varphi)}{dt} = \Omega \left[ e^{-\frac{\Delta F_0 - \delta F}{kT}} - e^{-\frac{\Delta F_0 + \delta F}{kT}} \right]
\]
\[
= 2\Omega e^{-\frac{\Delta F_0}{kT}} \sinh \left( \frac{\delta F}{2kT} \right).
\]
(2.45)
Here, \( \Omega \) is an attempt frequency prefactor that was calculated to be \([70]\)
\[
\Omega = \frac{L}{\xi} \sqrt{\frac{\Delta F_0}{kT}},
\]
(2.47)
where \( L \) is the length of the wire (so \( L/\xi \) reflects the number of possible independent phase slip centers) and \( \tau_{GL} \) is the Ginzburg-Landau relaxation time, \( \tau_{GL} = \pi \hbar / 8k(T_c - T) \). The corresponding voltage is found by combining Eqs. 2.42, 2.44, and 2.46:
\[
V_{LAMH} = \frac{h\Omega}{e} e^{-\frac{\Delta F_0}{kT}} \sinh \left( \frac{hI}{4ekT} \right).
\]
(2.48)

The LAMH theory of thermally activated phase slips was verified in experiments on Sn wires near \( T_c \) \([75]\). Later work on In wires, however, revealed an additional resistive process with a much weaker temperature dependence far below \( T_c \) (see Figure 2.3b) \([74]\). This observation was attributed to macroscopic quantum tunneling of \( \varphi \) through the energy barrier (dashed arrow in Figure 2.3a) \([74,76]\), or quantum phase slips. This results in a voltage drop given in the low current limit by \([74]\),
\[
V_{MQT} = \left( I \phi_0^2 / kT \right) \frac{16\sqrt{3}La_0^4}{\xi} \sqrt{\frac{\Delta F}{\hbar \tau_{GL}}} \exp \left[ -\frac{\beta AH_0^2 \xi \tau_{GL}}{18\hbar} \right],
\]
(2.49)
where \( \beta \) is a numerical constant of order unity and \( a_0 \) is a damping factor which is treated as a fit parameter. In this scenario, the total resistance of 1D wire is therefore
\[
R(T) = \frac{1}{I} (V_{LAMH} + V_{MQT}),
\]
(2.50)
consistent with what is seen in Figure 2.3b.

When the wire under consideration is not strictly 1D, meaning \( w \gtrsim 2\xi \), phase slip events will be affected by Abrikosov vortices. In 2D narrow wires, instead of the magnitude of the order parameter fluctuating to zero at a single point and allowing for a phase slip, an Abrikosov vortex can nucleate at a sample boundary, cross the
strip, and exit the opposite side [30, 77, 78], carrying with it a $2\pi$ phase change. Because $\xi$ is a function of temperature and field, a cross-over from a quasi-1D to a 2D wire can be observed, with a corresponding cross-over in phase slip mechanism.

### 2.6 Fluxoid quantization in superconducting loops

Consider now superconducting loops; the requirement that the GL order parameter from Eq. 2.10 be single-valued leads directly to the equation

\[ \oint \nabla \varphi \cdot d\vec{s} = 2\pi n, \]  

where $n$ can be any integer, and the integral in Eq. 2.51 is taken around any closed contour. Recalling the definition of $v_s$ from the kinetic energy term in Eq. 2.14, we see that

\[ \oint \nabla \varphi \cdot d\vec{s} = \frac{e^*}{\hbar c} \oint \left( \frac{m^* c}{e^*} \vec{v}_s + \vec{A} \right) \cdot d\vec{s}. \]  

Combining Eqs. 2.51 and 2.52, and noting that $\oint \vec{A} \cdot d\vec{s} = \phi$ is the magnetic flux threading the region of integration, yields the famous “fluxoid quantization” criterion,

\[ \Phi' \equiv \phi + \left( \frac{m^* c}{e^*} \right) \oint \vec{v}_s \cdot d\vec{s} = n\phi_0. \]  

Eq. 2.53 was originally experimentally verified in the case of cylinders with thick walls, such that a contour that encloses the central hole can be chosen where $\vec{v}_s \to 0$ [50, 51], and $\phi$ should be quantized in units of $\phi_0$. In fact, these experiments provided unambiguous support for the claim that the superconducting charge carrier possesses an effective charge of $2e$, rather than $e$, as the observed flux quantum was seen to take on the value $hc/2e$, not $hc/e$.

If we now consider the case of a superconducting loop with a thin wall, such that the contour of integration is a circle of radius $R$ along which $\vec{v}_s$ is parallel to $d\vec{s}$ and $|\vec{v}_s|$ is a constant not uniformly equal to 0 (a case distinct from that addressed in the experiments above), we arrive at an expression for $v_s$,

\[ v_s = \frac{\hbar}{m^* R} \left( n - \frac{\phi}{\phi_0} \right). \]  

The integer $n$ is chosen to minimize $v_s$. We show a plot of $v_s$ vs. $\phi$ in Figure 2.4a. The
modulation of $v_s$ produces a modulation of the kinetic energy of the supercurrent, which in turn produces a modulation of $T_c$ [57],

$$\frac{\Delta T_c(\phi)}{T_c} = 0.55 \frac{\xi^2}{R^2} \left( n - \frac{\phi}{\phi_0} \right)^2,$$

as shown in the lower panel in Figure 2.4a. This modulation in $T_c$ was first observed by Little and Parks [79] as a resistance modulation in a thin-walled Sn cylinder (see Figure 2.4b), confirming that it is indeed the fluxoid, and not simply the flux, that is quantized in a doubly-connected superconductor. The physical picture is that, in the presence of an external magnetic flux, the supercurrent in a loop will respond so as to satisfy Eq. 2.53 and maintain an overall phase change of zero (modulo $2\pi$). In Figure 2.4c, we depict schematically the case of a superconducting loop with $n = 1$. We see that the integer $n$ corresponds to the number of $2\pi$ windings of the GL order parameter phase; we therefore refer to $n$ as the “winding number” of the loop. In the ground state, $|n - \phi/\phi_0| \leq 1/2$.

When an Abrikosov vortex is added to the loop, there are two competing phase winding requirements. The global phase must wind by an integer multiple of $2\pi$ when circumscribing the central hole in the loop, and the local phase must wind by $2\pi$ around the vortex core. The vortex self-currents disrupt the circulating supercurrent, modifying the free energy and resulting magnetoresistance oscillations.
A number of crystalline superconductors exist. Among them is NbSe$_2$, a conventional type-II $s$-wave superconductor. NbSe$_2$ can be mechanically cleaved to monolayer thickness, enabling the extreme 2D confinement and minimized dissipation we seek. Additionally, this material is known to host a competing CDW state in both the bulk and 2D limit, and is therefore particularly useful as a model system for understanding the competing orders that are also present in the high temperature cuprate superconductors.

3.1 Physical properties of bulk NbSe$_2$

NbSe$_2$ (Figure 3.1a) is a transition metal dichalcogenide (TMDC). TMDCs have received immense attention recently owing to their wide range of electronic properties (metallic, semiconducting, superconducting) and their suitability for 2D electronics [80]. TMDCs exist in a variety of polytypes, but we focus on 2H-NbSe$_2$ (we will refer to this crystal as simply “NbSe$_2$” throughout this dissertation – the “2H” structure will be assumed).

NbSe$_2$ has a layered crystal structure with Se-Nb-Se “molecular layers” arranged in an A-B stacking as shown in Figure 3.1b. The unit cell is hexagonal, with lattice constants of $a = b = 0.34$ nm and $c = 1.25$ nm [81]. The interlayer bonding is van der Waals in nature, while the intralayer bonding is covalent. Thus, NbSe$_2$ crystals
are typically Se terminated [82].

### 3.2 Electronic properties of bulk NbSe$_2$

The first Brillouin zone of NbSe$_2$ is shown in Figure 3.1c. Several groups have calculated the electronic band structure of the bulk material [83–85]. Three bands cross the Fermi surface, as seen in Figure 3.2. The Se band has a hole-like nature, and there is one hole-like and one electron-like Nb band. At high temperatures, holes are the dominant charge carrier ($n_h \approx 1.4 \times 10^{22} \text{ cm}^{-3}$), but at low temperatures, the Hall voltage changes sign, indicating a transition to electron-dominated transport below approximately 30 K ($n_e \approx 1.1 \times 10^{22} \text{ cm}^{-3}$) [86].

For this dissertation, the most relevant properties of NbSe$_2$ pertain to supercon-
Table 3.1. Electronic and superconducting properties of NbSe$_2$ along three crystallographic axes.

<table>
<thead>
<tr>
<th>Property</th>
<th>$a$, $b$</th>
<th>$c$</th>
<th>Ref./Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_h(300K)$ (cm$^{-3}$)</td>
<td>$1.4 \times 10^{22}$</td>
<td></td>
<td>86, a</td>
</tr>
<tr>
<td>$n_e(7K)$ (cm$^{-3}$)</td>
<td>$1.1 \times 10^{22}$</td>
<td></td>
<td>86, a</td>
</tr>
<tr>
<td>$\rho(300K)$ ($\mu\Omega \cdot \text{cm}$)</td>
<td>$\lesssim 150$</td>
<td>$\lesssim 4000$</td>
<td>87</td>
</tr>
<tr>
<td>$\rho(7K)$ ($\mu\Omega \cdot \text{cm}$)</td>
<td>$\lesssim 10$</td>
<td>$\lesssim 500$</td>
<td>87</td>
</tr>
<tr>
<td>$\ell(300K)$ (nm)</td>
<td>1.5</td>
<td>.05</td>
<td>86,87, b</td>
</tr>
<tr>
<td>$\ell(7K)$ (nm)</td>
<td>26</td>
<td>0.5</td>
<td>86,87, b</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
<td>7.1</td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>$\Delta(0)$ (meV)</td>
<td>1.07</td>
<td>0.62</td>
<td>89,90</td>
</tr>
<tr>
<td>$B_{c1}$ (T)</td>
<td>0.0123</td>
<td>0.0050</td>
<td>88</td>
</tr>
<tr>
<td>$B_{c2}$ (T)</td>
<td>12.5</td>
<td>3.65</td>
<td>88</td>
</tr>
<tr>
<td>$J_c$ (A/cm$^2$)</td>
<td>$2.8 \times 10^4$</td>
<td>$2.6 \times 10^4$</td>
<td>c</td>
</tr>
<tr>
<td>$\xi(0)$ (nm)</td>
<td>9.5</td>
<td>2.8</td>
<td>88</td>
</tr>
<tr>
<td>$\lambda(0)$ (nm)</td>
<td>200</td>
<td>202</td>
<td>88</td>
</tr>
</tbody>
</table>

$^a$ Carrier densities calculated from Hall measurements assuming a single carrier model at each temperature.

$^b$ MFP calculated using $\ell = \left(\frac{3/4 \pi n}{a_0}\right)^{1/3} \times \frac{92\AA}{\rho}$ [91].

$^c$ Theoretical $J_c$ calculated using Eq. 2.28 and experimental parameters from Ref. [88].

...ductivity. Bulk NbSe$_2$ undergoes a superconducting transition below $T_c = 7.1$ K [88]. The characteristic length scales are given by $\xi = 9.5$ nm and $\lambda = 200$ nm, making NbSe$_2$ a strongly type-II superconductor with a Ginzburg-Landau parameter of $\kappa \sim 21$. The superconducting properties are anisotropic (see Table 3.1), with a ratio of the in-plane to out-of-plane coherence length of roughly 3.4. Angle resolved photoemission spectroscopy measurements of the superconducting gap (Figure 3.3) reveal that superconductivity is confined to the Nb bands, and that the gap, $\Delta$, is anisotropic, varying between 0 and a maximal value of $1.0 \pm 0.2$ eV [92], which is consistent with the BCS prediction from Eq. 2.37:

$$\Delta_{\text{BCS}} = \frac{3.528}{2} kT_c = 1.08 \text{ meV}. \quad (3.1)$$

NbSe$_2$ also hosts an incommensurate charge density wave (CDW) transition with three-fold symmetry below $T_{c,\text{CDW}} = 33.5$ K [93,94]. The CDW state is a 2D generalization of the Peierls transition in 1D. The physical lattice distortion
Figure 3.3. Momentum dependence of superconducting and charge density wave (CDW) gaps in NbSe$_2$ as measured by angle resolved photoemission spectroscopy. Color scale indicates magnitude of energy gap ($\Delta_s \propto T^2_c$), while thickness of gray bar on bands centered at K indicates relative contribution to gap from superconductivity. Superconductivity and CDW are seen to be anisotropic, anisotropic, and Fermi sheet dependent. Figure adapted from Ref. [92]

associated with the Peierls transition is accompanied by a periodically modulated electronic charge density [95]. $T'_c$ and $T_c$ have been shown to anticorrelate in NbSe$_2$ as a function of both pressure [96] and crystal thickness [97]. But, despite the competition, low-temperature ARPES measurements reveal the coexistence of both orders, with the CDW gap confined to a few “hot spots” (red regions centered on $K$ point in Figure 3.3), leaving most of the Fermi surface available for superconductivity [92]. The CDW state in NbSe$_2$ is likely driven by electron-phonon coupling [92,97], rather than Fermi surface nesting.

For sufficiently high quality crystals, the CDW phase is observable in resistivity measurements. Specifically, for crystals with $R/RRR \equiv R(300 \text{ K})/R(8 \text{ K}) \gtrsim 30$, a kink in $dR/dT$ marks the onset of the CDW phase [98]. The kink is attributed to the freezing out of CDW phase fluctuations below $T'_c$. For a complete transition,
the resistivity contribution from the CDW fluctuations would approach 0 as $T \to 0$, resulting in the maximal value of RRR.

3.3 Modified band structure of 2D crystals of NbSe$_2$

One issue we seek to address is the nature of vortex motion in crystalline superconductors – namely, whether vortices can move with macroscopic quantum coherence. The motion of normal electrons within the vortex core produces dissipation, and presumably decoherence. One way to reduce the effect of the normal electrons is to reduce their number by thinning the material system. As we discuss at length in Section 4.1, NbSe$_2$ cleaves readily along the $ab$ plane, and is therefore well suited to this particular application. Ultra-thin NbSe$_2$ features an electronic band structure distinct from the bulk. The theoretical band structure of bilayer and monolayer NbSe$_2$ is given in Figure 3.4. The Se band is seen to fall below the Fermi level, and in the monolayer limit only a single Nb band crosses the Fermi surface.

3.4 Superconductivity in 2D crystals of NbSe$_2$

The perturbation from the bulk band structure raises concerns as to whether superconductivity and CDW are preserved in the extreme 2D limit. At the onset of this dissertation work, this was an open question. Superconductivity in few-layer NbSe$_2$ has been investigated on several prior occasions. An early study by Frindt [82] observed a decrease in $T_c$ as a function of crystal thickness (Figure 3.5a),

Figure 3.4. Band structure of bilayer (upper panel) and monolayer (lower panel) NbSe$_2$. Figure adapted from Ref. [84].
and claimed to observe the survival of superconductivity to a single unit cell of NbSe$_2$. However, in that work, the thickness of the crystals was not directly measured, but was estimated using the bulk resistivity value, which is actual $\sim 7$ times smaller than the true value for thin flakes [100]. A recent investigation of crystals with thicknesses verified by atomic force microscopy revealed the same trend of decreasing $T_c$ with crystal thickness (Figure 3.5b) [99]. The thinnest crystals (2-3 layers) were found to be superconducting only after a sufficient in situ current annealing. Single layer NbSe$_2$ was originally observed to be semi-metallic [101], but concurrent with the preparation of this dissertation, multiple groups showed that both superconductivity and the CDW state are preserved even in a single layer of NbSe$_2$, provided care is taken to protect the crystal from ambient and processing conditions [97,102,103].

3.5 2D crystal superconductivity and vortex motion

The availability of 2D crystal superconductors enables the study of effects originating from the charge carriers residing in energy bands. The CDW ordering present in NbSe$_2$ in general competes with the superconducting order, and such competition may be highly relevant to the high transition temperature superconducting cuprates [104]. The CDW order parameter can be pinned to specific locations, potentially resulting in localized patches of CDW ordering. These patches may function as
pinning centers for Abrikosov vortices in a fundamentally different way than typical normal regions. The BKT transition, driven by the logarithmic vortex-antivortex interaction, may also be modified as a result of the influence of CDW order on the local value of $n_s$.

Even without considering the effects of the competing CDW order, the crystalline nature of NbSe$_2$ enables investigations of exotic effects related to vortex dynamics. It is known that the core of an Abrikosov vortex exhibits six-fold symmetry in NbSe$_2$ due to the crystal symmetry [105]. This will affect the intrinsic vortex properties in unknown ways. Furthermore, NbSe$_2$ crystals of 1, 3, 5, ... layers do not possess a center of inversion. Such non-centrosymmetric crystals can theoretically support a mixed superconducting pairing state [106]. This would be an exotic example of unconventional superconductivity, and would allow for a direct comparison between vortex dynamics in conventional and unconventional materials. Thus far, there have been no experimental searches for mixed pairing superconductivity in odd-layer NbSe$_2$. While the issues discussed in this section are not addressed experimentally in this dissertation, the techniques we develop in the following chapters allow for future devices aimed at such investigations.
Chapter 4

Fabrication of 2D crystal nanostructures

In this chapter, we detail the fabrication processes for the 2D crystal nanostructure devices for which we later present measurements using a conventional four-probe technique. Whereas the device fabrication methodology presented here represents a significant advance over previous approaches, the specific measurement techniques are mostly standard in the field. Therefore, we defer our discussion of the sample wiring, cooling, and measurement processes to the Appendix, and here focus solely on the preparation of nanostructures. All nanofabrication was performed at the Pennsylvania State University Materials Research Institute Nanofabrication Laboratory (Nanofab). Additional characterization such as Raman spectroscopy and electron microscopy was carried out in the Pennsylvania State University Materials Research Institute Materials Characterization Lab (MCL).

Before discussing individual details of the fabrication process, we find it instructive to present the final desired device. Figure 4.1 shows a schematic of a typical superconducting device for the study of vortex dynamics through electrical transport measurements. The device consists of a NbSe$_2$ nanowire (green) etched from an exfoliated micron-sized NbSe$_2$ crystal, contacted by measurement electrodes (gold), and supported on a rigid SiO$_2$/Si substrate (gray/blue).
4.1 Obtaining and identifying 2D crystals of NbSe$_2$

4.1.1 Mechanical exfoliation

NbSe$_2$ is a layered crystal featuring weak van der Waals interlayer bonding, for which the mechanical exfoliation of individual layers from a bulk crystal using a simple “Scotch tape” technique originally developed in the context of graphene research [101] is possible. In general, mechanical exfoliation is accomplished through the following 7-step process [107]: 1) Clean the target SiO$_2$/Si substrate; 2) Place a 1 mm$^2$ bulk NbSe$_2$ crystal onto the sticky surface of transparent Scotch tape; 3) Repeatedly cleave the NbSe$_2$ crystal by folding the tape onto itself and peeling apart; 4) Press freshly-cleaved NbSe$_2$ flakes onto target substrate; 5) Apply gentle pressure to backside of tape with soft tweezers or gloved finger; 6) Slowly remove tape from substrate; and 7) Locate and identify flakes using optical microscopy.

4.1.2 Substrate preparation

We chose a 500 µm thick single-crystal silicon wafer with a 300 nm thermally grown SiO$_2$ layer as our target substrate (purchased from Si-Tech, <100> face, $\rho \lesssim 5$ mΩ · cm). The top side of the wafer was mechanically polished to provide a smooth surface for exfoliation and further processing. The primary purpose of the oxide layer was to maximize the optical contrast of the ultra-thin exfoliated NbSe$_2$ flakes under white light. The silicon substrate could be heavily doped to allow it to function as a back electrode for electrostatic gating of the NbSe$_2$ devices.
However, most devices studied in this dissertation were too thick to allow for a substantial response to such gating. We also employed intrinsic silicon wafers to avoid potential parallel conduction channels through the substrate.

Because the success of the mechanical exfoliation process relies upon the van der Waals force between the NbSe$_2$ crystal layers and the SiO$_2$ surface overcoming the van der Waals force between adjacent NbSe$_2$ layers within the crystal, the cleanliness of the SiO$_2$ surface is crucial for 2D crystal yield. We developed a standard cleaning process that resulted in maximal yield (typically multiple crystals with $d \lesssim 10$ nm per $8 \times 8$ mm$^2$ silicon chip).

