

Electronic Spectroscopy of Topological Superconductor $\text{FeTe}_{0.55}\text{Se}_{0.45}$

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ABSTRACT

In condensed matter physics we study the behavior of crystals at finite density and low temperatures. By tuning and breaking the various materials, symmetries, and the topology of a crystal one can bring about brand new quantum phases of matter. These new phases of matter in turn produce emergent quasiparticles such as the cooper pair in superconductivity, the spinon in magnetic systems, and the Fermi arcs in Weyl semimetals.

Of particular interest are systems in which superconductivity interacts with topology. These systems have been theoretically predicted to produce anyonic quasiparticles which may be used as qubits in a future fault-tolerant quantum computer. However, these ideas usually require the use of the superconducting proximity effect to inject cooper pairs into the topological system. This in turn requires interfacing two different materials which not only requires extremely clean interfaces, but also matching Fermi surfaces, comparable Fermi velocities, and more. The ideal candidate for topological superconductivity would therefore be a material that is both superconducting and topologically non-trivial. One promising candidate is the iron-based superconductor $\text{FeTe}_{(1-x)}\text{Se}_x$, specifically at the $\text{FeTe}_{0.55}\text{Se}_{0.45}$ (FTS) doping which also has non-trivial topology. In this dissertation we address the fabrication of pristine interfaces using a new tool as well as new probes into the topology of FTS.

In Chapter II we discuss the motivation, construction, and use of the “cleanroom-

in-a-glovebox". This tool places an entire nanofabrication workflow into an inert argon atmosphere which has allowed us access to study a myriad of new materials and systems. A delightful offshoot of this glovebox is that it is a useful tool in training new scientists in fabrication techniques. The photolithography, Physical Vapor Deposition (PVD), and characterization tools in the glovebox are designed to be easy to use and thus afford new users a low-risk method of learning new techniques.

In chapter III we discuss a specific example of a new quantum phase of matter e.g. topological superconductivity in FTS. There, I discuss the fabrication requirements to probe this elusive phase as well as the unique measurement technique used to provide evidence that FTS is a higher-order topological superconductor. The characterization of FTS continues in Chapter IV where we reveal some exciting new results in the FTS system. These new results are direct evidence for the topological nature of FTS, a feat which has only been shown in Angle-Resolved Photo Emission Spectroscopy (ARPES) and Scanning Tunneling Microscopy (STM)

Chapter V concludes the dissertation with a summary of Chapters II, III, and IV. In addition, we give suggestions for future experiments to investigate the FTS system further as well as suggestions for insightful teaching programs with the cleanroom-in-a-glovebox.

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LIST OF ABBREVIATIONS

AR Andreev Reflection

DoS Density of States

STM Scanning Tunneling Microscopy

ARPES Angle-Resolved Photoemission Spectroscopy

PVD Physical Vapor Deposition

PAR Perfect Andreev Reflection

BTK Blonder-Tinkham-Klapwijk

LIA Lock-In Amplifier

BCS Bardeen-Cooper-Schrieffer

BdG Bogoliubov-de Gennes

ARPES Angle-Resolved Photo Emission Spectroscopy

FTS $\text{FeTe}_{0.55}\text{Se}_{0.45}$

TEM Tunneling Electron Microscopy

TI Topological Insulator

PVD Physical Vapor Deposition

MZM Majorana Zero Mode

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CHAPTER I

Introduction

At the beginning of the 20th century the world underwent the first quantum revolution. New ideas about wave-particles duality and quantization gave scientists the tools to explain previously observed phenomena such as the periodic table, chemical interactions, and electronic wavefunctions. With a deeper understanding, this new quantum theory drove revolutionary technologies such as electronic semiconductors thus bringing the world into the Information age. Now we are undergoing a second quantum revolution where we are no longer using quantum mechanics to simply explain observed phenomena, we are actively *controlling* quantum mechanics.[1] We are using quantum technologies to organize and build complex systems at the atomic level. This extraordinary leap forward has allowed us to create and research new quantum phases of matter and their associated new quasi-particles. Much as before, research into new quantum phases of matter is paramount for driving new technologies forward. For example, research into high-temperature superconductivity may lead us to room-temperature superconductivity, a phenomena which would massively reduce energy dissipation in modern electronics. However, it can be quite difficult to tell whether or not a system is in a new phase, especially if that phase is topological. Furthermore, once the system is in a new phase, robustly measuring the emergent modes requires new techniques and ideas. In this dissertation, we describe the development of new equipment to help build

these new quantum tools as well as the novel iron-based topological superconducting system such equipment has allowed us to study.

1.1 Scope

The works presented in this dissertation fall into two main parts: advances in nano-fabrication equipment and topological superconductivity. The first part introduces recent advances in condensed matter physics along with the difficulties associated with fabricating electronic devices to better study these new topics. In particular, we discuss nano-fabrication with materials that are acutely air-sensitive such as GdTe_3 as well as with materials where the bulk is stable in air but have air-sensitive surfaces such as FTS. The latter materials are of particular interest since the emergent modes that are indicative of a topological phase are often found on the surface of the material. The second part dives into the subject topological superconductors and higher order topology. Specifically, we focus on the iron-based superconductor $\text{FeTe}_{0.55}\text{Se}_{0.45}$, its topological properties, and some exciting new experiments.

The rest of this introduction will review pertinent background material. We introduce the notion of emergence and quantum phases of matter with specific applications to superconducting materials. We will leave some subjects of superconductivity, e.g. tunneling into a superconductor from a normal metal, to the appendices where these subjects can get a more in-depth treatment. A brief overview of topology will be given but more focus will be spent on how to treat the notion of topology in superconductivity.

1.2 Emergence and Topology

Emergence can be colloquially summarized as, "The whole is greater than the sum of its parts." Examples of emergence are all around us, from the biggest of scales where galaxies coalesce into superclusters to the smallest of scales where atoms emerge out of

the fundamental excitations of quantum fields. With such a huge subject, it is easy to see why studying emergence is of such importance, i.e., discoveries made about an emergent behavior may have useful applications in other disciplines. While this is exciting, it can also be easy to be sidetracked onto other topics and applications. Thus to keep this work on track we will use the sharper definition provided by Kivelson & Kivelson:

“An emergent behavior of a physical system is a qualitative property that can only occur in the limit that the number of microscopic constituents tends to infinity.”[2]

Phases of matter are a fantastic example of this definition as the same constituent material can display vastly different properties. Indeed, even small changes to the interactions between these microscopic constituents can lead a “classic” system (such as metals or insulators) to new phases of matter such as superconductivity and magnetism. Accompanying these phases are often new, useful quasi-particles such as the cooper pair and the magnon from the examples before. Not only do these new quasi-particles have value in real-world applications, they are also a critical method of identifying a new phase. Thus a governing question for the rest of this work is as follows, “What parameters can we tune to create a brand new phase of matter and what quasi-particles will this new phase produce?”

Many of electronic phases can be described elegantly through the language of symmetry and symmetry breaking[3–5]. However, starting in 1980 evidence began emerging that not all phases and phenomena could be explained by the use of symmetry alone. The first example of such a phase was the Quantum Hall Effect wherein a two-dimensional electron gas exhibits exactly quantized Hall voltages at large, perpendicular magnetic fields[6]. This phase consists of an insulating bulk with a perfectly ballistic 1-D edge mode around the bulk. Moreover, the phase does not immediately arise when time-reversal symmetry is broken but instead emerges at a finite magnetic field with no additional symmetries being broken. The Hall conductance increases by exact multiples

of the quantum of conductance (e^2/h) by further increasing the magnetic field, indicating more edge modes are emerging[7]. It was later shown that these quantized plateaus can be described using a topological invariant C_n called the Chern number.[8–11]

This Chern number is one example of a topological invariant arising from what is known as the Berry Phase[12]. The Berry phase is an additional, gauge-invariant phase factor acquired by a quantum mechanical system when it adiabatically evolves through a cyclical process and may be expressed as[12, 13]:

$$\gamma_n = i \oint_C \langle n(\mathbf{R}) | \nabla | n(\mathbf{R}) \rangle \cdot d\mathbf{R} \quad (1.1)$$

where γ_n is the Berry phase, $|n(\mathbf{R})\rangle$ is the wave function for an arbitrary parameter \mathbf{R} , and C is a closed loop in the parameter space. As an aside, this parameter \mathbf{R} is commonly either the crystal momentum k , or the spatial position, however the general theory describes a closed loop in *any* parameter space, which leads to some interesting topological phenomena[14, 15]. The Chern number arises when integrating this Berry phase of the wavefunction in momentum space and while defining and describing the Chern number in its full glory is fascinating, it is not within the scope of this dissertation as the rest of these works are focused on another topological invariant, the \mathbb{Z}_2 invariant.