The as-purchased silicon wafers were first patterned with Ti/Au finding markers for subsequent electron-beam lithography processing, coated in a protective layer of SPR 3012 photoresist, and diced into $8 \times 8$ mm$^2$ squares with a diamond saw. It is crucial to remove this protective resist, along with any other preexisting surface contaminants prior to attempting exfoliation. Our standard cleaning process is as follows: 1) 5 minute ultrasonic clean in acetone to remove majority of resist; 2) 5 minute ultrasonic clean in isopropyl alcohol to remove acetone residue; 3) Transfer to deionized water. This is a safety precaution, as solvents and acids are kept segregated in the Nanofab, and transferring directly from isopropyl alcohol to an acid bath is discouraged; 4) 10 minute clean in Cyantek Nanostrip at room temperature. Nanostrip is a corrosive mixture of sulfuric acid ($\text{H}_2\text{SO}_4$) and hydrogen peroxide ($\text{H}_2\text{O}_2$). It is extremely effective at cleaning organics from surfaces, especially at elevated temperatures. However, we found that for $T > 40\degree$C, Nanostrip will undesirably etch the patterned Ti/Au markers. Fortunately, even the room temperature clean proved adequate for subsequent exfoliation; 5) Spray thoroughly (at least 10 seconds) with deionized water and transfer to deionized water bath. Simply transferring from the acid bath to water bath does not sufficiently remove Nanostrip residue, and the extra rinse step must be included; 6) 5 minute ultrasonic clean in acetone; 7) 5 minute ultrasonic clean in isopropyl alcohol; 8) Blow dry with nitrogen or compressed dry air.

By carefully following this cleaning procedure, the SiO$_2$ surface is suitably prepared for exfoliation of NbSe$_2$ or other 2D crystals. In Figure 4.2a, we show a representative optical image of mechanically exfoliated NbSe$_2$ crystals on a properly cleaned silicon substrate. Note the large number of thick (gold color) crystals, the small amount of tape residue, and the presence of several thin (blue color) crystals.
Figure 4.2. a) Optical image of NbSe$_2$ crystals exfoliated onto SiO$_2$/Si substrate. High density of crystals indicates proper surface pretreatment. b) Optical image of NbSe$_2$ exfoliated onto improperly pretreated SiO$_2$/Si substrate. c) Optical image of thin NbSe$_2$ crystal. Bottom corner of main flake is bilayer NbSe$_2$. Four Ti/Au alignment markers for electron-beam lithography processing are visible.

This level of NbSe$_2$ coverage is typical for clean substrates once the exfoliation technique has been perfected. By contrast, in Figure 4.2b we show the result of exfoliating onto an improperly cleaned silicon substrate. The size of the field of view is the same as in Figure 4.2a, but there are very few crystals, and the ones that are visible are prohibitively small in the lateral dimensions.

We note that, while the cleaning process detailed here reliably results in few-layer NbSe$_2$ crystals, single-layer crystals were rare (only obtained on three occasions in several hundred attempts), and always with lateral dimensions less than 2 µm. It seems reasonable that further improvements to the cleaning process will improve the yield of monolayer crystals. In addition to chemical treating, a common method of cleaning oxide surfaces in semiconductor fabrication processes is exposure to an oxygen ion plasma. We investigated the efficacy of this cleaning step in the context of mechanical exfoliation of NbSe$_2$ and found it to be detrimental to our yield when included as an additional step after the above procedure. We hypothesize that the physical component of the plasma etch roughened the oxide surface, thereby decreasing the surface area available for the SiO$_2$ surface to “catch” a NbSe$_2$ layer through the van der Waals force.
4.1.3 Optical microscopy search

After cleaning the target substrate and exfoliating NbSe$_2$ with the Scotch tape technique, the next step is to locate suitable few-layer crystals. This is most readily accomplished with an optical microscope. We employed a Nikon Eclipse LV150 optical microscope with a 10x magnification eyepiece and 10x, 50x, and 100x objectives and an epi-illumination halogen light source. Similar to the actual exfoliation process, the art of locating NbSe$_2$ flakes takes some practice to fully develop. Typically, a standard silicon chip can be thoroughly scanned for moderately thin crystals in approximately 10 minutes, but the thinnest crystals ($d \lesssim 5$ nm) are difficult to see under low magnification due to small lateral dimensions, and a complete search for them might take twice as long.

In Figure 4.2c, we show a representative NbSe$_2$ crystal under 1000x magnification. The thickness of the resulting crystals can be quickly estimated by the color of the flake, as discussed in Section 4.1.4. The greenish blue regions are $\sim 10$ nm thick, whereas the lightest purple region is only 2 layers. The detection of even monolayer 2D crystals is made possible by the optical contrast, which we again note is optimized by the choice of oxide thickness on the target substrate.

4.1.4 Atomic force microscopy characterization

Optical microscopy is by far the fastest method of locating few-layer NbSe$_2$ crystals over a large substrate area, but it cannot provide accurate quantitative information. To precisely determine the thickness and uniformity of our crystals, we employed atomic force microscopy (AFM). In contact mode, the tip of the AFM is brought into direct contact with the crystal, which can result in damage to few-layer NbSe$_2$. In tapping mode, the tip is instead oscillated near its natural resonance frequency, and the change in the resonance frequency as a result of interactions with the sample is monitored. The latter method should be far less destructive for delicate samples.

We primarily used a Veeco Multimode SPM AFM operating in tapping mode for measurements of NbSe$_2$ crystals. We corroborated our height measurements with a Bruker Icon AFM which was calibrated against a manufacturer’s AFM standard. A sample 2D AFM map of an exfoliated NbSe$_2$ crystal is shown in Figure 4.3a. The height data scale ranges from 0 nm (dark brown) to 17 nm (yellow). A line trace
along the dashed white line is shown in Figure 4.3b. Sharp step edges corresponding to integer multiples of the interlayer separation of 6.5 Å are visible (note that NbSe$_2$ crystals cleave such that the $c$-axis is perpendicular to the substrate). Within a terrace, the flake is smooth, with the exception of aggregates of “dirt,” the origin of which remains unknown. Basic attempts at solvent cleaning were unsuccessful at removing the aggregates, so when possible, devices were fabricated in regions free of aggregates.

By measuring the height of many crystals of varying color, we were able to produce a calibrated color code relating the appearance of a crystal under white light to its thickness. The color code is given in Figure 4.3c. The accuracy of the color code is limited by several factors. Firstly, while it is straightforward to differentiate between single layer steps in a given flake, it is not as easy to compare the color of two spatially removed flakes owing to subtle differences in substrate color, lighting levels, and camera exposure times. Additionally, AFM measurements are not entirely reliable for determining the absolute thickness of a crystal due to an uncontrollable offset from the substrate, which arises from the presence of trapped adsorbates such as water or glue residue. As an example, the thinnest flake in the color code in Figure 4.3c was measured to be 2.6 nm thick. One would naively assume this corresponds to a 4-layer flake, given the NbSe$_2$ interlayer spacing of 6.5 Å. However, Raman spectroscopy indicates this flake is only 2 layers thick. Thus, the color code is only accurate on the order of 1-2 nm when determining
absolute flake thicknesses, but can readily distinguish a relative height difference of a single layer between terraces on a single crystal.

4.1.5 Raman spectroscopy

For determining the absolute height of an exfoliated NbSe$_2$ crystal, a more precise method was desired. Raman spectroscopy was used with great success to determine the number of layers in exfoliated graphene crystals. Early work on Raman spectroscopy with exfoliated NbSe$_2$ crystals suggested that the technique was less helpful for this material [99], as certain phonon mode peaks did not appear to evolve systematically with layer number, and the crystals themselves were prone to laser-induced damage. However, more recently, it was shown that there is a particular phonon mode – the shear mode – with a strong dependence on crystal thickness [97]. The shear mode is a low frequency mode, appearing less than 30 cm$^{-1}$ from the Rayleigh peak. We employed a Raman system with the necessary filters to confirm the thickness of a select few NbSe$_2$ crystals. It is on the basis of this confirmation that we confidently claim the thinnest crystal in our established color code is a single unit cell (2 layers) thick.

4.2 Filament shadow mask devices

While our ultimate NbSe$_2$ nanostructure devices required many individual processing steps to realize, it was sometimes desirable to fabricate test devices to isolate the effect of individual process steps such as the choice of electrode metal or surface pre-cleaning parameters. When this was the case, we employed a simple filament shadow mask to pattern two-terminal transport devices on exfoliated NbSe$_2$ flakes. This all-dry process has been detailed previously [107–109].

A quartz filament with diameter between 200 nm and 2 $\mu$m is prepared manually with the aid of an acetylene torch. The filament is then positioned on top of the NbSe$_2$ flake of interest using fine copper wire tools and a large working distance optical microscope. The filament serves as a shadow mask for a subsequent metallization step, resulting in a two terminal electrical device. The advantage to this process is its simplicity in terms of time, cost, and processing conditions. At no point must the NbSe$_2$ be exposed to anything beyond ambient atmospheric conditions. Thus,
Figure 4.4. a) Schematic of NbSe₂ device fabrication process. 1) Two layers of resist are applied to NbSe₂ flake on substrate. 2) Pattern for electrical contacts is exposed and developed. 3) Pattern is metallized. 4) Residual resist and undesired metal are removed. b) Optical image of NbSe₂ device after completion of process in (a).

the effect of individual processing conditions required for nanostructure fabrication, such as plasma cleaning, can be isolated.

4.3 Fabrication of nanostructure devices with “leads-first” approach

Our standard approach to device fabrication involved first making electrical contact to an exfoliated NbSe₂ flake with desired electrodes, then patterning the flake into a nanostructure geometry for low-temperature measurements.

4.3.1 Photolithography

For NbSe₂ flakes with large lateral dimensions \((l, w \gtrsim 20 \, \mu m)\), we used photolithography to pattern measurement electrodes. An overview schematic of the process can be seen in Figure 4.4a, followed by an optical image of a real device in Figure 4.4b. Because the properties of a 2D crystal are sensitive to residues resulting from this process, we provide here some discussion of the details of the photolithography process we used. In this process, a thin polymer resist is applied to the sample surface. When exposed to ultraviolet light (typically the 436 nm “g-line” or 365 nm “i-line” of a mercury lamp), the polymer chains break apart, enabling the dissolution of the film in a suitable developer. By selectively exposing the film through a
patterned chrome mask, certain regions of the polymer film can be removed while the unexposed regions remain. This allows the direct transfer of an arbitrary pattern onto the sample. We used the Suss MicroTec MA/BA6 contact aligner in the Nanofab for all photolithography processing. With proper selection of resist, exposure conditions, and develop conditions, feature sizes down to 3 \( \mu m \) were reliably obtained (see, for example, Figure 4.4b).

In practice, two layers of photoresist were typically applied to accommodate the subsequent metallization and liftoff steps (see Section 4.3.4). The underlayer is not sensitive to UV radiation, and develops at a faster rate than the top layer. This produces an undercut in the developed regions, such as can be seen in the second panel in Figure 4.4a. For thin NbSe\(_2\) crystals, we most commonly used MicroChem LOR-2A as an underlayer and either SPR 3012 or Microposit 1805 as a top layer. The specific processing conditions used for each resist can be found in Table 4.1. Note that the overhead lights in the Nanofab are filtered to prevent accidental exposure of resist, but the filtering is imperfect. Thus, best results were obtained by storing the samples in an opaque box between spin, exposure, and develop steps.

An example of a typical photolithography mask pattern is shown in Figure 4.5. The white regions correspond to transparent regions of the mask, and indicate where the resist will be exposed and developed away in preparation for the subsequent metallization step. The particular pattern shown here allows for 6 electrical contacts to a NbSe\(_2\) crystal in both four-terminal transport and Hall resistivity configurations. In practice, only the number of leads, and not their configuration, is important,
as a subsequent etch step is used to precisely define the measurement geometry (Section 4.3.5). The photolithography masks were designed by Dr. Conor Puls, a former graduate student of the laboratory.

The complete photolithography process can be summarized in the following steps: 1) Apply underlayer resist to substrate; 2) Bake resist to evaporate remaining solvent and establish develop rate; 3) Repeat steps 1) and 2) for top layer resist if applicable; 4) Expose pattern on NbSe$_2$ crystal using MA/BA6 contact aligner in hard contact mode; 5) Develop exposed resist. The advantage to photolithography is primarily the throughput, which is typically less than 30 minutes per device. The disadvantage, as alluded to above, is the relatively large minimal feature size, which necessitates the exfoliation of few-layer NbSe$_2$ crystals on the order of tens of micrometers.

### 4.3.2 Electron-beam lithography

A related technique is electron-beam lithography (EBL). The general idea is the same – a polymer resist is selectively exposed and developed to obtain a desired pattern on a sample. However, in EBL, the resist is exposed to a collimated beam of high-energy electrons (100 keV) rather than a UV lamp. The primary advantage of this approach is the minimal feature size, which is limited by the spot size of the electron column and the resolution of the resist. Under optimal conditions, feature sizes of 10 nm can be obtained. A second advantage is the “direct-write” capability. The electron beam is raster scanned across the sample, and can be blanked at arbitrary locations, allowing for the patterning of designs with every write. For photolithography, each device pattern requires the manufacture of a specific hard mask. We used the Vistec EBPG 5200 in the Nanofab for our EBL work.

The procedure for properly aligning an EBL pattern to an exfoliated crystal is

<table>
<thead>
<tr>
<th>Chemical</th>
<th>sec</th>
<th>sec</th>
<th>µm</th>
<th>°C</th>
<th>sec</th>
<th>mJ/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOR-2A</td>
<td>500</td>
<td>4000</td>
<td>45</td>
<td>0.2</td>
<td>195</td>
<td>60</td>
</tr>
<tr>
<td>1805</td>
<td>500</td>
<td>4000</td>
<td>45</td>
<td>0.5</td>
<td>110</td>
<td>60</td>
</tr>
<tr>
<td>3012</td>
<td>500</td>
<td>4000</td>
<td>45</td>
<td>1.33</td>
<td>95</td>
<td>60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Develop</th>
<th>sec</th>
<th>sec</th>
<th>mJ/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD-26</td>
<td>60</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td>CD-26</td>
<td>60</td>
<td>56</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1. Process parameters for photoresist application, exposure, and develop. Process assumes i-line Hg lamp and hard contact exposure mode.
non-trivial. In photolithography, the user can manually align the mask and the crystal under an optical microscope. The analog in EBL would be to use in situ scanning electron microscopy (SEM) imaging to align the crystal to the intended pattern, but the process of taking the SEM image would expose the electron beam sensitive resist, destroying the pattern. Instead, for EBL patterning, NbSe$_2$ crystals were exfoliated onto substrates with a pre-patterned array of Au alignment markers. A small region of the alignment marker pattern is shown in Figure 4.6a. A perpendicular grid of Arabic numerals and horizontal bars was used to identify the approximate location of an exfoliated flake. A separate grid of $20 \times 20 \ \mu m^2$ squares was used by the EBL tool to determine the $x$, $y$, and $\theta$ offset of the pattern, and a $50 \ \mu m$ grid of small finding markers was used to manually specify the precise location of the exfoliated crystals relative to the $20 \ \mu m$ squares. The presence of alignment markers appears to slightly reduce the yield of thin NbSe$_2$ flakes. In response, we developed an alternative process whereby the EBL alignment markers were deposited after the initial exfoliation. However, the additional processing steps required did not justify the minor increase in crystal yield, which could just as easily be achieved by increasing the number of exfoliation attempts.

The EBL pattern was drawn relative to the known positions of the $20 \ \mu m$ alignment marks with the aid of an optical microscope image and Tanner L-Edit IC Layout editor (see Figure 4.6). Consequently, the level of alignment was limited primarily by the quality of the $20 \ \mu m$ alignment marks and the resolution of the
Table 4.2. Composition of resists used in EBL processes.

<table>
<thead>
<tr>
<th>Resist</th>
<th>Polymer</th>
<th>Solvent</th>
<th>-Layer</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOR-2A</td>
<td>Poly(methyl glutarimide)</td>
<td>Cyclopentanone</td>
<td>Under</td>
<td>Not optimized for lateral resolution</td>
</tr>
<tr>
<td>P(MMA-MAA)</td>
<td>Poly(methyl methacrylate-methacrylic acid)</td>
<td>Ethyl Lactate</td>
<td>Under</td>
<td>Adversely reacts with NbSe$_2$</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
<td>Anisole</td>
<td>Over</td>
<td>Incompatible with LOR-2A</td>
</tr>
<tr>
<td>ZEP 520A 1:1</td>
<td>Methylstyrene, Chloromethyl acrylate</td>
<td>Anisole</td>
<td>Over</td>
<td>Compatible with LOR-2A</td>
</tr>
</tbody>
</table>

optical microscope used to generate the first image. We typically achieved alignment precision within 1 µm for an initial EBL write. Subsequent writes (such as the etch write discussed in Section 4.3.5) can be aligned within 100 nm to the first write if new 20 µm alignment marks are exposed at the same time as the measurement electrodes. We obtained electrode sizes down to 100 nm with EBL, though we rarely needed to pattern electrodes smaller than 300 nm, because our NbSe$_2$ crystals were typically at least 2 µm wide.

Similar to photolithography, there are a wide variety of available EBL resists. A summary of the resists we most commonly employed is given in Table 4.2. The highest lateral resolution for patterning electrodes was obtained with a bilayer stack of P(MMA-MAA)/PMMA A3, but the P(MMA-MAA) was found to react adversely with NbSe$_2$, preventing electrical contact. We ultimately chose LOR-2A as an underlayer, because of our success with that polymer in the context of photolithography. We modified the LOR-2A application process to improve the lateral resolution. Our electrode width was found to be 300 nm with the LOR-2A/ZEP 520A 1:1 stack. In Table 4.3, we provide the processing conditions for the full range of EBL resists employed in this dissertation.

4.3.3 Post-develop surface cleaning and contact resistance

After developing photoresists or electron-beam resists, it is common to use a low-power O$_2$ plasma to remove any thin residual layer of polymer prior to proceeding to metallization. However, we found an O$_2$ plasma to be extraordinarily counterpro-
productive when contacting NbSe$_2$. As a control experiment, we subjected unprocessed NbSe$_2$ crystals to an O$_2$ plasma before patterning electrodes with an all-dry filament-based process, and were unable to reliably make electrical contact. The plasma evidently modifies the top surface of the crystal, most likely through the formation of an oxide layer after the desorption of Se atoms, resulting in prohibitively high contact resistance. If resist residue does indeed remain after the develop step, it is possible that extraordinarily precise timing of the plasma step can remove the resist without damaging the underlying NbSe$_2$ surface, but such an approach results in an impractically low yield of measurable devices. Instead, we elected to avoid any post-develop surface cleaning. We discovered that LOR-2A left minimal residue with proper pre-bake and develop conditions, and allowed for low-resistance contact ($< 5 \, \Omega$ at low temperature). The P(MMA-MAA) copolymer, however, consistently resulted in high resistance contacts ($> 1 \, \text{k}\Omega$). While LOR-2A is not typically utilized as a polymer layer in EBL, it is compatible with the standard EBL resist ZEP 520 A, and we developed a bilayer lift-off process with a LOR/ZEP stack, the details of which can be found in Tables 4.3 and 4.4.