Before we move onto a discussion of the \mathbb{Z}_2 invariant and topological superconductivity I would like to make a quick note. The 1-D edge modes that arise in the Quantum Hall Effect are a beautiful example of how new phases often come with new quasiparticles. In the next section, we provide an example of another emergent quasi-particle. One that is central to the works presented in this dissertation, the Majorana Zero Mode.

1.3 Topological Superconductivity

The \mathbb{Z}_2 invariant as applied to 2D electronic systems first arose in 2005 when it was noted that imposing time-reversal symmetry in such systems leads to new topological

invariants[14, 16, 17]. While nonzero Chern numbers cannot be realized with time-reversal invariance, the “zero” Chern-number class instead can be subdivided into two pieces: “ordinary” insulators that do not in general have an edge state, and a “Quantum Spin Hall Effect” where a bulk topological invariant forces an edge state. The topological invariant in this case is not an integer, but rather a two-valued or \mathbb{Z}_2 invariant. Physically, this idea can be thought of as having two copies of the Quantum Hall Effect, one for spin-up electrons and one for spin-down, with opposite propagation directions. This system remains time-reversal invariant because time-reversal flips both the spin and propagation direction, thus both copies “transform” into each other under this operation. To understand how this leads to two-valued invariant rather than an integer invariant we need to take a look at how the time-reversal operator \mathcal{T} acts in Fermi (half-integer spin) systems. In 1930, H. A. Kramers showed that the square of the time-reversal operator is connected to a 2π rotation implying:

$$\mathcal{T}^2 = (-1)^{2S} \tag{1.2}$$

where S is the total spin quantum number of a state[18]. Plugging in half-spin shows that Fermion systems pick up a minus sign under two time-reversal operations. An immediate consequence of this is that every eigenstate of a time-reversal-invariant spin-half system is at least two-fold degenerate, also known as “Kramers pairs”. A non-rigorous proof is by showing that a time-reversal invariant perturbation H' cannot mix members of a Kramers pair.

$$\begin{aligned} \langle \mathcal{T}\psi | H' | \psi \rangle &= \langle \mathcal{T}\psi | H' | \mathcal{T}^2\psi \rangle && \mathcal{T} \text{ is antiunitary and } H' \text{ is TRS} \\ \langle \mathcal{T}\psi | H' | \mathcal{T}^2\psi \rangle &= -\langle \mathcal{T}\psi | H' | \psi \rangle && \mathcal{T}^2 = -1 \\ \therefore \langle \mathcal{T}\psi | H' | \psi \rangle &= -\langle \mathcal{T}\psi | H' | \psi \rangle = 0 && x = -x \implies x = 0 \end{aligned}$$

We can now combine this Kramers pair knowledge with the counter-propagating edge states mentioned above. If there is only a single Kramers pair of edge states then a right-moving excitation can only backscatter into its time-reversal conjugate, which we just showed is forbidden if the perturbation inducing scattering is time-reversal invariant. However, if we have two Kramers pairs of edge modes, then a right-mover can backscatter to the left-mover of the *other* Kramers pair, since it is not its time-reversal conjugate, which will eliminate the two Kramers pairs. Thus a system with an even number of Kramers pairs will pair down to zero Kramers pairs (making a trivial insulator), whereas systems with an odd number of Kramers pairs will wind up with a single, stable Kramers pair (a non-trivial insulator)[19]. Thus a topological system with time-reversal invariance will have a two-valued invariant that is either even or odd.

For an immediate consequence of this result on Fermionic systems we turn to the toy model of p-wave superconductivity on a 1D wire. We will start with the Bogoliubov-de Gennes (BdG) equations of which there is an in-depth derivation of presented in Appendix A, here we will use the final Hamiltonian from that appendix with some minor alterations. We will be closely following the works of Kitaev and Bernevig & Hughes[20, 21].

We begin by describing a 1-D chain of fermions, i.e., at each lattice site j on the chain there is a complex fermion c_j . For simplicity, we consider these complex fermions to either be spinless or fully spin-polarized due to a source of time-reversal symmetry breaking. Since a momentum-independent s-wave pairing potential is not possible for spinless fermions, we will use a momentum-dependent p-wave potential (in momentum space):

$$H_{\Delta} = \frac{1}{2} \left(\Delta p c_p^{\dagger} c_{-p}^{\dagger} + \Delta^* p c_{-p} c_p \right) \quad (1.3)$$

where c^{\dagger} and c are the creation and annihilation operators, p is the momentum, and Δ is

the superconducting pairing potential. The lattice BdG Hamiltonian (in real space) we need to solve is:

$$H_{BdG} = \sum_j \left[-t \left(c_j^\dagger c_{j+1} + c_{j+1}^\dagger c_j \right) - \mu c_j^\dagger c_j + |\Delta| \left(c_{j+1}^\dagger c_j^\dagger + c_j c_{j+1} \right) \right] \quad (1.4)$$

where $t > 0$ is the hopping parameter and μ is the chemical potential. To investigate how each parameter affects the superconducting gap, we take a lattice Fourier transform to convert back into momentum space:

$$H_{BdG} = \frac{1}{2} \sum_p \Psi_p^\dagger \begin{pmatrix} -2t \cos(p) - \mu & 2i|\Delta| \sin(p) \\ -2i|\Delta| \sin(p) & 2t \cos(p) + \mu \end{pmatrix} \Psi_p \quad (1.5)$$

where $\Psi_p = (c_p \quad c_{-p}^\dagger)$. Diagonalizing the Hamiltonian gives the energy eigenvalues as:

$$E_\pm(p) = \pm \sqrt{(2t \cos(p) + \mu)^2 + 4|\Delta|^2 \sin^2(p)} \quad (1.6)$$

These eigenbands are plotted in Fig 1.1 for various values of μ and setting t and $|\Delta|$ both to 1. From these bands we can see the gap closes when $\mu = -2t$ with energy gaps for both $\mu > -2t$ and $\mu < -2t$. As it turns out, the energy gaps for $\mu < -2t$ are topologically non-trivial while the energy gaps for $\mu > -2t$ are trivial. For an intuitive picture for why this is we will split the complex fermion operators into their Majorana fermion constituents. We replace each complex fermion c_j with two Majorana fermions, a_{2j-1}, a_{2j} via $c_j = \frac{1}{2}(a_{2j-1} + ia_{2j})$ and $c_j^\dagger = \frac{1}{2}(a_{2j-1} - ia_{2j})$. The Majorana operators are fermionic and are defined by their property $a_j = a_j^\dagger$ therefore they satisfy $\{a_j^\dagger, a_{j'}\} = 2\delta_{jj'}$ as well as $\{a_j, a_{j'}\} = 2\delta_{jj'}$. As an aside, due to the latter relation we can always break up a complex fermion operator into its real and imaginary Majorana components, although it may not always be a useful representation. Now, the

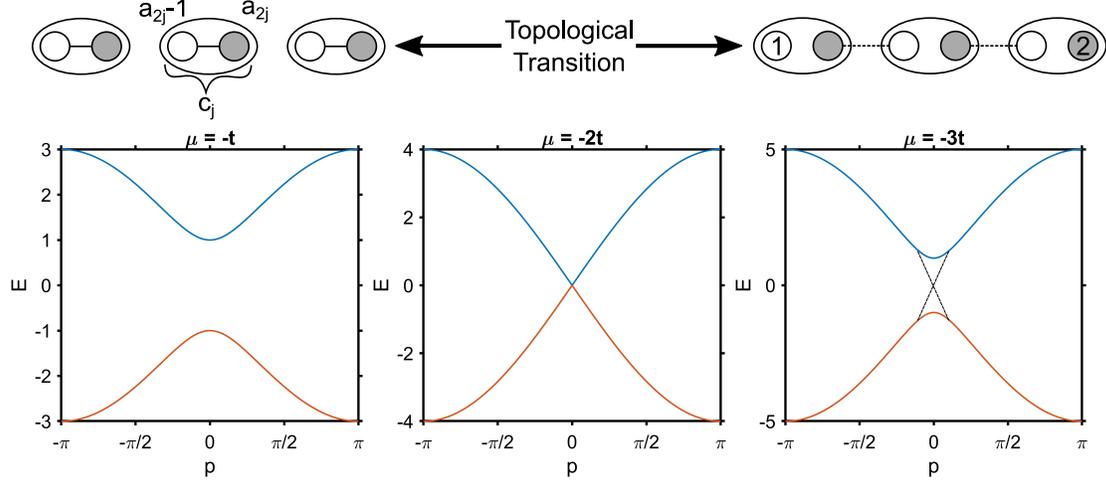


Figure 1.1: Dispersion relations of a 1D p-wave superconductor plotted at three different μ values. a) The trivial p-wave pairing scenario. The individual majorana particles each couple to the majorana on the same site. b) The critical value for μ where the gap closes. c) The topological p-wave pairing scenario. The majorana particles pair with majoranas on the nearest-neighbor site instead of on the same site. Two majorana zero modes are left on the edges of the wire, consistent with the bulk-boundary correspondence.

Hamiltonian for the lattice p-wave superconductor can be written as:

$$H_{BdG} = \frac{i}{2} \sum_p (-\mu a_{2j-1} a_{2j} + (t + |\Delta|) a_{2j} a_{2j+1} + (-t + |\Delta|) a_{2j-1} a_{2j+2}) \quad (1.7)$$

Here we can examine the difference between the two cases presented above by looking at two special limits.

The first limit is the trivial phase when we choose $\mu < 0$ and $|\Delta| = t = 0$. Here, the Hamiltonian reduces to,

$$H = -\mu \frac{i}{2} \sum_j (a_{2j-1} a_{2j}) \quad (1.8)$$

In this phase, the Majorana operators on each site are coupled together with an energy $\mu/2$ but there is no coupling between Majorana operators on different sites (see Fig 1.1).

This is denoted as the trivial phase since there will be no low-energy states on the end

of the chain if the boundaries are cut between sites. Said another way, the Majorana operators are localized to each site and are therefore in the atomic limit which is to say the trivial ground state.

The second limit is the topological phase where we choose $|\Delta| = t > 0$ and $\mu = 0$. Here, the Hamiltonian reduces to,

$$H = it \sum_j a_{2j} a_{2j+1} \quad (1.9)$$

This phase is the opposite of the previous phase as the Majorana operators on each site are only coupled to Majorana operators on *different* sites with an energy t . When the chain is cut the Majorana operators a_1 and a_{2L} (L is the last site) are “unpaired” and therefore there is a low-energy state on the each end of the chain (see Fig 1.1). Comparing to before, it is impossible to adiabatically tune this phase back to the atomic limit without closing the bulk gap (see Fig 1.1) and is thus a topologically non-trivial state. As a result, in the nontrivial phase the zero modes will not be destroyed until the bulk gap closes at a critical point.

This last point, along with the self-adjoint property, make Majorana Zero Mode (MZM) ideal candidates for fault-tolerant quantum computing. The self-adjoint property make MZM a topological quantum object called an “anyon”, a quasi-particle that is in between a boson and fermion. Anyons braid non-trivially: two counterclockwise exchanges do not leave the state of the system invariant, unlike in the cases of bosons or fermions[22, 23]. In this manner, MZM would be able to store information in the global wavefunction. That is to say the quantum state would be robust against local perturbations, drastically increasing the amount of quantum computations that could be made before the states decohere.

While the model presented above provides an intuitive understanding of how MZM arise out of the topological superconducting phase, there are no confirmed candidates for

materials that would realize it. Fortunately, there are quite a few other proposed models of obtaining topological superconductivity and/or observing MZM directly. These models include planar Josephson Junctions on a normal material that is subject to Rashba spin-orbit coupling[24–26], MZM arising as exotic excitations with fractional quantum numbers in Kitaev Quantum Spin Liquids[27, 28], or inducing superconductivity into a topological insulator[29]. What is apparent is that to study some of these systems, new methods of fabrication must be made so that we can study a wider variety of candidate materials, including materials that are sensitive to water and oxygen. With this in mind, we go directly into the next chapter which discusses a brand new instrument that is able to fabricate, characterize, and measure devices without the materials ever seeing ambient air.

CHAPTER II

Cleanroom-in-a-Glovebox

2.1 Introduction

Fabrication of devices at the nano-scale is central to future efforts in exploring novel quantum phases of matter and building next-generation devices. Previously this was achieved by creating dedicated facilities where the entire space is filtered and dust minimized via special air handling and attire for all who enter. While these cleanrooms minimize the amount of dust and other particles that can damage mesoscale devices, they do not protect the samples from either oxygen or water, at the same time they require extremely expensive and energy-intensive investments. In contrast, gloveboxes provide an inert atmosphere for working with oxygen and water sensitive materials, with greatly reduced initial and operational cost.[30] However, performing nanolithography in a glovebox risks contaminating the rest of the inert environment due to the various solvents involved. With these issues in mind, we've designed and constructed the cleanroom-in-a-glovebox to bridge the gap between these two approaches in order to prepare, fabricate, and characterize various scientific samples entirely within an inert argon atmosphere. The cleanroom-in-a-glovebox contains two separate work chambers where one chamber is devoted entirely to lithography and the other to preparation and characterization (Fig. 2.1a). The system can be operated with minimal training, no need for special attire (i.e. gowning), and far fewer demands on the building. As such, the

described cleanroom in a glovebox produces higher quality devices with air-sensitive materials, requiring far lower initial investment and operational cost than a traditional cleanroom. This makes the system described crucial in future efforts at training the quantum workforce and development of novel devices with a wider range of materials.