### Table 4.3. Process parameters for electron-beam resist application.

<table>
<thead>
<tr>
<th></th>
<th>Dispense</th>
<th>Spin</th>
<th>Bake</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RPM</td>
<td>RPM</td>
<td>µm</td>
</tr>
<tr>
<td>LOR-2A</td>
<td>500</td>
<td>5000</td>
<td>45</td>
</tr>
<tr>
<td>P(MMA-MAA)</td>
<td>900</td>
<td>5000</td>
<td>50</td>
</tr>
<tr>
<td>PMMA A2</td>
<td>900</td>
<td>4000</td>
<td>50</td>
</tr>
<tr>
<td>PMMA A3</td>
<td>900</td>
<td>5000</td>
<td>50</td>
</tr>
<tr>
<td>ZEP 520 A 1:1</td>
<td>500</td>
<td>4000</td>
<td>45</td>
</tr>
</tbody>
</table>

### Table 4.4. Process parameters for electron-beam resist exposure and develop.

<table>
<thead>
<tr>
<th></th>
<th>Beam</th>
<th>Dose</th>
<th>Develop</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nA</td>
<td>µC/cm$^2$</td>
<td>Chemical</td>
</tr>
<tr>
<td>LOR-2A</td>
<td>NA</td>
<td>NA</td>
<td>CD-26</td>
</tr>
<tr>
<td>PMMA A2</td>
<td>1</td>
<td>1650</td>
<td>MIBK:IPA 1:3</td>
</tr>
<tr>
<td>PMMA A3</td>
<td>25</td>
<td>300</td>
<td>MIBK:IPA 1:1</td>
</tr>
<tr>
<td>ZEP 520 A 1:1</td>
<td>8</td>
<td>155</td>
<td>n-amyl acetate</td>
</tr>
</tbody>
</table>

As a control experiment, we subjected unprocessed NbSe$_2$ crystals to an O$_2$ plasma before patterning electrodes with an all-dry filament-based process, and were unable to reliably make electrical contact. The plasma evidently modifies the top surface of the crystal, most likely through the formation of an oxide layer after the desorption of Se atoms, resulting in prohibitively high contact resistance. If resist residue does indeed remain after the develop step, it is possible that extraordinarily precise timing of the plasma step can remove the resist without damaging the underlying NbSe$_2$ surface, but such an approach results in an impractically low yield of measurable devices. Instead, we elected to avoid any post-develop surface cleaning. We discovered that LOR-2A left minimal residue with proper pre-bake and develop conditions, and allowed for low-resistance contact ($< 5 \, \Omega$ at low temperature). The P(MMA-MAA) copolymer, however, consistently resulted in high resistance contacts ($> 1 \, \text{k}\Omega$). While LOR-2A is not typically utilized as a polymer layer in EBL, it is compatible with the standard EBL resist ZEP 520 A, and we developed a bilayer lift-off process with a LOR/ZEP stack, the details of which can be found in Tables 4.3 and 4.4.
Figure 4.7. L-Edit CAD drawing of 90 nm wide nanowire. Purple regions will be exposed and etched, leaving white regions behind. Gray regions indicate areas where NbSe$_2$ remains, but is not electrically connected to the device of interest. Etch regions extend beyond field of view to contact electrodes.

4.3.4 Metallization and lift-off

Once an electrode pattern is generated with either photolithography or EBL, a 30 nm Au film is deposited over the entire sample by evaporating a source material (see Figure 4.4a, panels 3 and 4). This evaporation was typically performed at a pressure of $\lesssim 10^{-7}$ Torr in the Nanofab Kurt J. Leskar Lab-18 evaporator using either resistive heating or electron-beam bombardment to evaporate the source material. The remaining resist is then removed in a heated ($\sim 50^\circ$C) bath of MicroChem Remover PG (n-methyl pyrrolidone) in a process referred to as “lift-off.” Some care must be taken to ensure repeatable lift-off success. The evaporated film must be significantly thinner than the resist stack; the deposition angle must be as perpendicular to the substrate as reasonably achievable; and the solvent bath must be gently agitated with a pipette to assist with the peeling off of the unwanted film. It is important that the agitation be quite gentle, as Au does not wet SiO$_2$, and vigorous pipetting or sonication typically results in the loss of all electrodes. A Ti adhesion layer underneath the Au simplifies matters somewhat, but we found all-Au electrodes to give consistently lower contact resistance to NbSe$_2$. An optical image of a representative NbSe$_2$ device at this point in the process is shown in Figure 4.4b.
Table 4.5. Process parameters for etching NbSe$_2$ in PT-720 reactive ion etch system. Quoted process will etch through $\sim 10$ nm of NbSe$_2$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Flow rate</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Bias</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_4$</td>
<td>40 sccm</td>
<td>40 mTorr</td>
<td>25°C</td>
<td>200 V</td>
<td>15 s</td>
</tr>
</tbody>
</table>

4.3.5 Electron-beam lithography to pattern nanostructure

After depositing electrodes onto the NbSe$_2$ flake, we defined the nanostructure geometry. We used EBL to accomplish this, both for photolithography and EBL patterned electrodes. Our resist choice was always PMMA A2, with process parameters given in Tables 4.3 and 4.4. In the prior metallization step, we patterned EBL alignment markers simultaneously with the electrodes, so that the alignment between the electrodes and the nanostructure would be accurate. In Figure 4.7, we present a typical EBL nanostructure pattern. This pattern is for an 8-terminal nanostrip with both longitudinal and transverse voltage leads. An important obstacle to be aware of when patterning small EBL features is that the electrons scatter as they pass through the resist and substrate. The scattered electrons can expose unintended regions of the resist, resulting in a final pattern that appears “over-exposed.” This is referred to as the proximity effect, which is cumulative, so dense patterns are particularly susceptible to over-exposure. For features $< 100$ nm, this over-exposure can completely wash out the desired pattern. Software corrections can partly compensate for this effect, but we found a more effective approach was to only expose narrow lines to define our nanostructures. As can be seen in Figure 4.7, the nanostrip is outlined, but the majority of surrounding NbSe$_2$ is unexposed. By exposing lines of only 20 nm with a 10 nm beam, we were able to limit the over-exposure to 5 nm on a side, for a total exposed line width of 30 nm. Patterns were drawn with this ultimate over-exposure in mind, so a drawn nanostrip with an outlined width of 100 nm would result in a final structure with a width of 90 nm.

4.3.6 Plasma etching of nanostructure

Finally, the EBL patterned nanostructure was subjected to a CF$_4$ plasma in a PlasmaTherm 720 parallel plate reactive ion plasma etch tool in the Nanofab. In this process, positively charged ions in a plasma are accelerated towards the sample surface through a potential difference. At the surface, they interact physically
and chemically with the sample to provide a selective etch. The specific process parameters are given in Table 4.5. An important consideration in this step is the plasma-induced heating of the resist mask. It is beneficial to divide lengthy etches into multiple short steps with a cool-down period between each etch. Excessive heating of the resist mask will impede subsequent removal. In practice, we found that limiting etch steps to 20 seconds or less was sufficient.

In Figure 4.8, we show optical images of a representative NbSe$_2$ nanostructure device after a) exfoliation, b) electrode patterning and metallization, and c) nanostructure patterning and etching. The same nanostructure is shown again as a false-color SEM image in Figure 4.9. Electrodes are shown in yellow, the functional NbSe$_2$ nanostructure is shown in green, the electrically disconnected NbSe$_2$ is shown in blue, and the underlying SiO$_2$ substrate is shown in gray tones.

### 4.3.7 Post-etch cleaning

To remove the resist mask after etching the nanostructure, we again used heated Remover PG. This would remove the bulk of the mask, but we found a thin layer of PMMA to be insoluble in the solvent due to a chemical modification of the polymer during the CF$_4$ etch. Occasionally this layer would cover the sample of interest, but often it would peel off and redeposit in an innocuous location on the substrate. An O$_2$ plasma was effective at removing the remaining thin layer, but was undesirable due to the documented plasma-induced oxidation of the NbSe$_2$ surface. We elected to leave the thin layer untouched on the occasions it covered the sample, preferring
Figure 4.9. False color scanning electron micrograph (SEM) of NbSe$_2$ nanowire. Yellow regions are Au electrodes, blue regions are electrically isolated residual NbSe$_2$, gray regions are underlying SiO$_2$ substrate, and green regions are electrically contributing NbSe$_2$.

the possible additional level of disorder to the certain oxidation of the device.

4.4 Fabrication of nanostructure devices with “etch-first” approach

A major disadvantage of the “leads-first” approach presented in Section 4.3 is that the final devices do not represent idealized geometries. For instance, in the nanostrip shown in Figure 4.9, there are four nodes where the voltage electrodes intersect the horizontal nanostrip. These nodes are a perturbation of the ideal strip geometry, which would feature a uniform width along the entire device. In the case of nanoloops, the effect of superconducting electrodes can be dramatic [11]. It was therefore of interest to develop a process whereby a bare superconducting device geometry was defined first, and measurement electrodes were added afterwards.

4.4.1 Sub-10 nm alignment precision through device arrays

The main difficulty in an “etch-first” approach is the stringent alignment requirements. With the “leads-first” fabrication process, the necessary alignment between the metal electrodes and the etch pattern was no less than several hundred nanometers, because the electrodes could contact the NbSe$_2$ crystal far from the actual nanostructure, as seen in Figure 4.9. Aligning electrodes to a bare nanostructure
Figure 4.10. a) L-Edit CAD drawing of bare device “misaligned array.” Leads are intentionally offset from center of etched pattern in step sizes of $\delta x = 5\, \text{nm}$. Array also steps in $y$-direction (not shown). b) False color scanning electron micrograph of bare ring with sub-10-nm alignment between etch write and lead write. Color scheme follows Figure 4.9.

requires multi-step alignment tolerances less than 10 nm, though. With careful inclusion of well-defined alignment markers, the Vistec EBPG 5200 can reliably align multiple writes within 50 nm of each other, but we found it difficult to obtain alignment better than that. Our solution to this problem was to write an array of nanostructures followed by an array of contact electrodes. The $x$ and $y$ step sizes in the two arrays were intentionally made to differ by several nanometers, such as can be seen in Figure 4.10a (a 1D array is shown for simplicity, but in practice, the array was two-dimensional). In this way, the random $(x, y)$ offset between the etch and electrode writes would exactly cancel the designed offset between the bare device and electrodes at one location in the 2D array. We then imaged the array with an SEM to locate the device with the proper alignment, and used a final EBL step to extend the electrodes to measurement pads. Figure 4.10b shows an SEM image of a bare NbSe$_2$ ring fabricated in this fashion. The alignment between the electrode and ring is better than 10 nm, and the influence of superconducting nodes is completely eliminated.

### 4.4.2 Contact resistance of “etch-first” devices

The remaining disadvantage to the bare superconducting devices is the substantial processing that precedes the metallization of the electrodes. In addition to the possibility of processing steps unintentionally modifying the NbSe$_2$ surface, the
residue from the PMMA etch mask prevents low resistance contact between the electrodes and the device, and therefore must be removed in a way that preserves the sensitive NbSe$_2$ surface. This is subject of ongoing effort, with the most promising solutions being to first encapsulate the NbSe$_2$ flake with a protective 2D crystal such as graphene or boron nitride, or to transfer an unprocessed NbSe$_2$ crystal on top of predefined leads. Both approaches are enabled with the 2D crystal transfer station discussed in Section 4.7.

4.5 *In situ* annealing of devices

A common approach to cleaning 2D crystal devices after lithographic processing is to utilize current annealing [99], but we found that nanostructures of NbSe$_2$ were unable to sustain large currents to achieve noticeable cleaning. However, the commercial Physical Property Measurement System (PPMS) cryostat we employed is capable of heating samples to 400 K in a high vacuum environment. This is useful for cleaning water and other potential contaminants from the surface of samples prior to measurement.

In this dissertation, we present data on NbSe$_2$ 2D crystals ranging from two layers to more than 10 nm thick. While the effect of cleaning is most dramatic for thin samples, even relatively thick NbSe$_2$ surprisingly exhibits a response to *in situ* high temperature annealing. In Figures 4.11a-b, we show the $R(T)$ curves for an 11 nm
thick NbSe$_2$ nanoloop. At low temperatures, the as-processed device is insulating, rather than superconducting. After sufficient annealing, however, the device exhibits a superconducting transition near 4 K. Furthermore, the residual resistivity ratio, which reflects the quality of the crystal in the normal state, is improved from 2.5 to 4.1 after annealing. In Figure 4.11c, we show the resistance of this device during the anneal process at 400 K. The curve resembles a decaying exponential, and provides a means of determining when the device has been sufficiently annealed without the time-consuming task of cooling below the expected $T_c$.

There is a potential risk to in situ annealing. The melting point of indium is 430 K, and occasionally the indium spheres we used to attach the gold leads would flow during the annealing process. Upon recooling, the contracting indium would tear the thin evaporated gold pads free from the SiO$_2$ substrate, breaking electrical continuity. This effect could be mitigated in one of three ways: reinforcing the indium contacts with silver epoxy, which would not flow, including an adhesive titanium underlayer beneath the gold pads, or annealing at lower temperatures. Annealing at temperatures as low as 370 K resulted in improved crystal quality, with a substantially reduced rate of failure from indium reflow.

In situ annealing was originally pursued in an attempt to improve contact resistance. The noticeable affect on device quality, especially the superconducting properties, was unanticipated in thick devices, where surface adsorbates were thought to be unimportant. We return to a detailed discussion of the physical consequences of surface adsorbates in 2D crystals of NbSe$_2$ in Chapter 5.

### 4.6 Interface characterization by transmission electron microscopy

When dealing with 2D crystals, interfaces and surfaces are of paramount importance. An invaluable tool for characterizing the quality of an interface is the transmission electron microscope (TEM), which can achieve atomic resolution visualization of properly prepared samples. We used the Quanta 200 3D Dual Beam Focused-ion-beam (FIB) system in the MCL to prepare cross-sectional TEM samples from NbSe$_2$ nanostructures. The FIB uses a focused beam of gallium ions to cut a site-specific cross-sectional sample and then thin it to electron transparency ($\lesssim 100$ nm).
Figure 4.12. a) High resolution transmission electron micrograph of NbSe$_2$ crystal underneath Ti/Au measurement electrode. Inset line traces indicate relative elemental composition as measured by energy dispersive x-ray spectroscopy. b) Average transmitted electron intensity from (a). NbSe$_2$ triple layers visible in blue region, but not in green region.

Imaged the samples in a JEOL 2010F TEM with a probe size of 1.6 Å.

Shown in Figure 4.12a is a high resolution TEM image of a 9-nm thick NbSe$_2$ crystal underneath a Ti/Au electrode. The lattice planes of NbSe$_2$ are clearly visible as the vertical triple layers on the left. The inset curves give the relative atomic concentrations of the indicated materials, as measured simultaneously by energy dispersive x-ray spectroscopy (EDX). There are several things to note from this image. Firstly, the ratio of Nb:Se is as expected near the SiO$_2$ substrate (namely, 1:2), but a pronounced Se deficiency is apparent near the top surface of the flake. Secondly, the Ti underlayer of the electrode has diffused into the NbSe$_2$ crystal, as seen by the overlapping Ti and Nb signals. Finally, the top several layers of NbSe$_2$ crystal are restructured beginning near 7 nm and corresponding with the Se deficiency. This restructuring can be seen more clearly in Figure 4.12b, which is a plot of the average transmitted electron intensity over a reduced lateral
Figure 4.13. Energy dispersive x-ray spectroscopy line traces of indicated elements in exfoliated NbSe$_2$ crystal on SiO$_2$. A region of oxidized niobium centered at 14 nm is visible. O line scale increased by a factor of three due to low detector efficiency for O.

range. Below 7 nm, the Se-Nb-Se triple layer is evident with the expected lattice constant of 0.65 nm. Above 7 nm, the triple layer is replaced with a single repeating structure with a reduced lattice constant.

The most likely explanation for the restructuring and Se deficiency is the formation of a niobium oxide at the top surface of the NbSe$_2$ flake. Oxygen is difficult to detect in EDX measurements due to its low atomic number. This effect is further complicated because of the proximity of Au, which strongly scatters the incident electrons, so we prepared TEM samples of processed NbSe$_2$ crystals in regions not covered by measurement electrodes. A representative EDX spectrum from such a sample is shown in Figure 4.13. We observe the same Se deficiency at the top surface of the crystal, and we also observe a corresponding peak in the concentration of O (note the different scale for the O line trace). High resolution TEM images of this sample (data not shown) reveal the same restructuring found in Figure 4.12. Thus, we conclude that O displaces Se in the top few crystal layers, resulting in the formation of a niobium oxide region.

We performed several additional TEM measurements on a variety of NbSe$_2$ samples in an attempt to isolate the conditions under which the oxide layer forms. We observed oxidation both underneath measurement electrodes and on exposed regions of the crystal, indicating the Ti diffusion is not to blame. Furthermore, we observed oxidation in devices both with and without an in situ anneal, and in both photolithography and EBL prepared devices. The oxidation is evidently related to the standard processing conditions common to all devices. Fortunately,
the formation of a thin oxide layer apparently does not prohibit low-resistance electrical contacts. However, a sufficiently thick oxide, such as may be incurred by an O\textsubscript{2} plasma, will result in insulating contacts which prevent low-noise voltage measurements.

Thick NbSe\textsubscript{2} devices (≥ 5 layers) reliably exhibit superconductivity, but the thinnest devices we measured showed insulating behavior, consistent with previous results on lithographically-processed NbSe\textsubscript{2} [100,101]. Interestingly, superconductivity was previously observed in bilayer NbSe\textsubscript{2} transport devices fabricated with a lithography-free process [99], and, concurrent with this dissertation, in monolayer NbSe\textsubscript{2} protected by graphene [102] or boron nitride [97]. Thus, process-induced oxidation is almost certainly the reason for the insulating behavior of the thinnest crystals reported in this dissertation. Ultimately, we wish to study the dynamics of vortices in nanostructures of single-layer NbSe\textsubscript{2}, and process-induced oxidation is therefore unacceptable. This led us to develop the 2D crystal encapsulation technique outlined in Section 4.7.

4.7 Fabrication of 2D crystal heterostructures

Motivated in part by the necessity of protecting ultra thin 2D crystals of NbSe\textsubscript{2} from ambient and processing conditions, we developed a process to encapsulate exfoliated NbSe\textsubscript{2} crystals with single-layer graphene, which has itself been demonstrated to be quite robust to standard lithographic processing conditions. Broadly, the process involves transferring an exfoliated graphene flake onto an exfoliated NbSe\textsubscript{2} flake within an inert atmosphere. A major advantage to this technique is its flexibility – it can be applied to any 2D crystal that can be mechanically exfoliated – and the potential applications extend well beyond simple protection of a sensitive underlayer. For example, a freshly-cleaved crystal can be transferred onto predefined contact electrodes, eliminating the risk of process-induced degradation of electrical contacts. In this section we describe the implementation of this 2D crystal transfer process in our lab.
Figure 4.14. a) Schematic of 2D crystal transfer process. 1) Exfoliate 2D crystal onto PMMA/PAA substrate. 2) Place substrate on top of DI water bath. 3) Wait for PAA to dissolve and PMMA layer to release. 4) Suspend PMMA over hole in aluminum slide. 5) Invert slide, position over second 2D crystal, and heat to > 100°C to transfer. 6) Dissolve PMMA in acetone. b) Optical images of transfer process in (a). 1) Monolayer graphene exfoliated on PMMA/PAA substrate. 2) Few-layer NbSe$_2$ exfoliated on standard SiO$_2$/Si substrate. 3) Final graphene/NbSe$_2$ heterostructure on SiO$_2$/Si after transfer but prior to removing PMMA. 4) Final graphene/NbSe$_2$ heterostructure on SiO$_2$/Si after removing PMMA.

4.7.1  Heterostructure overview

A schematic of the heterostructure fabrication process is shown in Figure 4.14a. First, the 2D crystal to be transferred is mechanically exfoliated onto a specially prepared bilayer stack of poly(methyl methacrylate) (PMMA) and polyacrylic acid (PAA) applied to a silicon substrate. The thickness of the stack is tuned to provide maximum optical contrast for exfoliated 2D crystals, similar to the role of the 300 nm thermal oxide layer utilized for standard mechanical exfoliation onto silicon substrates. PAA is water soluble, whereas PMMA is insoluble in water. The substrate is then placed into a bath of distilled water. Surface tension is sufficient to suspend the substrate on the surface, as seen in the second panel of Figure 4.14a, but the water meniscus climbs high enough to dissolve the PAA. After several minutes, the PAA is completely dissolved, and the silicon substrate falls to the bottom of the bath, leaving the highly hydrophobic PMMA layer and exfoliated 2D crystal floating on the surface.