An overview of the system is shown in Fig. 2.1a, with the lithography chamber, (discussed in the “Fabrication” section), containing a Heidelberg μ PG101 Direct-Write system, an Angstrom NexDep Thermal Deposition and Plasma Etching system, and a Spin-Coating Systems G3 Spin Coater. The characterization chamber contains a WITec alpha300R confocal Raman system (Fig. 2.1b & Fig. 2.2b), a Nanomagntics ezAFM (Fig. 2.2a), a home-built 2D material dry-transfer system, electronic BNC and banana cable feedthroughs. These two chambers are connected via a small antechamber which allows us to transfer samples into and out of the gloveboxes while also enabling simple transfer between boxes without contamination. Lastly, attached to the back of the glovebox is an intermediate chamber for attaching a vacuum suitcase (Fig. 2.2d). This allows receiving from and transferring to a wide array of UHV systems, providing compatibility with electron-beam systems, scanning tunneling microscopy (STM), molecular beam epitaxy (MBE), angle resolved photoemission spectroscopy (ARPES) and other cutting edge tools. As such our processes and design enable a range of scientific tools on nanoscale, air-sensitive materials, while simultaneously reducing the time, training and cost involved.

2.2 Materials Characterization

Atomic force microscopy (AFM) is an invaluable tool for characterizing materials. In the case of mesoscale physics, AFM is used to discern the thickness of exfoliated 2D materials. In other cases it characterizes the roughness of a substrate (such as in 2.2a) or sample. In order to resolve such small features, great care was taken to isolate the AFM system from environmental vibrations. This is more difficult than usual in a glovebox,

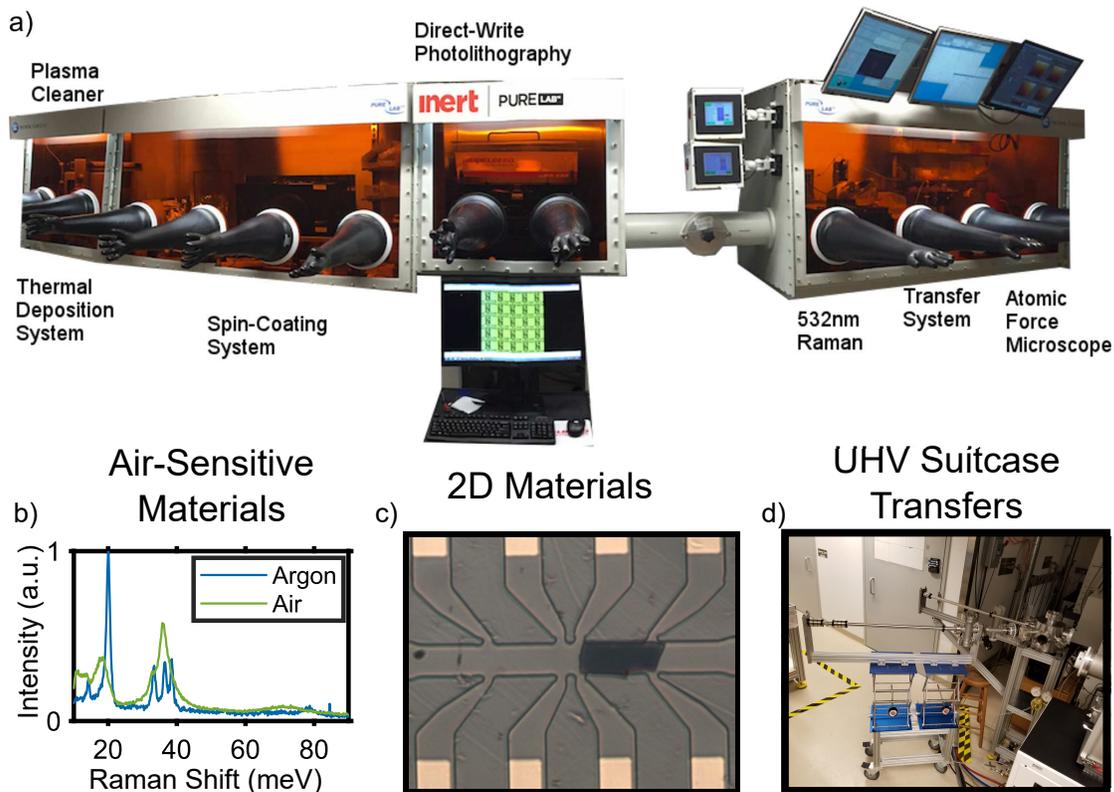


Figure 2.1: 1a) Picture of the Cleanroom-in-a-Glovebox. b) Raman spectra measured on αRuCl_3 showing the difference exfoliation in the inert atmosphere makes. Raman measurements were taken using the WITec Raman System installed in the glovebox. c) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ exfoliated onto a thin film of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. The film was then etched into a double hall-bar structure around the flake. d) Photo of the UHV suitcase during a device transfer from the glovebox to the low-temperature Raman system. The UHV suitcase is attached to the back of the glovebox.

as there are quite a few vibrations that arise from the gas-circulation system as well as sudden pressure changes from users inserting their hands into the glovebox to work on other tasks. To combat these vibrations the ezAFM and transfer stage were placed on a large granite slab. An additional Minus-K Vibration isolation stage was employed for the ezAFM and care was taken to ensure the cables were well secured to each other but did not touch the glovebox directly. The results of this are seen in Fig. 2.2a where we took an AFM scan of Mica, an atomically flat substrate. The noise levels of the scan are less than 5 angstroms in magnitude (the resolution of the ezAFM). To ensure rougher features can be resolved, this was compared with the AFM from HfO₂ film on a Si substrate grown by atomic-layer deposition. We note that ezAFM works with voice coils and thus is substantially less expensive and easier to use than a typical AFM system. Nonetheless, we anticipate a further reduction in noise with more traditional piezo-based scanning probes.

Raman spectroscopy can be used to tell the quality, doping level, thickness, symmetry, and cleanliness of samples.[31–36] For example, the ratio of the 2D peak to the G peak in graphene is commonly used to discern how disordered the sample is.[37] With our Raman system’s mapping capabilities, we determined the spatial distribution of the disorder after the fabrication of CVD graphene such as in Fig. 2.2b. The WITec system also allows us to measure photoluminescence (PL) with a simple switch of energy ranges. PL is a useful measurement technique when working with materials such as MoS₂, as it quickly identifies single-layer flakes, and provides insight into the interaction of MoS₂ with the substrate.[38–40] We observed another advantage of the glovebox here. Namely, Mica is known to have charged potassium ions on the surface after cleaving but is quickly neutralized in air.[41] When exfoliating MoS₂ directly to the mica we found the PL consistent with the mica taking the MoS₂ from n-type to intrinsic.[42, 43] (see Fig. 2.2c)

It is crucial to overcome the “glovebox-specific” problems to obtain the high-quality

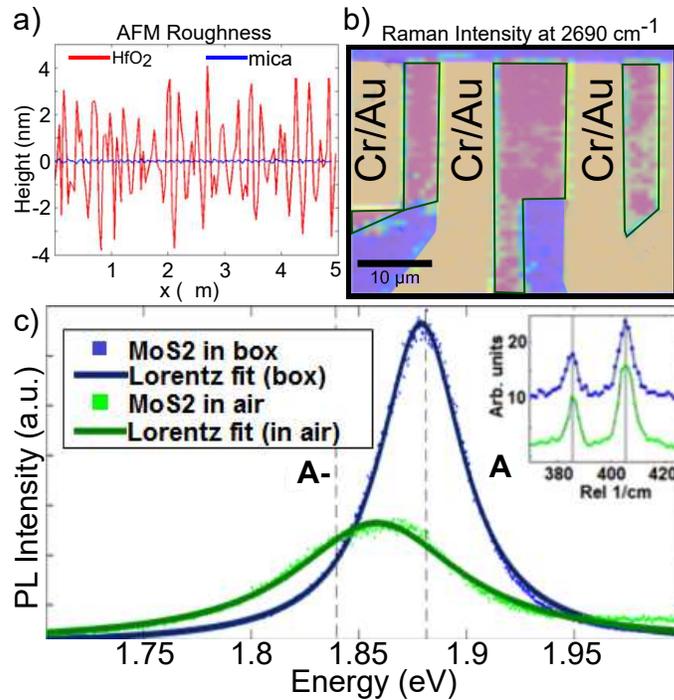


Figure 2.2: a) Line scan using the *in-situ* AFM on a hafnium oxide and mica substrate. This data demonstrates both the effectiveness of our vibration isolation methods and the atomically flat surface of mica. b) Area scan of a patterned CVD graphene device using the *in-situ* Raman system. Graphene is outlined in green while color represents the intensity of the 2D-peak. c) Photoluminescence of MoS₂ exfoliated on mica. Blue data represents MoS₂ which was exfoliated onto mica in the glovebox while green represents exfoliation in the ambient environment. The inset shows Raman spectroscopy in the same conditions as the PL. We note that since the phonon modes do not shift in energy we can attribute this drastic change in PL to the inert glovebox environment and not to the dielectric characteristics of the substrate.