Next, the floating PMMA is removed from the bath with an anodized Al slide with a 3 mm diameter hole. The diameter of the hole is important — we found that a larger hole caused a wrinkling of the thin film, whereas a smaller hole made it
difficult to correctly position the crystal of interest. Likewise, the choice of anodized Al for the slide material results in the most controllable positioning of the PMMA film when removing from the bath. The positioning is accomplished by holding the Al slide just beneath the water surface and using the bulb end of a plastic pipette to manipulate the film. It is crucial that the pipette bulb not actually contact the film, as this will result in wrinkles and tears, but rather, the bulb is used to locally deform the surface of the water near the PMMA, and this deformation can be used to “push” the film. By carefully noting the precise location of the desired crystal relative to the edges of the substrate before dissolving the PAA, it is possible to center the exfoliated crystal within the hole in the Al slide. Precise centering is not essential, but the crystal must obviously be on a region of film that is suspended over the hole, rather than supported on the solid part of the slide.

Once the film is removed onto the slide, it is inverted (film side down) on a pair of plastic spacers and allowed to dry in a sealed container overnight. Any attempt to speed the drying process always resulted in a wrinkled film. At this point, the second crystal in the desired heterostructure is exfoliated onto a standard Si/SiO$_2$ substrate. For the case of sensitive crystals, such as monolayer NbSe$_2$, this exfoliation and subsequent transfer is performed within a N$_2$ dry box. With the aid of an optical microscope and custom-built micro-manipulator transfer station, the 2D crystal on the PMMA film is positioned directly above the 2D crystal on the Si/SiO$_2$ substrate and brought into as close proximity as possible (typically $\lesssim$ 30 $\mu$m). A localized stream of N$_2$ gas is applied to the backside of the film to bring it into contact with the substrate, which is heated to $\sim$ 110$^\circ$C. When the PMMA contacts the heated substrate, it softens and adheres. The Al slide can then be removed, and the PMMA dissolved in acetone, leaving the 2D crystal heterostructure on the Si/SiO$_2$ substrate. Figure 4.14b shows optical images of a representative NbSe$_2$/graphene heterostructure at various steps in the process.

A summary of the 2D crystal heterostructure fabrication process follows: 1) Exfoliate 2D crystal to be transferred onto PMMA/PAA substrate; 2) Dissolve PAA in water bath; 3) Remove PMMA film from bath onto Al slide with predrilled hole; 4) Dry film overnight; 5) Exfoliate 2D crystal to be covered onto Si/SiO$_2$ substrate; 6) Use micro-manipulator transfer station to align crystals; 7) Heat substrate and blow film into contact using compressed N$_2$; 8) Dissolve PMMA film in acetone.
Table 4.6. Process parameters for application of polymer stack to Si substrate for 2D crystal transfer process.

<table>
<thead>
<tr>
<th></th>
<th>Dispense</th>
<th>Spin</th>
<th>Bake</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RPM</td>
<td>RPM</td>
<td>°C</td>
</tr>
<tr>
<td>5% PAA</td>
<td>900</td>
<td>5000</td>
<td>60</td>
</tr>
<tr>
<td>PMMA A3</td>
<td>900</td>
<td>4000</td>
<td>60</td>
</tr>
</tbody>
</table>

4.7.2 Substrate preparation

For the water-soluble layer in the 2D crystal transfer process, we used a solution of 5% PAA in H₂O. A small amount of saturated NaOH was added to neutralize the pH level of the solution. The necessary amount of NaOH was determined by iteratively adding droplets of NaOH to the PAA solution and checking the pH level with litmus paper, so the final pH was only accurate to ±1. PAA is commercially available in varying concentrations; we began with a solution of 25% PAA in water with 50,000 g/mol molecular weight. We diluted the commercial solution in order to obtain the proper thickness when applying the PAA to a Si wafer. The final bilayer stack of PAA/PMMA needs to provide maximal optical contrast between an exfoliated 2D crystal and the substrate. Practically, this means to the unaided eye, the wafer should appear the same deep blue color that a Si wafer with 300 nm thermal oxide appears. Obtaining the proper thickness of the final stack was simply a matter of trial and error. Table 4.6 gives the processing conditions we found to result in suitable contrast (for a comparison to the contrast of Si/SiO₂ wafers, see panels 1 and 2 in Figure 4.14b). Note that the top PMMA layer was not baked – this was to allow for better conforming to the target substrate during the transfer process.

The application of PAA must be performed at a dedicated spin bench. A common adhesion promoter in lithography is hexamethyldisilazane (HMDS), which reacts strongly with water, releasing ammonia gas. As a safety precaution, therefore, HMDS and the water-based PAA solution must not be stored nor applied at the same station. Instead, to promote adhesion between the PAA and Si wafer, we performed an O₂ plasma clean on the wafer prior to applying the PAA, the specific parameters of which can be found in Table 4.7.
Table 4.7. Process parameters for cleaning Si wafer in preparation for application of PAA.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Flow rate</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Power</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>100 sccm</td>
<td>10 mTorr</td>
<td>25°C</td>
<td>75 W</td>
<td>120 s</td>
</tr>
<tr>
<td>Ar</td>
<td>8 sccm</td>
<td></td>
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Figure 4.15. a) Micromanipulator 2D crystal transfer station. Anodized aluminum slide is rigidly mounted to 3-axis micromanipulators (not visible) and suspended over brass heater block. Large working distance optical microscope permits alignment at 500x magnification. b) Custom-designed 10 ft³ nitrogen dry box encasing 2D crystal transfer station. Boxed region indicates field of view in (a).

4.7.3 Micromanipulator 2D crystal transfer station

The micro-manipulator transfer station used in the fabrication of 2D crystal heterostructures was custom-designed to be compatible with our existing Nikon Eclipse LV150 optical microscope. The manipulation was achieved with a 3-axis micromanipulator (Thorlabs PT3A XYZ Translation Stage with Differential Adjusters) featuring a resolution of 25 µm per revolution and 25 mm travel range along each axis. The manipulator was mounted to the stage of the optical microscope by a custom-built aluminum adapter (lower silver piece in Figure 4.15a). An aluminum “forklift” (upper silver piece in Figure 4.15a) was bolted to the manipulator to support the anodized Al slide with PMMA film. The slide was clipped to the top of the forklift during transfer. To facilitate heating of the substrate during the transfer process, a 32 W, 1/4” diameter cartridge heater was encased in a brass heater block and mounted to the microscope stage below the Al forklift. The temperature was monitored with a thermocouple inserted into a separate hole near the top surface of the heater block, and controlled with a variable AC voltage transformer.
The maximum obtainable temperature in this configuration exceeded 140°C, but transfers were typically performed at 110°C.

It was important that the surface of the Al slide be parallel to the surface of the substrate mounted on the brass heater block. Any discrepancy in angles would limit the minimal achievable vertical distance between the 2D crystals during the transfer. To obtain lateral alignment accuracy within 1 μm, it was necessary to bring the crystals closer than 30 μm vertically before applying the pressurized N\textsubscript{2} gas. While all components of the transfer station were designed with this requirement in mind, we maximized the alignment of the slide to the heater block by including foam washers between the manipulator and microscope adapter piece. The bolts holding the manipulator to the adapter were selectively tightened against the foam washers to compensate for any inadvertent rotation between the slide and the heater block. This alignment was repeated every several weeks to compensate for the normal wear and tear on the system.

4.7.4 Nitrogen dry box for inert atmosphere 2D crystal transfer

To minimize exposure to oxygen and water during the encapsulation process, the transfer station was encased in a custom-built N\textsubscript{2} dry box, shown in Figure 4.15b. The dry box featured a load lock with independent gas lines for purging, a workspace for exfoliating NbSe\textsubscript{2} flakes, the aforementioned microscope and transfer station, and a compartment for silica gel desiccant. The lowest achievable moisture level within the dry box was limited by a diffusive gas path through the optics of the microscope. To mitigate this, we operated the box at a positive pressure of dry N\textsubscript{2} gas. To prevent unnecessary waste of the N\textsubscript{2} gas, the box was only pressurized during and immediately before a series of transfers. We found that acceptably low levels of moisture (<10% relative humidity) could be achieved after approximately 24 hours of operation. The continuous operation of a portable dehumidifier in the vicinity of the dry box was also found to help decrease the moisture level within the box. To further mitigate the effects of moisture, the transfer process was performed rapidly, with as little as 30 minutes separating the initial exfoliation of NbSe\textsubscript{2} and the final encapsulation with graphene.

A representative heterostructure is shown in Figure 4.16a. The darkest purple region is 4-layer NbSe\textsubscript{2}, the lighter purple region is bilayer NbSe\textsubscript{2}, and the faintest
Figure 4.16. a) Optical image of bilayer NbSe$_2$ (light purple) covered with single-layer graphene (outlined with dashed white line). b) Optical image of heterostructure in (a) after lithography and metallization. c) Resistance ($R$) vs. temperature ($T$) for heterostructure in (b).

region, outlined in the dashed white line, is single-layer graphene transferred on top of the NbSe$_2$. The same heterostructure is shown after EBL and metallization in Figure 4.16b. Note that the unprotected NbSe$_2$ has changed color, likely due to oxidation during device processing. The encapsulated NbSe$_2$, on the other hand, is optically unaffected by the lithography process, indicating the effectiveness of the encapsulation technique. The lead configuration allows for both transport and planar tunneling measurements on the graphene/bilayer NbSe$_2$ heterostructure. In Figure 4.16c we present the low temperature resistance of the heterostructure. A superconducting transition at $T_c \approx 4.5$ K is apparent.
Vortex entrance and crossing of 2D crystal nanowires

In this chapter, we present electrical transport measurements on NbSe$_2$ nanowires. We present experimental evidence and theoretical analysis in the London approximation of sample-specific magnetoresistance variations in 2D crystal nanowires based on vortex crossing of the nanowire by overcoming a free energy barrier. The understanding we gain from this system regarding the relevant energy barriers for vortex crossing and trapping is utilized in the design of NbSe$_2$ nanoloops for vortex manipulation.

5.1 Experimental devices

Our experimental 2D crystal NbSe$_2$ nanowires were fabricated with the “leads-first” technique outlined in Chapter 4. We typically fixed the length of the nanowires at $L = 2.0$ $\mu$m or $4.0$ $\mu$m. Nanowires with average widths of 25, 55, 90, and 96 nm were measured. In this chapter, we present primarily results from two representative nanowires: Sample 120117_4_1 ($w \approx 96$ nm, $d \approx 15$ nm, Figure 5.1a) and Sample 130401_15_3B ($w \approx 90$ nm, $d \approx 9$ nm, Figure 5.1c). In Section 5.4, we discuss our results on the more narrow nanowires. All measurements were performed in a four-terminal geometry with the measurement configurations shown in Figure 5.1. Unless explicitly stated otherwise, the magnetic field was orientated perpendicular to the plane of the device (parallel to the $c$-axis of NbSe$_2$).
A crucial limitation to the fabrication technique outlined in Chapter 4 is the resulting edge roughness of the NbSe$_2$ nanostructures. This roughness arises from both the resolution of the EBL resist along with the uniformity of the plasma etch. In Figure 5.1b, we present a histogram of the width of nanowire Sample 120117_4_1 as measured by scanning electron microscopy, with each count representing the average width along an independent 2.2 nm segment. This deviation from the ideal nanowire geometry has implications for both phase slip events and vortex crossing events.

In Figure 5.2, we present a general characterization of Sample 130401_15_3B. We find this sample to be fully superconducting with an onset transition temperature of $T_{c}^{\text{onset}} = 5.6$ K (Figure 5.2a), which is somewhat reduced from the bulk value of 7.1 K, but consistent with previous measurements on thin NbSe$_2$ crystals [99]. The
residual resistivity ratio ($RRR \equiv R(300\,\text{K})/R(8\,\text{K})$) is 4.1 for this loop, which is typical for this thickness of NbSe$_2$, [99,100] indicating the processing did not degrade the quality of the original crystal. We observe a critical field of $\mu_0 H_c^2 = 3.6\,\text{T}$ (Figure 5.2b). Using Eq. 2.26, along with the measured $H_c^2(1.8\,\text{K})$ yields a coherence length of $\xi(1.8\,\text{K}) = 9.6\,\text{nm}$, consistent with the bulk value for NbSe$_2$. Finally, Sample 130401_15_3B exhibits a critical current of $I_c = 5.5\,\mu\text{A}$ (Figure 5.2c).

5.2 Temperature dependence of nanowire resistance

The LAMH theory of thermally activated phase slips of the order parameter was outlined in Section 2.5. The phase slip induced voltage was given by Eq. 2.48. For a measurement current small relative to $I_0 \equiv h/4\epsilon kT$, the hyperbolic sine can be replaced by its argument, yielding an effective “phase slip resistance,”

$$R_{\text{LAMH}} = \frac{V_{\text{LAMH}}}{I} = \frac{\pi h^2 \Omega}{2e^2 kT} e^{-\Delta F_0 / kT}.$$  \hspace{1cm} (5.1)

The height of the phase slip barrier, $\Delta F_0$, is in principle given by Eq. 2.43 in terms of $H_c, A,$ and $\xi$. In practice, it is easier to use standard GL relationships [57]
to express $\Delta F_0$ in terms of experimentally measurable quantities such that [8,110]

$$\Delta F_0 \approx 0.83 \frac{kT_c R_q}{\xi} \left( \frac{L}{R_N} \right),$$

(5.2)

where $R_q = h/(2e)^2 \approx 6.5$ kΩ is the quantum of resistance for paired electrons, and $R_N$ is the normal state resistance of the nanowire. Because we are explicitly considering a case where the resistance of the superconducting channel is non-zero, it is also important to account for the parallel conductance through the normal channel in the nanowire. Thus, we expect the total resistance of our nanowire to follow the form

$$R = \left( \frac{1}{R_{LAMH}} + \frac{1}{R_N} \right)^{-1},$$

(5.3)

where $R_N$ is essentially independent of temperature.

We first investigated the resistive transition of Sample 120117_4_1 as a function of temperature in the absence of an applied magnetic field. In Figure 5.3a, we show the $R(T)$ trace on a semi-log scale. The filled circles are experimental data points. We found that Eq. 5.3 (which essentially depends only on $\xi$ and $T_c$) failed to fit the measured curve when we assumed bulk values for $\xi(0)$ and $T_c$ (failed fit not shown). While it is not evident in the semi-log plot, $T_c$ of this nanowire is very close to the bulk value of $T_c^{\text{bulk}} = 7.1$ K, as can be seen in Figure 5.3b, which shows the same data as Figure 5.3a, but on a linear scale near $T_c$. We likewise expect $\xi(0) \approx \xi(0)^{\text{bulk}}$, based upon the observed $H_{c2}$ in similar devices (see Figure 5.2b).
Thus, we are not free to treat $\xi$ and $T_c$ as variable fitting parameters.

We found that by including an *ad hoc* suppression of the energy barrier in the form of

$$\Delta F = \frac{\Delta F_0}{\alpha},$$

we could obtain an excellent fit to the experimental data over five orders of magnitude with the parameters $T_c = 7.1$ K, $\xi(0) = 9.5$ nm, and $\alpha = 7.1$ (solid line in Figure 5.3a). This suppression of the energy barrier from the theoretical value has several potential origins. In the full LAMH theory, the barrier height is expected to decrease with measurement current as $I^2$ \cite{69,70}, and our measurements were performed at $I/I_0 \approx 10$. Additionally, because $\Delta F_0$ is proportional to the product $A\xi$ (Eq. 2.43), a reduction in the effective cross-sectional area can cause a suppression from the theoretical value \cite{74}. Phase slips would then tend to nucleate at the locations along the wire with the lowest barrier height. Preferential nucleation of phase slips at local weak points was observed recently in ultra-long Nb nanowires \cite{111}. As can be seen in the histogram in Figure 5.1b, the width (and therefore $A$) of the nanowire varies along its length. The possible existence of a normal region near the etched edges and top surface of the nanowire may enhance the relative variation of $A$.

We now turn to a study of the resistive transition of the nanowire in finite magnetic fields. In Figure 5.4, we plot the transition at fields ranging from 1.4 T to 4.4 T in steps of 0.1 T from right to left. For low fields, the general shape of the transition resembles the LAMH theory. At higher fields, however, a resistive tail
with a weaker temperature dependence emerges. The approximate location of this
tail is indicated by the shaded region in Figure 5.4.

It is tempting to ascribe this resistance tail to quantum tunneling of the order
parameter at low temperatures [74,76,112]. While early work on Nb nanowires [113]
failed to find any evidence for quantum tunneling of phase slips in high magnetic
fields, subsequent work on Al nanowires [114] instead suggested that quantum
phase slips do become increasingly dominant in high magnetic fields. We attempted
to fit our curves to a phenomenological equation similar to Eq. 2.50 combining
both thermal activation and quantum tunneling of the order parameter. However,
to obtain satisfactory fits required an unphysical evolution of $\xi(H)$ and $T_c(H)$,
suggesting that some mechanism other than phase slips of the order parameter
begins to dominate the resistive transition of our NbSe$_2$ nanowires at finite fields.

5.3 Magnetoresistance variations

The derivation of Eq. 5.3 assumes a 1D (or quasi-1D) system in which $\psi$
cannot vary appreciably along the width of the wire (meaning, $w \lesssim \xi$). Very near $T_c$, where
$\xi$ diverges, this is a reasonable approximation for our system. However, far below
$T_c$, the approximation is clearly invalid. As discussed in Section 3.1, NbSe$_2$ is a
type-II superconductor, and thus can support Abrikosov vortices in finite magnetic
fields. Consequently, we expect vortices to play a role in the transport properties
of our NbSe$_2$ nanowires at sufficiently high fields.

5.3.1 Vortex trapping in London approximation

In 2D narrow strips, instead of the magnitude of the order parameter fluctuating
to zero at a single point and allowing for a phase slip, an Abrikosov vortex can
nucleate at a sample boundary, cross the strip, and exit the opposite side [30,77,78],
carrying with it a $2\pi$ phase change. The voltage induced by this localized phase
change is given by the Josephson relation, $\partial \varphi / \partial t = 2eV/\hbar$ [57]. As in the 1D case,
the phase change rate, and therefore the induced voltage drop, is determined by a
 corresponding energy barrier.

For a spatially isolated single vortex crossing event, this energy barrier at
zero applied field can be calculated in the London approximation by considering
Figure 5.5. (a) Calculated vortex energy \( V_{in} \) vs. position \( v \) and applied field \( \mu_0 H \) for nanowire Sample 130401_15_3B. Energy scale is in arbitrary units, with red being highest energy and purple being lowest. Plot generated assuming \( \xi = 9.6 \) nm, \( \lambda = 200 \) nm, \( d = 9 \) nm, \( w = 90 \) nm, and \( T = 1.8 \) K. Colored solid lines indicate location of cuts shown in panel (b). Gray plane intersects plot at \( V_{in} = 0 \). (b) Cuts of \( V_{in}(v,H) \) from (a) at applied fields of \( \mu_0 H = 0.16, 0.26, 0.36, \) and \( 0.46 \) T, top to bottom. Vortex trapping field is found to be \( \mu_0 H_{c1} = 0.36 \) T.

The energy, \( V_{in}^0 \), of a test vortex placed at a position \( v \) along the width of a nanowire [15,115–117]:

\[
V_{in}^0(v) = \frac{\phi_0^2}{8\pi \Lambda^2} \ln \left( \frac{2w}{\pi \xi} \sin \left( \frac{\pi v}{w} \right) \right),
\]

(5.5)

where \( \Lambda = 2\lambda^2/d \) is the Pearl penetration depth, which is valid in the limit \( d \ll \lambda \). The unphysical divergence of the logarithm term near the nanowire edges is cut off by the finite size of the vortex core, which is on the order of \( \xi \). Specifically, we observe that \( V_{in}^0(v) = 0 \) when \( v \approx \xi/2 \) or \( v \approx w - \xi/2 \). The generalization of Eq. 5.5 to finite magnetic fields is not straightforward, and is actually most easily accomplished by considering a limiting case of the more general Eq. 6.14 developed later in the context of superconducting loops. We therefore defer the full derivation of \( V_{in}(v,H) \) to Section 6.1. Even that approach does not yield a simple closed-form expression for \( V_{in}(v,H) \), so we content ourselves with numerical calculations.

In Figure 5.5a we plot the numerically calculated \( V_{in} \) as a function of vortex position, \( v \), along the width of the wire and applied magnetic field, \( \mu_0 H \), in the absence of an applied current. The parameters used to generate these curves mimic nanowire Sample 130401_15_3B, namely, \( \xi = 9.6 \) nm, \( \lambda = 200 \) nm, \( d = 9 \) nm, and \( w = 90 \) nm. The semi-transparent gray plane placed at \( V_{in} = 0 \) highlights the field.
regime in which $V_{in}$ acquires a global minimum within the nanowire. In Figure 5.5b, we show cuts of $V_{in}(v, H)$ along the planes of constant $H$ indicated in Figure 5.5a. In the case of zero applied current, the free energy acquires a global minimum within the nanowire at a critical field, $H_{c1}$. This is the field at which a vortex can first be trapped within the nanowire [118]. Vortex trapping is a result of a global free energy minimum arising purely from the interplay between screening currents and the vortex self-currents, and is distinct from the concept of vortex pinning by defect sites, which will be discussed in Section 5.3.4. For our experimental system, we obtain a trapping field of $\mu_0 H_{c1} = 0.36$ T in the absence of an applied current (see Fig 5.5b).

In the limit $\xi/w \ll 1$, an analytic expression for $H_{c1}$ is obtained [15]:

$$H_{c1} \approx \frac{2\phi_0}{\pi w^2} \ln\left(\frac{2w}{\pi \xi}\right).$$

(5.6)

Our nanowire features $\xi/w \approx 0.1$, and so it is not surprising that the value of $\mu_0 H_{c1} = 0.29$ T estimated from Eq. 5.6 somewhat underestimates the more rigorously valid numerical calculation. We present Eq. 5.6 for completeness, however, as the general trend of $H_{c1} \sim w^{-2}$ will become relevant as we discuss thinner nanowires.

The experimental signature of vortex trapping in a nanowire is not clear from this formalism. But in Section 5.4, we present indirect evidence of vortex trapping in the evolution of the critical current with applied field, and in Chapter 6, we present direct evidence for vortex trapping in nanoloops. We introduce the theory of vortex trapping here in preparation for our discussion of vortex crossing in the next section.

### 5.3.2 Free energy barrier for vortex crossing

The London formalism does predict a clear experimental manifestation of vortex crossing of a nanowire. An external transport current will introduce an additional energy term to the curves in Figure 5.5, because a net current exerts a transverse Lorentz force on a vortex (see Eq. 2.38). If we assume any transport current is uniformly distributed within the nanowire, this results in the addition of a linear energy term, giving rise to the free energy shown in Figure 5.6a. In this case, the
transport current flows out of the page, applying a force in the negative $x$-direction on the vortex. The condition $F(x \leq 0) < F(x > 0)$ will cause a net flow of vortices across the width of the nanowire, provided the local energy barriers can be overcome. The rate of vortex flow is dependent upon the height of the two energy barriers shown in Figure 5.6a; $F_e$ is the barrier for a vortex to enter the nanowire, and $F_x$ is the barrier for a vortex to exit the nanowire. Because a vortex must both enter and exit the nanowire to complete a crossing cycle, and the probability of surmounting an energy barrier is exponentially dependent upon the barrier height, the crossing rate is primarily determined by the larger of the two barriers. In Figure 5.6b, we plot $F_e$ and $F_x$ for a nanowire with 1 $\mu$A applied current as a function of external field. The barrier which most influences the crossing rate at a given field is drawn with solid lines. At $\mu_0H = 0.37$ T, the two barriers are equal, resulting in a local maximum in the crossing rate. It is this local maximum that leads to the non-monotonic magnetoresistance variations of the nanowire that are the focus of this section.

The curves shown in Fig. 5.6a represent the free energy of a single vortex within a nanowire. The vortex energy does not depend upon its position along the nanowire length, as the system is considered to be uniform in that direction. But experimental devices always feature inhomogeneities, so there will be some
preferential location for vortex trapping due to local variations in the nanowire width (see Figure 5.1b) and the location of defect sites. Above \( H_{c1} \), vortices will first become trapped at these preferential sites. Subsequent crossing vortices will interact with the trapped vortices as well as the screening and transport currents, and the free energy of the crossing vortices will not be adequately described by the curves in Fig. 5.6a. The addition of pinning sites featuring a suppressed order parameter further perturbs the energy calculation. However, the crossing rate will still be determined by the effective barriers, which will exhibit non-monotonic behavior due to a similar interplay between screening currents and vortex self-currents as before. These variations will be sample-specific, reflecting the sample-specific nature of the inhomogeneities.

5.3.3 Magnetoresistance variations from vortex crossing

We now turn to magnetoresistance measurements of nanowire Sample 130401_15_3B (see Fig. 5.7). At a temperature of 1.8 K, the nanowire exhibits vanishing resistance in an applied magnetic field below 0.30 T. Above 0.30 T, we observe aperiodic magnetoresistance variations superimposed on an increasing background resistance. The locations of the relative extrema are insensitive to temperature (Fig. 5.7a) and measurement current (Fig. 5.7b) within our measurement resolution, and the first resistance maximum occurs at 0.42 T. These variations are not dependent upon field history (Fig. 5.7c). The maximum amplitude of the variations is \( \lesssim 1\% \) of the normal state resistance. While we will focus exclusively on measurements on nanowire Sample 130401_15_3B in this section, we note that similar magnetoresistance variations were observed in all nanowires of sufficient width. As an example, we show the magnetoresistance variations of nanowire Sample 120117_4_1 as an inset to Figure 5.7a. The steps visible at the phase boundary are an artifact of the measurement resolution. Notably, the variations are absent in nanowires with \( w \lesssim 50 \) nm (data not shown), which is consistent with our measurements of \( I_c(H) \) in Section 5.4, which suggest vortex penetration is not possible in wires of that width.

The field-dependent behavior of the vortex crossing energy barrier shown in Figure 5.6 explains the magnetoresistance variations both qualitatively and quantitatively. The observed resistance arises from crossing vortices, and is proportional
Figure 5.7. (a) Color plot of resistance ($R$) vs. magnetic field ($\mu_0 H$) and temperature ($T$) at 500 nA for nanowire Sample 130401_15_3B. Resistance normalized to $R_N = 5.5$ k$\Omega$ and plotted on log scale to emphasize variations. White region indicates where resistance drops below measurement noise level. Inset: $R(H,T)$ for nanowire Sample 120117_4_1 showing similar variations. (b) $R(H)$ at 1.8 K and 0.1, 0.5, 1.0, and 1.5 $\mu$A (bottom to top) for same nanowire as (a). (c) $R(H)$ at 1.8 K and 1 $\mu$A in increasing (red circles) and decreasing (blue triangles) field for same nanowire as (a) showing lack of hysteresis.

to the crossing frequency, which depends upon the height of the two energy barriers. At 1.8 K, the first resistance maximum is reached at 0.42 T, which is in agreement with the local minimum in the crossing barrier calculated to occur at $\mu_0 H = 0.37$ T in Fig. 5.6b. Subsequent resistance maxima at higher applied fields cannot be addressed quantitatively within the framework developed in Section 5.3.2, which applies only to a spatially isolated crossing event. At higher fields, the vortex density will increase, and crossing events will no longer be spatially isolated, leading to a modification of the crossing barrier. In fact, at 0.37 T, simple geometric considerations suggest a chain of crossing vortices is located approximately every $6.5\xi$ along the length of the nanowire. It is reasonable to expect that the proximity of crossing events will modify the crossing barriers seen in Figure 5.6. To further complicate the picture, it is plausible that vortex trapping and vortex
crossing events can coexist under appropriate conditions. At higher fields (data not shown), the curves in Figure 5.6a will again develop a global minimum within the nanowire. At this point, vortices can be trapped, and the barrier for additional crossing vortices will be modified by the interaction with the trapped vortices. The assumption of spatially isolated vortex crossing events is reasonable at low fields, where overlapping vortices are energetically unfavorable. However, it has been demonstrated in geometrically confined systems that giant multi-quanta vortices can form in certain field ranges [20,23]. Thus, it is conceivable that a vortex may cross the nanowire along a path which passes near, or even intersects, a trapped or pinned vortex.

While the London formalism is not suited to addressing the case of non-isolated crossing events, Berdiyorov et al. have investigated the magnetoresistance of superconducting nanowires utilizing a time-dependent Ginzburg-Landau (TDGL) phenomenology [78]. The Ginzburg-Landau approach allows for treatment of systems where spatial variations in the order parameter are significant, such as is the case with a high density of vortices. While the TDGL equations are only rigorously justified in the case of a gapless superconductor [57], the results obtained are often in qualitative agreement with experimental observations.

Berdiyorov observed that at low fields, vortices were excluded from a superconducting nanowire, whereas at high fields, vortices were immobilized within the nanowire. At both extremes, the lack of net vortex flow results in a vanishing voltage signal. At intermediate fields, TDGL simulations revealed a series of chains of vortices periodically crossing the nanowire. This crossing cycle repeats with a frequency \( f^{-1} \sim 100\tau_{GL} \), where \( \tau_{GL} \) is the GL relaxation time, \( \tau_{GL} = 4\pi\lambda^2\sigma_n/c^2 \) (\( \sigma_n \) is the normal state conductivity). The system experienced two local maxima in the free energy vs. time trace in the entry-crossing-exit process. These maxima were defined as effective entry and exit barriers. The frequency of vortex crossing was correlated with the relative heights of the two local maxima, and observed to vary non-monotonically with field in intermediate field ranges. At fields well above the first magnetoresistance maximum, TDGL simulations revealed additional magnetoresistance peaks. These subsequent peaks apparently resulted from additional chains of crossing vortices, and were typically superimposed upon a resistive background, indicating that at sufficiently high fields and current densities, vortices are always in motion, and not immobilized within the nanowire. Our observations
in Fig. 5.7 are consistent with this prediction. The results of the TDGL simulations are complementary to the theoretical considerations in Section 5.3.2. The London formalism describes two energy barriers in the space domain resulting from the interplay between applied, screening, and vortex self-currents, whereas the TDGL simulations observe two free energy maxima in the time domain resulting from a particular spatial distribution of the order parameter.

### 5.3.4 Effects of vortex pinning

In addition to geometric constraints, which provide a means of vortex trapping, experimental 2D systems also feature finite levels of disorder, which result in vortices being preferentially pinned at locations where the order parameter is artificially reduced [61]. The strength of this pinning force is expected to decrease with decreasing crystal thickness for relatively thick NbSe$_2$ samples [119], though there have been no direct measurements of the pinning force in 2D crystal superconductors. Weak pinning centers need not necessarily immobilize a vortex, but they will locally lower the free energy of the vortex, which can result in either an effective increase or decrease in the crossing barrier depending on the location of the pinning center within the nanowire.

It is clear that the idealized free energy shown in Figures 5.5 and 5.6 will be modified by the presence of defect regions in experimental devices. We investigated this situation experimentally by comparing the magnetoresistance of two independent and nominally identical nanowires. In Figure 5.8, we plot the magnetoresistance variations for the left and right segment of the nanowire shown in Fig. 5.1c. Both curves have been normalized to the normal state resistance of the respective segment, which differed by < 3%. Each segment exhibits magnetoresistance variations, and, significantly, the field at which the first resistance maximum appears is independent of nanowire segment and field sign. The constant value of this first maximum for the two segments is anticipated, as the effective width is essentially uniform along the nanowire, and in the London formalism, it is the nanowire width alone that determines the first crossing rate maximum. However, the amplitude and position of relative extrema appear uncorrelated between the segments. We note that a similar irreproducibility was observed in the magnetoresistance signatures of Pb nanowires [120], but their sample fabrication method did not allow measurements
Figure 5.8. Normalized resistance ($R/R_N$) vs. magnetic field ($\mu_0H$) for the two independent sections of nanowire Sample 130401_15_3B. Left segment (red circles) is measured from $V_1$ to $V_2$, and right segment (blue triangles) is measured from $V_2$ to $V_3$ (see Figure 5.1c).

of independent nanowire segments as used in the present study.

Specifically, two single-crystal NbSe$_2$ nanowires made as identically as possible showed differing magnetoresistance patterns, which can only be ascribed to the influence of differing configurations of pinning sites on the free energy in Figures 5.5 and 5.6. This sample-specific response to magnetic field is also anticipated in the TDGL simulations. By including regions with a suppressed superconducting order parameter, Berdiyorov et al. were able to shift the location and amplitude of the original magnetoresistance peak, as well as introduce additional peaks at higher fields [78]. The disordered region pinning sites were observed to form “easy-flow” channels where vortices preferentially crossed the nanowire. In the complementary language of the London formalism in Section 5.3.2, the pinning sites modify the entry and exit barriers at certain locations along the nanowire length. The location of pinning sites varies between samples, which causes different configurations of “easy-flow” channels, and therefore sample-specific magnetoresistance variation signatures. This sample-specific pattern of the magnetoresistance variations, which should be seen only in sufficiently long nanowires where multiple independent vortex crossing locations can exist, can be called a “magneto fingerprint” of the sample-specific configuration of vortex pinning centers in a 2D crystal superconducting nanowire.

The ultra-thin nature of our device appears to make it sensitive to surface defects and adsorbates, consistent with the recent finding that surface contamination can suppress superconductivity in atomically-thin NbSe$_2$ [97,102]. We measured the full
nanowire in two different ambient conditions – a low vacuum helium environment \((P \sim 3\ \text{Torr})\) and a high vacuum \((P \lesssim 10^{-5}\ \text{Torr})\) environment. As shown in Figure 5.9, the magnetoresistance variations differ in the two situations. This suggests that surface adsorbates also affect the magnetoresistance variation. This is consistent with the observed lack of hysteresis in the magnetoresistance variations seen in Figure 5.7c, because we would expect surface defects to generate only a weak pinning potential in our sample, which is several unit cells thick. It would be useful to correlate these measurements with a high-resolution magnetic imaging technique to determine precise vortex positions. Finally, we note that, while the magnetoresistance variations depend on the pinning potential, the initial appearance of finite resistance is dictated by \(H_{c1}\), rather than by vortex depinning (Eq. 2.41). This can be clearly seen in Fig. 5.7b, which shows the field at which finite resistance appears is essentially unaffected by the measurement current.

### 5.3.5 Comparison with previous work

Magnetoresistance variations attributed to the motion of Abrikosov vortices were considered in superconducting nanowires previously [26,27,120–126]. It is therefore useful to compare the sample-specific magneto fingerprint picture based on vortex crossing to these previously considered pictures. We first note that the magnetoresistance variations observed in our system are distinct from the critical current oscillations observed in nanowires of disordered aluminum [26] and \(a: \text{InO}\) [125], which are due to the formation of a “Webber blockade” [16,127], wherein static
vortices are added to a nanowire one at a time in analogy to the Coulomb blockade in quantum dots [128]. In the Webber blockade picture, periodic magnetoresistance oscillations arise from the magnetic charging energy required to add an additional flux quantum to the nanowire, and therefore exhibit a period on the order of $\frac{\phi_0}{A_0}$, where $A_0$ is the area of the nanowire perpendicular to the applied field. For our system, that corresponds to a period of $\sim 60$ Oe, which is more than an order of magnitude smaller than any reasonable definition of period from Figure 5.7. Additionally, the variations remain quite pronounced even at temperatures above $0.5T_c$ (Figure 5.7a), well beyond the point at which thermal fluctuations should mask any Webber blockade quantum oscillations [16,125]. This insensitivity to temperature and dramatically inconsistent “period” rule out the Webber blockade interpretation in this system.

A second potential origin of magnetoresistance variations within a nanowire is the geometric rearrangement of a confined vortex lattice at discrete matching fields [121,123]. Such a rearrangement has been directly observed by scanning tunneling measurements in linear channels hundreds of nanometers wide in NbSe$_2$ [129]. The rearrangement was also shown to produce magnetoresistance peaks at matching fields of [123]

$$\mu_0 H_N = \frac{\sqrt{3}\phi_0}{2} \left(\frac{N}{w}\right)^2. \quad (5.7)$$

For our system, Eq. 5.7 predicts the first three resistance peaks to occur at $\mu_0 H = 0.22$, 0.88, and 1.98 T, which clearly contradicts our experimental observations.

Other mechanisms, such as fabrication-induced normal regions creating effective doubly-connected geometries (which would then feature Little-Parks-like oscillations), have been suggested [120], but such an interpretation seems extraordinarily unlikely in the present case, given the single-crystal nature of our devices and the extreme sensitivity to surface adsorbates (which are unlikely to drive the entire thickness of the crystal normal).

### 5.4 Critical current kink from vortex trapping

In Section 5.3, we argued that the observed magnetoresistance variations in our NbSe$_2$ nanowires arose from the non-monotonic dependence of the vortex crossing barrier on the applied magnetic field. The London formalism successfully predicted
the field of the first magnetoresistance maximum, and the crossing barrier was clearly shown to be further modified locally by the presence of weak pinning centers. While the evidence for vortex crossing dominating the magnetoresistance is compelling, the London formalism also predicts vortex trapping above $\mu_0 H_{c1}$. Vortex trapping in nanostructures is particularly interesting, as it represents the first step towards controlled manipulation of vortices in confined systems, which is the primary goal of this dissertation.

Static, trapped vortices produce no voltage drop (Eq. 2.39), making their detection with magnetoresistance measurements somewhat complicated. However, the presence of a trapped vortex does modify the free energy of the system, which was previously shown to affect the critical current in the context of the Webber blockade [16, 26, 127]. Thus, a possible experimental signature to characterize in our search for evidence of vortex trapping in NbSe$_2$ nanowires is the critical current. While not all nanowires we measured exhibited complete zero resistivity, we can define an effective $I_c$ as the current at which the differential resistance of the nanowires is maximal. Below $I_c$, the nanowires display either vanishing resistance or a weak persistent resistance tail. The evolution of $I_c$ as a function of applied field is shown in Figure 5.10a for five nanowires with differing average widths. The solid lines are for the magnetic field oriented parallel to the $c$-axis, and the dashed lines are for the magnetic field oriented perpendicular to the $c$-axis.

Figure 5.10. (a) Critical current ($I_c$) vs. applied magnetic field ($\mu_0 H$) for NbSe$_2$ nanowires. $I_c$ is normalized to the value at $H = 0$. Solid lines are for field applied parallel to NbSe$_2$ $c$-axis. Dashed lines are for field applied perpendicular to NbSe$_2$ $c$-axis and current flow. Nanowire widths (thicknesses) are indicated for parallel (perpendicular) field measurements. Arrow indicates kink associated with vortex trapping in wide samples. (b) Calculated vortex trapping field ($\mu_0 H_{c1}$) vs. nanowire width ($w$) from Eq. 5.6.
For nanowires with $w \gtrsim 50$ nm, a kink is evident in the $I_c(H)$ trace (indicated with arrow in Figure 5.10a). This kink may be related to vortex entry, especially considering the lack of a corresponding kink for the narrower samples. In fact, it was shown in the London approximation that above a critical field, $H^*$, which is proportional to $H_{c1}$, the critical current of a nanowire changes from a linear to inverse linear dependence on applied field [115,130,131], leading to an apparent kink. A similar response was obtained in Ginzburg-Landau simulations of superconducting nanowires [132]. Note that by orienting the field along the $ab$ plane but perpendicular to the direction of current flow, the effective “width” of the nanowire is actually the crystal thickness, $d$, which is quite small compared to the coherence length. In this orientation, the kink in $I_c(H)$ is also absent, though the increase in $H_{c2}$ in this orientation prevents us from characterizing the entire phase diagram. In Figure 5.10b, we plot the calculated value of $\mu_0H_{c1}$ from Eq. 5.6 as a function of wire width, assuming bulk NbSe$_2$ superconducting parameters. The trapping field is seen to increase rapidly as the nanowire width is reduced, making vortex entry into thin nanowires unlikely.
Chapter 6

Manipulating vortex motion in 2D crystal nanoloops

The magnetoresistance measurements on NbSe$_2$ nanowires suggest that vortices may be manipulated and detected in nanostructures. A scanning superconducting quantum interference device (SQUID) and magnetic force microscope were employed previously in planar films of YBa$_2$Cu$_2$O$_{6.354}$ [133] and Nb [134] to manipulate and study vortices. So far little work has been done on the manipulation of vortex motion in extremely geometrically confined nanoscale superconductors.