Raman and PL data. These are two-fold, first additional light contamination adding unwanted background signals and change in focus or position of the sample due to vibrations, air currents, and temperature fluctuations. To minimize these effects a simple casing was placed around the entire system, using black plastic sheets and 80-20 aluminum bars. Combined with careful isolation of the fibers and wires via foam sealing to the glovebox, the case enabled high-resolution Raman and PL area-scans like the one shown in Fig. 2.2b and c.

2.3 Sample Fabrication

The ability to create mesoscopic heterostructures has been crucial in the study of 2D materials, by enabling new physical effects and allowing encapsulation for removal to air.[30, 44–50] However, this relies on minimizing additional contaminants from solvents. Thus we constructed a standard dry-transfer system in the characterization chamber. To ensure excellent alignment and minimal drift during transfer, the stage was placed on a thick granite slab, with the required wires and tubing isolated from touching the glovebox chamber directly. The transfer stage has six, fully-motorized stages, three of which are piezo-based Picomotor stages with a 30 nm step size providing precise positioning of the samples relative to one another, such as the heterostructure shown in Fig. 2.1c. Furthermore, this system has produced a number of complex devices including the realization of Coulomb Blockade into atomic defects in a 2D heterostructure[51], observation of hinge modes in a higher order topological superconductor,[52] and CVD graphene sensors of bacteria with single cell resolution[53].

One of the key features of our cleanroom in a glovebox is our photolithography capabilities. In our fabrication chamber, we have an SCS G3 Spin Coater, Angstrom Engineering NexDep physical vapor deposition system, a UHV suitcase transfer system, and a Heidelberg μ PG101 Direct-Write system. The glovebox column has a solvent scrubber installed, which allows for small amounts of solvent to be removed from the system. This keeps the rest of the environment clean while using the photolithographic, lift-off, and cleaning solvents. We employ the use of Qorpak bottles to limit the exposure of solvents to the glovebox atmosphere. These bottles have a PTFE liner in the caps that are resistant to most chemicals while also providing a low moisture transmission rate. In addition, we use activated charcoal as a passive solvent absorbent. Raman, PL, and AFM scans of materials before and after long term exposure to the fabrication chamber revealed no evidence for additional contamination. This is further attested to by our ability to observe quantum oscillations at relatively low fields in graphene devices

fabricated inside (Fig. 2.3c).

The lack of contamination along with the alignment abilities of the mask-less system was crucial in creating high-quality devices and periodic structures (see Fig. 2.3d and 2.3e). The μ PG101 has a resolution of $1\ \mu\text{m}$ with a $20\ \text{nm}$ registry, optical auto-focus and can write up to a 5-inch wafer in one run. We note optical auto-focusing is required as the changing dynamics of the glovebox air prevented the use of standard pressure alignment. The μ PG101 stage runs on an air-bearing that is normally supplied with compressed air from the building, but this is not possible while in a glovebox as the unfiltered air would vent directly into the clean environment. Instead, we inserted a T-junction into the argon path from the cylinder where one side of the junction goes into the cylinder to supply the glovebox and the other supplies the stage with argon for the air-bearing. Not only does this solve the air-bearing problem but it also vents excess solvents and water from the clean atmosphere more quickly. To shut off the air-bearing when the system is not in use, we installed a cutoff valve after the T-junction that is shut when the stages don't need to move.

In a typical nanofabrication process, one must develop and dry the samples in air before moving them into a deposition tool. With an *in-situ* thermal deposition system glovebox users are able to develop and dry the sample in the inert argon environment before transferring them into the deposition tool. Furthermore, the deposition tool contains an *in-situ* plasma-cleaning system so samples can be de-scummed in high vacuum immediately before the deposition of metals. This step can be critical in establishing good electrical contact to certain materials. Following the deposition, small amounts of aluminum can be evaporated onto the samples followed by exposure to a 0.1% oxygen environment, creating an air-protection layer of alumina.[54] This layer of alumina can also be used to protect samples against photoresists during nanofabrication processes as it is easily removed by TMAH-based developers. For example, when fabricating CVD graphene devices we first deposit a layer of alumina before spin-coating