In this chapter, we use electrical transport techniques to detect vortex trapping in and crossing of a superconducting nanoloop. The free energy barrier for vortex crossing is a function of superfluid velocity, which is a periodic function of the global winding number of the superconducting phase as well as the applied flux. This leads to a periodically varying rate for vortex crossing [28,30] and, consequently, a periodically varying magnetoresistance. Significantly, as we show in Section 6.1, a vortex can also be trapped in the nanoloop arms under suitable conditions. The trapping of such a vortex, which demands the local phase winding around the vortex core be superimposed on the global phase winding, is predicted to have observable effects on the magnetoresistance signature, as shown below. Furthermore, we demonstrate our ability to manipulate the critical field for vortex trapping along with the locations of the trapped and crossing vortices, thereby enabling future experiments directed toward quantifying fundamental properties of vortices in 2D crystal superconductors.
6.1 London calculation of free energy

To obtain the conditions under which Abrikosov vortices can be trapped in a superconducting nanoloop, we follow the analysis of Kogan, Clem, and Mints [15] using the London equations in the limit $d \ll \lambda$, where $d$ is the loop thickness and $\lambda$ is the magnetic penetration depth. Our experimental NbSe$_2$ devices typically feature $d < 10$ nm, placing us well in the regime of applicability of the London approximation.

The sheet current density, $\vec{g}$, in a superconducting loop containing a single vortex (+) or anti-vortex (-) at position $\vec{v}$ can be calculated by solving the equations

\[
\frac{2\pi \Lambda}{c} \nabla \times \vec{g} = \pm \phi_0 \delta(\vec{r} - \vec{v}) - \vec{H}, \tag{6.1}
\]

\[
\nabla \cdot \vec{g} = 0, \tag{6.2}
\]

where $\Lambda(T) = 2\lambda(T)^2/d$ is the Pearl length and $\vec{H}$ is the applied field. No distinction needs to be made between the applied and local field, because if the radius of the loop, $r$, satisfies $r \ll \Lambda$, as is the case with the devices considered in this chapter, the self-fields of the currents within the loop are negligibly small. By introducing a scalar stream function,

\[
\vec{g} = \nabla \times Gz, \tag{6.3}
\]

Eq. 6.2 is automatically satisfied, and Eq. 6.1 can be expressed as

\[
\frac{2\pi \Lambda}{c} \nabla^2 G = \mp \phi_0 \delta(\vec{r} - \vec{v}) + H. \tag{6.4}
\]

The linearity of Eq. 6.4 allows for solutions of the form

\[
G = G_v + G_H, \tag{6.5}
\]

where

\[
\nabla^2 G_v = \mp \frac{c\phi_0}{2\pi \Lambda} \delta(\vec{r} - \vec{v}) \tag{6.6}
\]

and

\[
\nabla^2 G_H = \frac{c}{2\pi \Lambda} H. \tag{6.7}
\]

The latter equation is readily solved, and the former can be solved using
techniques from electrostatics. Eq. 6.6 is analogous to that of an electric charge trapped between two grounded, concentric cylinders, for which the exact solution is given by Jacobi elliptic functions. For loops of the size considered in Ref. [15] as well as this dissertation, the exact solution can be approximated by [58]

\[ G(r, \theta) \approx \frac{cH}{8\pi \Lambda} r^2 + G_0 \ln \frac{r}{a} \]

\[ \pm \frac{c\phi_0}{4\pi^2 \Lambda} \text{Re} \left\{ \ln \frac{\sin[\pi \ln(vre^{i\theta}/a^2)/2 \ln(b/a)]}{\sin[\pi \ln(v/re^{i\theta})/2 \ln(b/a)]} \right\}, \]  

(6.8)

where

\[ G_0 = -\frac{c\phi_0}{4\pi^2 \Lambda} \left[ N \pm \frac{\ln b/v}{\ln b/a} \right], \]  

(6.9)

and \(a\) and \(b\) are the inner and outer radii, respectively. Here we have adopted polar coordinates with the origin located at the center of the loop. The presence of a vortex leads to an ambiguity in defining the winding number, \(N\), so we follow the convention of Ref. [15] that with a vortex present, contours enclosing the annulus hole and the point \(\vec{v}\) acquire a phase of \(2\pi(N+1)\), whereas contours enclosing just the annulus hole acquire a phase of \(2\pi N\). As an example, in Figure 6.1a, we schematically represent the superconducting phase in a loop with \(N = 1\) and a single vortex positioned at \((r, \theta) = ((b + a)/2, 0)\).

Using Eqs. 6.3 and 6.8, we can generate the current distribution within a superconducting nanoloop for an arbitrary geometry, vortex position, and external magnetic field. We show in Figure 6.1b the ground state current distribution for a nanoloop without a vortex. The geometric and material parameters used in the calculation are as follows: \(a = 73\) nm, \(b = 158\) nm, \(d = 6\) nm, \(\mu_0H=0.39\) T, \(T = 1.8\) K, \(\xi(0) = 10\) nm, and \(\lambda(0) = 200\) nm. The physical dimensions are chosen to imitate our ultimate experimental devices, and the material parameters correspond to literature values for bulk NbSe\(_2\) (Table 3.1). For this field, the ground state corresponds to \(N = 7\). The current streamlines (indicated by white arrows) are seen to form counterpropagating concentric circles, which necessarily cancel completely at some radius in the interior of the loop.

The distribution becomes more complex with the addition of a stationary Abrikosov vortex. In Figure 6.1c, we consider the same loop as in Figure 6.1b, but with a single vortex fixed at the point \((r, \theta) = ((b + a)/2, 0)\). Near the vortex, the current density diverges. Therefore, a cutoff is introduced at \(|\vec{r} - \vec{v}| \leq 1.2\xi\) to
Figure 6.1. (a) Schematic of $\psi$ for a loop with $n = 1$ and a single trapped Abrikosov vortex (black dot). Adapted from Ref [135]. (b) Color plot of current density in a 6 nm thick loop with inner radius $a = 73$ nm and outer radius $b = 158$ nm. Applied field is 0.39 T, which corresponds to a ground state of $n = 7$. Plot generated assuming $\xi(0) = 10$ nm and $\lambda(0) = 200$ nm. Loop boundaries are shown in black, and current streamlines are shown in white. (c) Same as (b), but with a vortex fixed at $(r, \theta) = (115, 0)$ nm (black disk).

facilitate the plotting. The current streamlines are clearly influenced by the vortex self-currents, and the free energy of the loop will be correspondingly affected.

Once the exact current distribution is known, the free energy ($F$) of the loop can be calculated as the sum of the kinetic and magnetic energies. This energy calculation is the main result of Ref. [15]. Kogan et al. obtain

$$F(N, v, H) = \epsilon_v(v) +$$

$$\epsilon_0 \left[ \left( N + \frac{\ln(b/v)}{\ln(b/a)} \right)^2 - 2 \left( \frac{H}{H_0} \right) \left( N + \frac{b^2 - v^2}{b^2 - a^2} \right) + \chi \left( \frac{H}{H_0} \right)^2 \right] \quad (6.10)$$

where

$$\epsilon_v(v) = \frac{\phi_0^2}{8\pi^2 \Lambda(T)} \ln \left[ \frac{2v \ln(b/a)}{\pi \xi(T)} \sin \frac{\pi \ln(v/a)}{\ln(b/a)} \right] \quad (6.11)$$

is the self-energy of the vortex, $\epsilon_0 = \phi_0^2 \ln(b/a)/8\pi^2 \Lambda(T)$ is a characteristic energy scale, $\chi = \frac{b^2/a^2+1}{\frac{b^2/a^2+1}{b^2/a^2+1}} \ln(b/a)$ is a geometric factor, and

$$H_0 = \frac{2\phi_0 \ln(b/a)}{\pi(b^2 - a^2)}. \quad (6.12)$$
The energy of the vortex-free state is then
\[
\mathcal{F}_0(N, H) = \epsilon_0 \left( N^2 - 2N \left( \frac{H}{H_0} \right) + \chi \left( \frac{H}{H_0} \right)^2 \right). \tag{6.13}
\]

Finally, the free energy difference between the vortex-trapped and vortex-free states is given by
\[
V_{in}(N, v, H) = \mathcal{F}(N, v, H) - \mathcal{F}_0(N, H). \tag{6.14}
\]

\(V_{in}\) determines the stability of a vortex at a given position within the arms of the loop. In Figure 6.2a we plot \(V_{in}\) for the loop in Figure 6.1c at different values of applied magnetic field. \(H_{c1}\) is defined as the field at which a global minimum of \(V_{in}\) is first found in the sample [118]. We see \(\mu_0 H_{c1} \approx 0.38\) T, as indicated by the purple curve. If we consider a thinner loop with \(a = 70\) nm and \(b = 108\) nm, we find \(\mu_0 H_{c1} \approx 1.54\) T (Fig. 6.2b). We will return to experimental devices which mimic both of these dimensions. We note that Eq. 6.14 was applied to the case of a nanowire in Chapter 5 by taking the limit \(a, b \to \infty\) while holding \(b - a = w\) constant.

At this point, we will discuss the limitations of the London approach. The finite size of the vortex core (on the order of \(\xi(T)\)) is not considered in Eq. 6.1. Thus, in a physical system, the formalism breaks down within \(\sim \xi(T)\) of the edges of the
Figure 6.3. False color scanning electron micrographs of (a) thin wall square NbSe$_2$ loop ($d \approx 9$ nm, $w \approx 35$ nm, $s \approx 155$ nm), (b) thick wall square NbSe$_2$ loop ($d \approx 9$ nm, $w \approx 80$ nm, $s \approx 200$ nm), (c) thick wall square NbSe$_2$ loop with constrictions ($d \approx 6$ nm, $w \approx 80$ nm, $s \approx 200$ nm). Color scheme follows Figure 4.9. Measurement geometry is indicated.

sample. To avoid an unphysical divergence, the authors of Ref. [15] set $\epsilon_0 = 0$ within $\xi(T)/2$ of the sample boundaries. Unfortunately, this essentially arbitrary choice has a direct impact on the numerically calculated $H_{c1}$ when $b - a \sim \mathcal{O}(\xi(T))$. For instance, if we instead choose to set a cutoff of $\xi(T)$, we calculate $\mu_0 H_{c1} \approx 0.32$ T for the same geometry as considered in Fig. 6.2a. For the sake of consistency, we maintain the cutoff employed in Ref. [15], but the level of quantitative agreement between theory and experiment must be understood in light of these limitations. We stress, however, that the qualitative results reported in Sections 6.4 and 6.5 are unaffected by the choice of cutoff.

6.2 Experimental devices

Our experimental 2D crystal NbSe$_2$ devices were again fabricated with the “leads-first” technique outlined in Chapter 4. We performed measurements primarily on three geometries: a square “thin loop” with arm width $w \approx 35$ nm and median diameter $s \approx 155$ nm (Figure 6.3a), a square “thick loop” with $w \approx 80$ nm and $s \approx 200$ nm (Figure 6.3b), and a square “thick loop with constrictions” with $w \approx 80$ nm, $s \approx 200$ nm, and two artificial constrictions with width $w_0 \approx 30$ nm (Figure 6.3c). Multiple devices with each nominal geometry were measured, and the resulting magnetoresistance signatures were in good qualitative agreement within a given geometry. Thus, in this chapter, we present data only from the three
Figure 6.4. (a) Zero field resistance ($R$) vs. temperature ($T$) for sample 140203_16 (Figure 6.3c) showing superconducting transition at $T_c = 4.2$ K. Inset: $R(T)$ over full temperature range. Units on axes are same as in main panel. (b) $R$ vs. magnetic field ($\mu_0 H$) at 1.8 K for same sample showing $\mu_0 H_{c2} = 2.8$ T. (c) Voltage ($V$) vs. current ($I$) trace at 1.8 K and zero field for same sample showing $I_c = 850$ nA.

representative devices pictured in Figure 6.3. All measurements were performed in a four-terminal geometry with the measurement configuration shown in Figure 6.3. The magnetic field was consistently orientated perpendicular to the plane of the device, with positive field pointing out of the page, as indicated in Figure 6.3b.

In Figure 6.4, we present a general characterization of Sample 140203_16. We find this sample to be fully superconducting with transition temperature of $T_c = 4.2$ K (Figure 6.4a), which is again somewhat reduced from the bulk value of 7.1 K, but consistent with our observations in the thinnest nanowires discussed in Chapter 5. The residual resistivity ratio ($RRR \equiv R(300\text{ K})/R(8\text{ K})$) is 3.9 for this loop, which is typical for this thickness of NbSe$_2$ [99,100], indicating the processing did not degrade the quality of the original flake. We observe a critical field of $\mu_0 H_{c2} = 2.8$ T (Figure 6.4b), which is also somewhat reduced from the bulk value of 3.6 T. We will discuss the fine features visible in Figure 6.4b in a later section. Finally, Sample 140203_16 exhibits a critical current of $I_c = 850$ nA (Figure 6.4c). Assuming a uniform current distribution in the nanoloop, and neglecting the influence of the nodes and corners, this corresponds to $J_c = 8.9 \times 10^4$ A/cm$^2$, several orders of magnitude below the theoretical upper limit set by the pair-breaking velocity in Eq. 2.28. The onset of a finite voltage at this current instead proceeds from the induced motion of vortices. We note that the resistive transition as a function of applied current is quite broad, and full normal state resistance is not reached until 1.3 $\mu$A.
There are several differences between the geometry considered theoretically in Section 6.1 and our experimental devices. An unavoidable complication with transport devices is the presence of measurement leads. While the addition of leads does not affect the topology of the system or the expected oscillation period, it has been shown to modify the overall energy of the superconducting condensate [11]. This will likely contribute to quantitative discrepancies with the presented theory, but the qualitative features should be preserved.

A second difference between our devices and the theoretical system is that our devices are fabricated in a square loop, rather than circular loop geometry, as it is difficult to fabricate smooth curves at this lower limit of nanofabrication capabilities. Again, we expect this modification to affect only quantitative predictions of the theory. In principle, the energy calculations and electrostatic analogy can be repeated for a square loop geometry, but this is likely ultimately unprofitable, because we are still left with the influence of the measurement leads. Nonetheless, we would like to attempt some manner of quantitative comparison between experiment and theory. To apply the results above to our square loops, we employ the following procedure. We first apply the transformations:

\[ w = b - a, \]  
\[ s^2 = \pi \left( \frac{b + a}{2} \right)^2. \]

This preserves the two key geometric properties of the circular loop, namely, the arm width and the area enclosed by the median diameter. Then, we hold \( a \) fixed and vary \( b \) until the predicted magnetoresistance oscillation period \( (H_0, \text{Eq. 6.12}) \) matches the experimentally observed oscillation period, \( \Delta H \). In all cases, Eq. 6.12 was found to overestimate the oscillation period by \( \lesssim 4\% \) after the direct transformations in Eq. 6.15 and 6.16, so only minor adjustments were necessary. This specific procedure is somewhat arbitrary, but we applied it systematically across device geometries to maintain some amount of consistency between our theoretical calculations and experimental observations.
Figure 6.5. (a) Resistance ($R$) vs. field ($\mu_0 H$) for sample 140203_16. (b) Measured magnetoresistance oscillation amplitude (red dots) vs. temperature ($T$) for sample in (a). Solid line is fit to London theory of vortex crossing (Eq. 6.22). Fit parameters are indicated. Dashed line is Little-Parks prediction using measured $dR/dT$.

6.3 Magnetoresistance oscillation amplitude

In the Little-Parks scenario, the $T_c$ modulation of a doubly-connected loop in a magnetic field leads to a resistance oscillation with an amplitude of [57]

$$\Delta R \approx 0.14T_c \left( \frac{\pi \xi(0)^2}{A_0} \right) \frac{dR}{dT},$$

(6.17)

where $A_0$ is the effective area enclosed by the structure. For a square loop with finite arm width, $A_0 = s^2$.

In Figure 6.5a, we plot the MRO for Sample 140203_16 at low applied fields. Clear oscillations with a well-defined period and amplitude are visible, as we expect. Using Eq. 6.17 and the measured $dR/dT$ from Figure 6.4a, we can describe the temperature dependence of the MRO amplitude. We plot this prediction with the dashed line in Figure 6.5b. By contrast, the experimentally measured amplitude is indicated with the solid red circles in the same figure. Eq. 6.17 is seen to be inconsistent with the data. A similar result has been observed previously in other doubly-connected type-II superconducting systems [28–31,136], and explained in terms of a vortex crossing mechanism [28,30].

To understand how vortex crossing events produce the observed MRO, we return
to Eq. 6.14. In the limit of a thin ring \((w \ll a)\), Eq. 6.14 simplifies to [15]

\[
V_{in} \approx E_v + E_0 z \left( 2N - 2 \frac{H}{H_0} + z \right), \tag{6.18}
\]

where

\[
E_v = \frac{\phi_0^2}{8\pi^2 \Lambda} \ln \left( \frac{2w}{\pi \xi(T) \sin(\pi z)} \right) \tag{6.19}
\]

is the now position independent vortex self-energy, \(E_0 = \frac{\phi_0^2}{8\pi^2 \Lambda} \left( \frac{w}{a} \right)\), and \(z \equiv \frac{b-w}{b-a}\).

Eq. 6.18 has a maximum value at \(z = 1/2\), and this maximum acts as an effective barrier for vortex crossing of the ring. Standard thermodynamic averaging of the four distinct crossing situations (corresponding to a positive or negative vortex entering or exiting the loop) leads to an overall effective crossing barrier of [28]

\[
\Delta E_{\text{eff}} \approx (E_v + E_0/4) - E_0^2 \frac{(N - H/H_0)^2}{k_B T}. \tag{6.20}
\]

This results in a resistance that varies according to [137]

\[
\frac{R}{R_n} = \left[ I_0 \left( \frac{\Delta E_{\text{eff}}}{2k_B T} \right) \right]^{-2}, \tag{6.21}
\]

where \(I_n\) is the \(n^{th}\)-order modified Bessel function of the first kind. Finally, the amplitude of the MRO is given by [28]

\[
\Delta R = R_n \left( \frac{E_0}{2k_B T} \right)^2 \frac{I_1(\alpha)}{(I_0(\alpha))^3}, \tag{6.22}
\]

where \(\alpha \equiv (E_v + E_0/4)/(2k_B T)\).

The solid line in Figure 6.5b is a fit of our experimental data to Eq. 6.22. The only free parameters are \(\xi(0), \lambda(0),\) and \(T_c\), with the temperature dependence of \(\xi\) and \(\lambda\) given in Eqs. 2.22 and 2.23, respectively. The obtained fit values are \(\xi(0) = 3.9\) nm, \(\lambda(0) = 2.1\) \(\mu\)m, and \(T_c = 4.3\) K. The fit value for \(T_c\) reproduces our measured \(T_c\) quite well, and the reduction in \(\xi(0)\) from the bulk value can be understood in terms of a reduced mean free path. The significant increase of \(\lambda(0)\) from the bulk value has been observed in similar systems [28, 138], and may be attributable to a suppression of \(\psi\).

We note that Eq. 6.22 is derived with the assumption \(w \ll a\), which essentially
ensures that the vortex energy plots shown in Figure 6.2 never acquire a local minimum. We expect this to be a valid assumption for the “thick loop with constrictions” geometry of Sample 140203_16 shown in Figure 6.3c. The vortex crossing events should be confined to the constricted regions, which are substantially thinner than the effective loop radius, and the energy barrier at the constrictions should not acquire a local minimum within the arms of the loop.

6.4 Phase shift at $H_{c1}$ from vortex trapping

As discussed in Section 6.1, above $H_{c1}$, which is defined to be the field at which a global minimum in Eq. 6.14 is found within the arms of the loop, a vortex can be trapped within the arms of a superconducting nanoloop. At the applied field at which this occurs, the MRO are expected to acquire a rigid phase shift. In this section, we derive this result, and present the first experimental verification of this prediction.

6.4.1 London calculation of phase shift

The free energy ($F$) of the superconducting loop as a function of global winding number ($N$), vortex position ($v$), and magnetic field ($H$) was calculated in Section 6.1. In Figure 6.6a, we plot the free energy of the nanoloop in Figure 6.1c both with a trapped vortex (purple curves, Eq. 6.10), and without a vortex (black curves, Eq. 6.13). As the magnetic field increases, the free energy of the loop is represented as consecutive parabolas with different $N$. For the vortex-free loop, the transition from state $N - 1$ to state $N$ requires the system overcome a free energy barrier with a local maximum at $H/H_0 = N - 1/2$. However, when a vortex is trapped in the loop, a different set of parabolas are generated. The backgrounds of the two sets of parabolas have different slopes, and at the lower critical field, $H_{c1}$, the state with a vortex becomes energetically more favorable than that without one, as shown in Figure 6.6b. At this field, $V_{in}$ first acquires a global minimum within the arm of the loop. The background of the free energy originates from the kinetic energy of the induced currents required by the global phase winding [139]. The crossing of the two curves suggests that the disruption of this current distribution resulting from the introduction of a vortex into the loop leads to the lowering of
Figure 6.6. (a) Ground state free energy (F) in units of \( \epsilon_0 \) versus normalized applied magnetic field \( (H/\Delta H) \) for loop in Figure 6.1b. Black curves are for vortex-free state, and purple curves are with a single vortex trapped at a radius \( v = 115 \) nm. Vortex trapping field is indicated. (b) Zoom in on blue boxed region in (a). Multiple intersections of the free energy curves are visible near \( H_{c1} \). (c) Zoom in on red boxed region in (a). The phase shift (\( \delta_v \)) between vortex-trapped and vortex-free states is indicated.

The vortex-trapped parabolas are phase shifted from the vortex-free parabolas by an amount \( \delta_v \), as shown in Figure 6.6c. To calculate the magnitude of the phase shift, we look for solutions to \( F(N - 1, v, H_N) = F(N, v, H_N) \) and see that

\[
H_N/H_0 = \left( N - \frac{1}{2} \right) + \frac{\ln(b/v)}{\ln(b/a)}.
\]

The acquired phase shift is \( \delta_v = \ln(b/v)/\ln(b/a) \). It is interesting to note that an apparent free energy oscillation phase shift accompanied by a period change may occur in nanoloops as a result of a field-dependent crossover between effective singly- and doubly-connected geometries [13]. However, in the mechanism considered in the present work, the phase shift is not accompanied by a change in oscillation.
Figure 6.7. Ginzburg Landau calculation of free energy \( F \) vs. applied magnetic field \( \mu_0 H \) for square loop in Figure 6.3b. Black curves are for vortex-free state, and purple curves are with a single trapped vortex. The phase shift \( \delta_v = 0.026 \text{ T} \) arising from vortex trapping is indicated. Figured adapted from Ref [138].

period, and therefore corresponds to a different scenario. Vortex trapping discussed here is also distinct from pinning. In vortex pinning, a vortex preferentially occupies a spot where superconductivity is locally suppressed by a material defect. In the scenario presented here, the trapping potential originates from the image force even in the absence of local defects.

6.4.2 Ginzburg-Landau calculation of phase shift

In Chapter 5, we showed that the London and GL theories provided complementary interpretations of the observed magnetoresistance variations in superconducting nanowires. The two theories likewise predict equivalent phenomena in the case of superconducting nanoloops. We are indebted to Dr. Kevin Roberts, who assisted us by numerically solving the Maxwell-Ginzburg-Landau differential equations for a NbSe\(_2\) loop in the geometry of Figure 6.3b for the vortex-free and vortex-trapped cases [138]. The results are shown in Figure 6.7. As with the analytic London calculation, the GL calculation predicts a phase shift in the free energy oscillations with the trapping of an Abrikosov vortex. In the magnetic field range Roberts considered, the vortex-trapped state was not the ground state. However, it is likely that a crossover to a stable trapped vortex state would be observed at higher fields.
Figure 6.8. (a) Magnetoresistance of Sample 150126_1_4 and Sample 140203_16 at 1.8 K. Sample 150126_1_4 data is after subtraction of a smooth background; Sample 140203_16 data has no subtraction, but is rigidly shifted horizontally by 0.012 T to compensate for observed temperature-dependent field offset. Curves offset vertically and scaled for clarity. Dashed lines are separated by $\Delta H = 520$ Oe, and the phase shift, $\delta_v \approx 0.3 \Delta H$, is indicated. (b) Magnetoresistance of Sample 140203_16 at 1.8 K and 900 nA for increasing (red) and decreasing (blue) magnetic fields showing lack of hysteresis in phase shift feature. Dashed lines are separated by $\Delta H = 520$ Oe.

6.4.3 Experimental verification of vortex trapping

It is quite interesting to see if the phase shift predicted theoretically can be detected in a real system. For devices recently reported in the literature [28–30], the measurements appear to have been performed at fields below $H_{c1}$, which depends on the sample size and geometry (Figure 6.2). Furthermore, as seen in Eq. 6.23, $\delta_v$ depends upon the vortex position within the loop, which may not be fixed. Additionally, near the trapping field, the energy difference between the vortex-trapped and vortex-free states is quite small. Indeed, the free energy curves intersect multiple times (Figure 6.6b), potentially prohibiting a clean transition between the vortex-free and vortex-trapped states.

In Figure 6.8a, we present the MRO of Sample 140203_16 over a larger field range at 1.8 K. The oscillations have a period of $\Delta H \approx 520$ Oe, which is consistent with the measured geometry. We see that the local maxima in resistance coincide with half-integer values of $H/\Delta H$ (dashed lines) up to $\mu_0 H \approx 0.25$ T. Above 0.25 T, the oscillations acquire a phase shift, $\delta_v \approx 0.3 \Delta H$, which is the expected signature of vortex trapping. The field at which this phase shift occurs is in reasonable agreement with the calculated value of $\mu_0 H_{c1} = 0.38$ T from Fig. 6.2a. To emphasize the robustness of this observation, we also plot in Figure 6.8a the
MRO for Sample 150126_1_4, which features the same geometry, but without the artificial constrictions (Figure 6.3b). We found it necessary to first subtract a smooth background from the data for this sample (see Section 6.6), but a phase shift of identical magnitude is observed in the vicinity of 0.3 T. We observe no hysteresis in the magnetoresistance (Fig. 6.8b), confirming the vortex trapping is not the result of strong pinning centers, but is instead determined by the field-dependent free energy.

We can use Eq. 6.23 to estimate the radial positive of the vortex, $v$. We obtain $v = 125 \text{ nm}$, or approximately $0.6w$. This is a reasonable result, as we would expect a minimum energy by positioning the vortex far from the boundaries of the nanoloop. However, we should be cautious in applying Eq. 6.23, as our experimental geometry does differ in significant ways from the theoretical geometry. It would be more fruitful to employ a high resolution magnetic imaging technique [140] to explicitly verify the vortex location.

### 6.5 Tuning $H_{c1}$ with external parameters

We can lend further support to the role of vortex trapping in generating the experimentally observed phase shift in our NbSe$_2$ nanoloops by demonstrating an ability to tune the trapping field, $H_{c1}$, in accordance with theoretical predictions. In this section, we focus on the response of the vortex trapping field in Sample 140203_16 to various external parameters.

#### 6.5.1 Evolution of $H_{c1}$ with applied current

In Figure 6.9a we plot the magnetoresistance oscillations of Sample 140203_16 around 0.25 T at various applied currents. The dashed vertical lines are placed at the expected (unshifted) fields of the $N = 4$, 5, and 6 peaks. At low currents, the $N \leq 5$ peaks are not phase-shifted, but the $N = 6$ peak is (along with subsequent higher peaks not shown), indicating $4.5H_0 \leq H_{c1} \leq 5.5H_0$. At higher currents, the first phase-shifted peak is the $N = 5$ peak, indicating the vortex stability field has decreased to $3.5H_0 \leq H_{c1} \leq 4.5H_0$. At all currents, the phase shift is equal in magnitude, as demonstrated by the consistent position of the $N = 6$ peak. We also observe an additional local maximum in the magnetoresistance curves which
Figure 6.9. (a) Normalized resistance ($R/R_0$) of Sample 140203_16 versus applied field ($\mu_0 H$) at 1.8 K and 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 $\mu$A (top to bottom). Vertical dashed lines indicate the expected (unshifted) positions of peaks 4, 5, and 6. Slanted solid lines track approximate value of $\mu_0 H_{c1}$ as indicated by local resistance maxima. Curves offset vertically for clarity. (b) Calculated $\mu_0 H_{c1}$ versus applied current ($I$) at 1.8 K. Horizontal dashed lines are placed at half-integer multiples of $H/H_0$.

The observed features agree with the expectations of the theoretical picture presented above and demonstrate that the applied current provides an additional means of manipulating the trapped vortex. Assuming that the applied current is uniformly distributed within the loop, an additional Lorentz force on the vortex is expected, resulting in the addition of a linear term to the $V_{in}$ curves in Figure 6.2. Numerical solutions for $H_{c1}$ as a function of applied current and temperature are shown in Figures 6.9b for the thick loop geometry. $H_{c1}(I)$ should be an even function for our system, since in our measurement geometry, current counter propagates in both arms, but in Figure 6.9b, we consider $H_{c1}$ in only one arm due to an experimentally observed asymmetry in the the trapping field between the arms (see Section 6.7). We see that $H_{c1}$ is indeed predicted to evolve systematically with applied measurement current, consistent with our experimental observations.

The discontinuities in the calculated $H_{c1}$ curves can be understood by considering the energy difference between the N and N+1 states at a given applied field. $\mathcal{F}_0(N+1, H) - \mathcal{F}_0(N, H)$ is periodic in $H$ (Eq. 6.13) and maximal just above half-integer values of $H/H_0$ (indicated by dashed lines in Figs. 6.9b). Going from a vortex-free to vortex-trapped state is similar to increasing the winding number from $N$ to $N + 1$, and is therefore most energetically costly where $\mathcal{F}_0(N+1, H) - \mathcal{F}_0(N, H)$
is maximal. Our measured $R(H, I)$ curves appear to be consistent with a jump in $H_{c1}$. The observed resistance peaks are sufficiently sharp so that both the non-shifted and shifted $N = 5$ peaks would be seen at intermediate currents if the critical field for vortex stability evolves smoothly. Given that only one or the other is found experimentally, and that the additional local resistance maximum jumps discontinuously between the 0.6 and 0.7 $\mu$A curves, at least a rapid decrease in $H_{c1}$ from $H \approx 5H_0$ to $H \lesssim 4.5H_0$ is present as $I$ increases, if not an actual discontinuity.

### 6.5.2 Evolution of $H_{c1}$ with temperature

A similar effect is observed when sourcing a fixed current but varying the temperature of the system (Fig. 6.10a). The magnetoresistance oscillations broaden with increasing temperature, but it is still clear the first phase-shifted peak changes from $N = 6$ to $N = 5$ as temperature increases. We again performed numerical calculations to investigate the temperature dependence of $H_{c1}$ in the London theory. The temperature dependence of $V_m$ is primarily determined by the $\xi(T)$ term. We plot the results of our numerical calculations in Figure 6.10b. Again we find that the experimental trend agrees well with the theoretical predictions, in that an increase in temperature is expected to result in a decrease in $H_{c1}$, and the decrease will be very rapid near $N + 1/2 \leq H_{c1}/H_0 \leq N$.

![Figure 6.10](image-url)
Figure 6.11. (a) Calculated field of first vortex stability ($\mu_0 H_{c1}$) in circular loop. Inner radius ($a$) is fixed at 70 nm, and outer radius ($b$) is varied. (b) Calculated energy from Eq. 6.14 ($V_n$) versus vortex position ($v$) along radius of loop with $a = 70$ nm and $b = 108$ nm at applied fields of 16.3, 17.3, 18.3, and 19.3$H_0$ (top to bottom). (c) Magnetoresistance of Sample 140124_12 at multiple temperatures after subtracting off a smooth background. Magnetic field is given in units of $H_0 = 840$ Oe. Shaded region indicates field range where oscillations are not strictly periodic.

6.5.3 Engineering $H_{c1}$ with nanoloop geometry

The field of first vortex stability in a nanowire was given by Eq. 5.6, and was found to increase as $w^{-2}$ as the width of the nanowire was reduced. When the limit $w \ll r$ is not valid, the dependence of $H_{c1}$ on the geometry of a loop must be calculated numerically from Eq. 6.14, but the general trend is maintained. In Figure 6.11a, we plot the numerically calculated $H_{c1}$ for a loop with inner radius $a = 70$ nm and an outer radius $100$ nm $\leq b \leq 175$ nm. The inverse quadratic dependence is observed clearly. This suggests that by fabricating loops with different arm widths, we can tune the field at which the vortex trapping MRO phase shift is observed.

We investigated the MRO in thin arm nanoloops such as the one shown in Figure 6.3a. Sample 1401224_12 features an arm width of $w \approx 35$ nm and a median
diameter of $s \approx 155$ nm. In Figure 6.11b, we reproduce Figure 6.2b, which plots $V_{in}$ for a dimensionally equivalent circular loop ($a = 70$ nm, $b = 108$ nm) at several magnetic fields. Here, we give the fields in units of $H_0$ for ease of comparison to Figure 6.11c. We find $\mu_0 H_{c1} = 18.3 H_0 \approx 1.54$ T.

In Figure 6.11c, we present the measured magnetoresistance of Sample 140124_12 with the magnetic field given in units of $H_0 = 840$ Oe. At a given temperature, there is a finite range of magnetic fields over which the oscillation amplitude is sufficiently large to reliably track. Therefore, due to the large predicted value of $H_{c1}$, it was necessary to observe the oscillations at several temperatures, as can be seen by the three distinct curves in Figure 6.11c. We ensured the magnetic field ranges had substantial overlap between different temperature curves to rule out artifacts resulting from the temperature dependence of $H_{c1}$. We observe strictly periodic MRO over the range $0 \leq H/H_0 + 1/2 \leq 15$. In the field range $15 < H/H_0 + 1/2 < 18$, the oscillations lose their periodicity, as can be seen by the offset between the observed local maxima and the predicted local maxima (vertical dashed lines). This field range is in reasonable agreement with the predicted value of $H_{c1} = 18.3 H_0$.

### 6.6 Directing crossing vortices to artificial constrictions

In Figure 6.12, we plot the vortex crossing barrier (Eq. 6.14) at an applied external field of $0.15$ T for the thin loop (black curve) and thick loop (purple curve) geometries. The abscissa is scaled from 0 to 1 for both widths for ease of comparison. The ordinate axis is plotted in units of eV, rather than what has become our convention of normalizing to $\epsilon_0$, because the definition of $\epsilon_0$ depends upon the ratio $b/a$. The use of physical units allows a direct comparison of the barrier heights for the two geometries. However, we stress that the absolute scale, which suggests an essentially insurmountable barrier far exceeding $k_B T$ at low temperatures, does not represent an inconsistency in our interpretation of the vortex crossing mechanism. The height of the barrier scales with $\lambda^{-2}$, and from Section 6.3, we see that the literature value for the penetration depth in bulk NbSe$_2$ underestimates the true value in our devices by more than an order of magnitude. Thus, the ordinate axis should
likely be reduced by several orders of magnitude. Nevertheless, the qualitative
dependence of barrier height on nanoloop arm width is clear: the crossing barrier
is reduced for nanoloops with narrow arms. Therefore, by fabricating artificial
constrictions in the arms of a thick nanoloop, we direct the vortex crossing to
the constrictions with a minimal crossing barrier and simultaneously isolate the
trapped vortex from the crossing events by confining it to the wider regions where
$H_{c1}$ is lowest (Fig. 6.2). Intuitively, we expect this to result in experimental MRO
that more closely follow the predictions from the London theory in Sections 6.1
and 6.3, which are valid in the limit of isolated vortices.

In Figure 6.13, we present the unprocessed data for the thick loop without
constrictions (Figure 6.13a) and the thin loop without constrictions (Figure 6.13b)
near $H_{c1}$. For loops without artificial constrictions, the observed magnetoresistance
oscillations are superimposed on a resistive background. To more clearly observe
the vortex-related oscillations and phase shift in both samples (Figures 6.8a and
6.11c), we subtracted a smooth background from the measured resistance data.
The dashed line shows the polynomial fit used for the background subtraction.

Our interpretation of the smooth background on which the expected oscillations
and phase shift are superimposed is as follows. In a uniform circular loop, vortex
crossing events can happen with equal probability at any angular position. Unavoid-
able fabrication induced inhomogeneities will modify the local energy landscape,
along with the local value of $H_{c1}$. This will result in a global free energy that
is “smeared.” This effect is exacerbated by the presence of corners and nodes in

\[
\begin{align*}
\text{Figure 6.12.} & \quad \text{(a) Calculated energy ($V_{in}$) versus normalized vortex position along radius} \\
& \quad \text{of two loops at applied field of 0.15 T. Purple line is for $a = 73$ nm and $b = 158$ nm.} \\
& \quad \text{Black line is for $a = 70$ nm and $b = 108$ nm.}
\end{align*}
\]
Figure 6.13. (a) Magnetoresistance of Sample 150126_1_4. The smooth resistive background indicated by the dashed line is subtracted to obtain the oscillations in Fig. 6.8a. Inset: Comparison of raw (red) and background subtracted resistance data (blue) near 0.36 T (dashed box in main panel). Curves shifted vertically for clarity. The dashed line indicates the expected (unshifted) position of the \( n = 7 \) resistance maximum. (b) Magnetoresistance of Sample 140124_12. A smooth resistive background is still apparent (indicated by the dashed line).

the experimental geometry. By contrast, if we intentionally provide an easy crossing channel where the barrier is significantly artificially reduced, vortex crossing events will be strongly spatially confined, and the local free energy and value of \( H_{c1} \) will dominate the measured MRO. This interpretation is consistent with our experimental observation that both thick and thin uniform loops exhibit a smooth resistance background and a “shoulder” feature near \( H_{c1} \), while the thick loop with constrictions shows neither.

We note that it is possible to attribute the observed phase shift in the thick loop sample (Figure 6.8a) to an improper background subtraction near \( H_{c1} \). However, we can be confident that the observed phase shift is not an artifact of a poor background subtraction for three reasons. Firstly, the phase shift is seen in the constricted thick loop without a background subtraction. Secondly, the magnitude of the phase shift is the same for the background subtracted thick loop as for the non-background subtracted constricted thick loop, which would be highly unlikely if the apparent phase shift in the former case was a subtraction artifact. Thirdly, we can directly compare the position of the extrema before and after the background subtraction. In the inset to Figure 6.13a, we plot the unprocessed resistance data (red) and the background-subtracted resistance data (blue) for the thick loop without constrictions. The curves have been shifted vertically for ease of
Figure 6.14. Magnetoresistance of Sample 140203_16 at 1.8 K and 650 nA over extended field range. Vertical lines are separated by $\Delta H = 520$ Oe except where indicated. Shaded regions denote where oscillations acquire phase shifts as determined by comparing consecutive magnetoresistance maxima.

comparison. We see that the background subtraction produces no substantial shift in the position of the resistance maximum within the resolution of our measurement. For comparison, the expected location of this maximum in the absence of vortex trapping is indicated by the dashed line.

6.7 Asymmetry of trapping with field direction

We return once more to the MRO in Sample 140203_16 – the thick loop with artificial constrictions. In Figure 6.14, we plot the MRO at 1.8 K over an expanded field range for both positive and negative field orientations. The vortex trapping phase shift at $\mu_0 H_{c1}^+ = +0.28$ T is visible. But in the negative field orientation, the phase shift does not occur until $\mu_0 H_{c1}^- \approx -0.38$ T, though the phase shift in each orientation is equal in magnitude ($0.3 H_0$, see shaded regions in Figure 6.14). This asymmetry, $\mu_0 H_{c1}^+ \neq \mu_0 H_{c1}^-$, can be understood in light of the theory presented in Section 6.1.

For a uniform square loop in the absence of a measurement current, a vortex is equally likely to stabilize in either of the two arms above $H_{c1}$. The presence of a net measurement current, however, introduces an additional term to the free energy. In our measurement setup, current propagates clockwise through the top arm, and counter clockwise through the bottom arm. This introduces an asymmetry in the relevant $V_m$ curves. We demonstrate this explicitly in Figure 6.15a. The black curve
Figure 6.15. (a) Vortex energy ($V_{\text{in}}$) vs. vortex position ($v$) for different measurement conditions. Black curve is for zero measurement current, and is independent of the specific arm the vortex is located in. Blue (red) curve is with 2.5 $\mu$A applied current and with vortex located in bottom (top) arm. Note the opposite trend of $\mu_0 H_{c1}$ for the two trapping configurations. (b) Magnetoresistance of Sample 140203_16 for positive (red) and negative (blue) fields at 1.8 K and 650 nA. Negative field data is reflected about local minimum nearest 0 T. Arrows indicate where local magnetoresistance maxima coincide between two field orientations.

shows $V_{\text{in}}(v)$ for our thick loop at $H_{c1}$ in the absence of a measurement current, and it applies equally well to a vortex trapped in either arm. The blue (red) curve shows $V_{\text{in}}(v)$ for a vortex trapped in the bottom (top) arm at the same field, but with an applied measurement current of 2.5 $\mu$A. We see that the value of $H_{c1}$ is increased (reduced). Thus, the effect of the measurement current is to break the symmetry between the arms and establish a preferred arm for the vortex.

Additionally, it is likely the vortex trapping field is not uniform along the circumference of the loop due to local variations in $w$ or $\psi$. If we assume the trapping field has some global minimum ($H_{c1}^*$) as a function of position along the circumference of the loop, there will be a preferred vortex trapping side, even in the absence of a measurement current. With the addition of a finite current, $H_{c1}$ will either be increased or decreased, depending on the direction of current flow. Reversing the direction of the current is equivalent to reversing the orientation of the field. So we expect to see different values of $H_{c1}^-$ and $H_{c1}^+$. It is tempting to claim

$$H_{c1}^* = \frac{H_{c1}^+ + |H_{c1}^-|}{2}. \tag{6.24}$$

However, Eq. 6.24 assumes a high degree of symmetry in terms of current distribution and free energy barriers. Given that this discussion began with the assumption
that the loop is non-uniform, it seems unlikely that Eq. 6.24 can be considered at all rigorous. Instead, we are left with the more conservative inequality,

\[
\min \left( H^+_{c1}, |H^-_{c1}| \right) \leq H^*_c \leq \max \left( H^+_{c1}, |H^-_{c1}| \right).
\]  

(6.25)

Once a vortex is trapped in an arm, it generates a phase shift of fixed magnitude. In Figure 6.15b, we overlay the positive and negative field MRO for Sample 140203_16. The black arrows indicate the MRO maxima that exactly coincide. At \( H^+_{c1} \), the curves separate, but above \( |H^-_{c1}| \), they line up again, indicating the resulting phase shift is identical in both field orientations. Interestingly, at higher fields, the misalignment/realignment process repeats.

### 6.8 Additional phase shifts above \( H_{c1} \)

In the case of the loop with constrictions, several phase shifts are evident at different applied fields (see shaded regions in Fig. 6.14). These phase shifts may result from subsequent vortex trapping events, though the present theory does not address this situation. The electrostatic analogy employed in Section 6.1 can be extended to the case of \( n \) charges equally spaced around two grounded concentric cylinders. This extension is beyond the scope of this dissertation. Qualitatively, it is reasonable to expect each subsequent vortex trapping event to be accompanied by an additional phase shift in the magnetoresistance oscillations. Alternatively, the additional phase shifts may simply reflect a change in the location of the trapped vortex, since the phase shift depends on \( v \) (Eq. 6.23).

### 6.9 Temperature dependent offset from self-inductance

A careful inspection of Figure 6.14 reveals that \( \mu_0 H = 0 \) does not precisely correspond to the local magnetoresistance minimum as we would expect from either Eq. 2.55 or Eq. 6.13. This can naively be explained by trapped magnetic flux, either within the superconducting magnet generating the field or in the sample itself. However, given the importance of the MRO phase in our interpretation of vortex trapping, further characterization of this zero field offset is warranted.

In Figure 6.16a, we plot the low field MRO of Sample 140203_16 at a series
of different temperatures for positive (solid lines) and negative (dashed lines) current. We observe a clear, temperature dependent phase shift between the current directions. The maximum value of the shift between current directions is \( \Delta \phi/\phi_0 \approx 0.33 \) at 1.8 K, and the value is reduced to essentially 0 above \( T = 3.7 \) K. This is inconsistent with the picture of trapped magnetic flux in the superconducting magnet, which cannot depend upon the temperature of the sample. The offset is unchanged after thermally cycling the sample through \( T_c \), ruling out the possibility of trapped flux within the sample itself, as well. Additionally, we find that the offset between current directions does not depend upon the magnitude of the applied current (see Figure 6.16b).

This asymmetry with bias current direction is commonly observed in conventional SQUIDs. A SQUID is composed of a doubly-connected superconductor interrupted by two weak links. Like the nanoloops considered in this chapter (and for essentially the same reasons), a SQUID exhibits MRO with a period of \( \phi_0 \), with the first local maximum occurring at \( \phi/\phi_0 = 1/2 \). Each junction in a SQUID features a critical current, \( I_{0,k} \) \((k \in \{1, 2\}, \text{and indexes the junction})\). In a perfectly symmetric SQUID, \( I_{0,1} = I_{0,2} = I_0 \). However, in real devices, the critical current can differ between the two arms of the SQUID such that

\[
I_{0,1} = I_0(1 - \alpha I) \tag{6.26}
\]
\[
I_{0,2} = I_0(1 + \alpha I), \tag{6.27}
\]
where $\alpha_I$ is a dimensionless parameter characterizing the degree of asymmetry in the junction critical currents. There can also exist a second asymmetry, $\alpha_L$, which characterizes the difference in the self-inductances of each arm of the SQUID. In this case, it can be shown [141] that, at $I_c \approx 2I_0$, the local minimum in the MRO are phase shifted by an amount

$$\Delta \phi = \beta_L (\alpha_I + \alpha_L) \phi_0,$$

(6.28)

where

$$\beta_L = \frac{2LI_0}{\phi_0},$$

(6.29)

and $L$ is the self-inductance of the SQUID. Furthermore, if the bias current is varied, the MRO shift along the flux axis by an amount proportional to $\alpha_L$, independent of $\alpha_I$. This enables independent experimental determination of the two asymmetry constants.

The flux dependence of SQUIDs was originally calculated for the case of a superconducting loop featuring two insulating barriers (Josephson junctions), but any “weak link” (such as a normal metal barrier or geometric constriction) produces the same behavior [141]. Thus, we apply the above analysis to our thick nanoloop with artificial constrictions. We see readily from Figure 6.16b that $\alpha_L \approx 0$ for our system. In the size regime of our nanoloops, the inductance of our loop is dominated by the kinetic inductance, $L_k$, which arises from the inertial mass of the charge carriers [142], rather than the geometric inductance, $L_g$, [143] and is given by

$$L_k = \frac{8\mu_0 \lambda^2 s}{wd}.$$

(6.30)

If we take a value of $\lambda = 2.1 \mu m$, which is justified in light of the results in Section 6.3, we use Eqs. 6.29 and 6.28 to recover the observed shift in Figure 6.16a with the values of $I_0(1.8 \text{ K}) \approx 70 \text{ nA}$ and $\alpha_I(1.8 \text{ K}) = 0.5$. We did not perform independent tests to verify $I_0$, but we can see from Figure 6.16b that $I_0 < 100 \text{ nA}$. We do not claim any confidence in the particular choice of $\alpha_I$; we merely demonstrate that the observed zero field phase shift can be numerically obtained with plausible choices for both parameters. The observation that $\Delta \phi \to 0$ as $T \to T_c$ is unsurprising, as both $\alpha_I$ and $I_0$ necessarily approach zero in that limit. Such a zero field offset was not observed in either the thick loops or thin loops without constrictions, lending
further support to the claim the shift has its origin in a non-zero $\alpha_I$ caused by the inclusion of the artificial constrictions.
Chapter 7

Conclusions

In this dissertation, we have presented two main accomplishments: the development of a fabrication process enabling transport measurements on 2D crystal nanostructures of NbSe$_2$ in arbitrary planar geometries and the manipulation of Abrikosov vortices within such nanostructures. Taken together, these two accomplishments set the stage for fundamental investigations of vortex dynamics in confined crystalline superconductors, which may shed light on several outstanding issues such as the vortex mass, the possible quantum motion of vortices, and the effect of competing long-range orders in single-crystal superconductors. The novel process we developed for fabricating nanoscale transport devices prepared on mechanically exfoliated 2D crystals of type-II superconductor NbSe$_2$ overcame technical difficulties such as achieving low resistance electrical contacts to the nanostructures, aligning measurement electrodes to transport devices with nanometer precision, and protecting the thinnest NbSe$_2$ crystals from oxidation under processing conditions. The resulting nanostructures of few-layer crystalline superconductors with feature sizes a few times the zero temperature coherence length have not been achieved prior to this work.

Superconducting nanowires of 2D crystal NbSe$_2$ were found to show thermally activated phase slips near $T_c$ in zero magnetic field. In finite magnetic fields, the system exhibited magnetoresistance variations arising from a non-monotonic vortex crossing barrier predicted theoretically in the London approximation. Another main result was the demonstration that the presence of weak pinning centers produced by surface adsorbates locally modifies the vortex crossing barrier, resulting in a sample-specific magnetofingerprint that reflects the configuration of pinning centers.
In sufficiently wide nanowires, we also observed a kink in the evolution of the critical current as a function of applied field; we tentatively associate this kink with vortex trapping in the nanowire, suggesting that both crossing and trapped vortices can coexist in nanostructures. Our analysis of the Abrikosov vortex dynamics in single-crystal nanowires guided our design of more complex structures aimed at the control and manipulation of vortices.

We observed periodic magnetoresistance oscillations with an enhanced amplitude arising from vortex crossing events in single-crystal superconducting nanoloops. We also observed a rigid phase shift in the magnetoresistance oscillations of a nanoloop resulting from the trapping of an individual vortex within the arm of the loop above the lower critical field, $H_{c1}$. By fabricating artificial constrictions in a nanoloop, we were able to direct the crossing events to the constricted regions, demonstrating an ability to manipulate dynamic vortices in NbSe$_2$ nanostructures. We tuned the critical field by means of an external transport current, temperature, and loop geometry, all in agreement with theoretical calculations in the London approximation, demonstrating that crossing and trapped vortices can coexist in superconducting nanoloops under suitable conditions, thereby making it possible to manipulate both crossing and trapped vortices in a 2D crystal nanostructure.

The manipulation of individual Abrikosov vortices within a 2D crystal nanostructure is expected to enable experiments probing fundamental properties of superconductivity in reduced dimensions, and is the first step toward the study of the possible quantum nature of Abrikosov vortices. For example, by modulating the electronic charge on a central island within a superconducting loop, quantum interference of vortices may be observed [39] – this Aharonov-Casher effect [144] is the predicted dual of the verified Aharonov-Bohm effect [145] for charged particles. Additionally, quantum tunneling of Abrikosov vortices may be explored in a suitable structure [38].

Because the band structure of NbSe$_2$ evolves with crystal thickness in the few-layer limit, a systematic study of nanostructures of varying thicknesses may reveal band-structure dependent phenomena of superconductivity and vortex motion, especially related to the interplay of the presumably competing CDW and superconducting orders in this material. Similarly, pairing symmetry effects related to the symmetry of the crystal structure – specifically, the lack of inversion symmetry in NbSe$_2$ crystals with odd numbers of layers – may be observable [146].
Cryogenic electronic transport measurement techniques

In this appendix, we describe how NbSe$_2$ nanostructures are wired to measurement electronics, cooled to cryogenic temperatures, and characterized with electrical transport measurements.

A.1 Wiring nanostructure devices to measurement electronics

Typical devices prepared by EBL or photolithography had metallic contact pads approximately $300 \times 300 \ \mu m^2$. These pads were connected to measurement electronics by means of three levels of additional wiring. A schematic of a wired device is shown in Figure A.1a. We attached 25 $\mu m$ diameter gold wire to the gold contact pads using pressed indium dots (described below). The other end of the gold wire was soldered to a copper pad on separate rigid header. A 75 $\mu m$ diameter copper wire was soldered to the other end of the copper pad, completing the sample “header.” The free end of the copper wire was then soldered to the cryostat-specific sample mount. The sample mount was connected to room temperature measurement electronics through electrical feedthroughs.

We found that pressed indium dots were the most reliable means of contacting the gold pads on the devices while minimizing the risk of damage to the nanodevice from electrostatic discharge. The process for attaching gold wires to contact pads
with indium dots is as follows (see Figure A.1b): 1) Under an optical microscope, position 200 µm diameter indium sphere (Part No. SPHEREIN-41016, Indium Corporation of America) on corner of contact pad using fine wooden tip; 2) Deform sphere into pancake using blunt tweezers; 3) Press gold wire lightly into indium pancake using sharp tweezers. Care must be taken at this point to not sever the indium pancake with the sharp tweezers; 4) Repeat steps 1) and 2) with a second indium sphere on top of the gold wire. The final result should consist of a gold wire encased in two indium pancakes. In some cases, the original indium sphere will not adhere well to the pad/substrate. The most frequent cause is a dirty substrate, and this can be rectified with a short isopropyl alcohol rinse if necessary. The indium sphere technique works well for gold contact pads, but occasionally resulted in low-temperature contact failure on aluminum pads. To prevent this, we would reinforce the indium sphere connection with a small amount of cured silver epoxy when wiring to aluminum pads.

A.2 Protection from electrostatic discharge

Unintentional electrostatic discharge (ESD) poses the greatest threat to electrical transport nanodevices. The most probable time for ESD damage is during the wiring process, when the sample comes into direct electrical contact with potential charge reservoirs. To protect the NbSe$_2$ nanodevices, we instituted a series of standard wiring procedures, resulting in $>80\%$ of devices surviving the wiring process. All wiring was performed at a static-free station designed previously [109].
The station consisted of a grounding mat, grounding wrist strap, and Chapman volume static eliminator workstation ionizer. The wiring process consists of several steps, outlined in Section A.1. The solder steps must be completed first, with the indium dot bonds being the final step. In this way, electrical contact to the device of interest is avoided for the majority of the wiring process.

The next most probable time for ESD is when connecting and disconnecting measurement electronics. Each measurement cryostat has electrical feedthroughs terminating in a BNC connector “breakout” box. The measurement electronics were connected to the BNC outputs on the breakout box. When changing the measurement configuration, the leads of the measurement electronics were first shorted together through a secondary, low-resistance path to provide an alternative current path in the event of ESD. Both a grounding wrist strap and workstation ionizer were employed when connecting and disconnecting measurement leads.

A.3 Low temperature techniques

A.3.1 Liquid nitrogen probe station

The fabrication of a NbSe$_2$ nanodevice represents a significant investment of resources. Whenever possible, the success of each fabrication step was confirmed before proceeding to the next one. Of primary concern was the quality of the electrical contact between the metallized electrodes and the NbSe$_2$ crystal. We used a room-temperature probe station (consisting of electrically conducting tungsten tips mechanically attached to micro manipulators) to measure the two-terminal resistance of our devices. In this way, we could gain a sense of the contact resistance without needing to first wire each sample to a header.

We found that devices with similar room temperature contact resistances could exhibit diverging behavior at low temperatures depending on the nature of the contact. Thus, we devised a technique to quickly measure the contact resistance of a batch of samples over a large range of temperatures. A copper sample block was mounted to a styrofoam container, and the device under test was attached to the block with double-sided tape. A small amount of liquid nitrogen was poured in the container, cooling the sample block. The apparatus was constructed to be small enough to fit within the size restrictions of the probe station, and a resistance
vs. temperature measurement was performed between 300 K and 77 K. In our experience, if the contact behaved metallically to liquid nitrogen temperatures, it would continue to do so to helium temperatures, and therefore allow for low-noise transport measurements.

The implementation of this technique assumes a high degree of correlation between the behavior of multiple contacts across a single batch of samples. It is impractical to measure every contact in a batch of devices in this way, especially because moisture condenses on the cold sample surface, potentially contaminating the device. We typically only measured the contact of a few representative samples from each batch that were not candidates for further processing (for reasons such as incomplete metal liftoff or improper electrode alignment).

A.3.2 Liquid helium dip probe

When a high device throughput was desired, but liquid nitrogen temperatures were insufficient, we used a liquid helium dip probe. Samples were wired to a copper block with an attached Cernox thermometer. The entire assembly was lowered into a liquid helium storage dewar. The temperature was controlled by controlling the height of the block above the liquid surface, and was smoothly varied between 300 K and 4.2 K. This enabled measurements of the superconducting state of NbSe$_2$ in the absence of an applied magnetic field. The dip probe was primarily used to confirm contact resistance and superconductivity in devices without incurring the expense of cooling a conventional cryostat.

A.3.3 Quantum Design Physical Property Measurement System

For the transport measurements presented in this dissertation, we employed a commercial Quantum Design Physical Property Measurement System (PPMS). This system has a base temperature of 1.8 K, which is achieved by using a mechanical pump to lower the boiling point of liquid helium. The vaporized helium is pulled through a cooling annulus surrounding the sample chamber, rather than brought into direct contact with the sample as in the case of the dip probe, and temperature is controlled ($\pm 5$ mK) by varying the flow rate of the cooling gas. A resistive heater on the sample mount allows for in situ heating up to 400 K. The system contains a superconducting magnet capable of applying fields of $\pm 9$ T, and a high-vacuum
cryopump capable of reducing the sample chamber pressure to $\lesssim 10^{-5}$ Torr to aid in removing surface adsorbates.

**A.3.4 Helium reliquefier system**

The PPMS system vaporizes liquid helium at a rate of approximately 10 liquid L/day under normal operating conditions. For both economic and environmental reasons, it is prudent to recover and recycle this gas. Our lab is connected to a department-owned Cyromech LHeP60 helium reliquifier for this purpose. We constructed a gas handling manifold to connect the PPMS to this reliquifier system (shown in Figure A.2). It is important that only gaseous helium be sent to the reliquifier, as other materials with higher melting temperatures will freeze in the cold heads and block the flow of liquid helium. Because the mechanical pump controlling the flow rate of cooling gas is also used to pump the atmosphere out of the PPMS sample chamber upon loading a new sample, a bi-directional valve on the manifold is used to direct the flow of pump exhaust either into the recovery system or into a vent line, depending on the state of the PPMS. With this setup, we recover and reliquefy more than 90% of the helium consumed by the PPMS, with the majority of the losses occurring during the initial stage of helium refills of the PPMS dewar.
A.4 Measurement configuration and electronics

All data presented in this dissertation come from four-terminal electrical transport measurements. In this configuration, a DC current is applied between two terminals of a device, and after a brief stabilization period, the resulting voltage is measured across two additional terminals. In this way, only the voltage contribution from the device under test is detected, and the influence of parasitic contact and measurement electrode resistance can be removed. To account for the thermoelectric offset voltage present under any measurement condition, we measured the voltage at a particular bias current, remeasured the voltage in the absence of current, and subtracted the two values to obtain an accurate voltage reading.

The commercial PPMS system includes a set of measurement electronics, but we typically bypassed that in favor of our custom low-noise measurement system. We installed RF filters (Low Pass LC Filter Modules, Coilcraft Item P7LP-304L, 3 dB cutoff at 0.30 MHz) at room temperature between the PPMS electrodes and our custom breakout box. For a current source, we used a Keithley Model 6221 AC and DC current source, featuring sub-pico ampere resolution, and for a voltmeter, we used a Keithley Model 2182 Nanovoltmeter, featuring nanovolt resolution. When reporting resistance values, we assume a linear relationship between current and voltage. In cases where this assumption is not valid (for instance, near $J_c$), we typically report voltage values, instead.

A.5 Data acquisition

Nearly all data acquisition was automated through National Instrument’s programming language, Labview. Communication between the controlling computer and the measurement electronics (as well as the PPMS) was accomplished through a General Purpose Interface Bus (GPIB, IEEE-488) connection. We coded the high-level measurement programs ourselves, and relied on freely available sub-programs from Keithley and Quantum Design for interfacing with the electronics and PPMS.
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Vita
Shaun Mills

Shaun Mills was born in Philadelphia, Pennsylvania, and spent his childhood in rural southern New Jersey. His interest in physics was largely obscured by his passion for tennis and Classical piano in his youth. He received his Bachelor of Science degree from Grove City College in 2010 with a double major in Applied Physics and Mathematics. That summer, he married Rachel Stelzer and moved to State College to begin his graduate studies in the low-temperature transport laboratory of Dr. Ying Liu. Shaun now has three children – Benjamin, Levi, and Abigail – but still finds the time to maintain some level of proficiency at both tennis and piano. He and his wife are active members of Oakwood Presbyterian Church in State College, where he serves in the nursery, on the Worship Team, and on the Service Team.

Selected Publications:

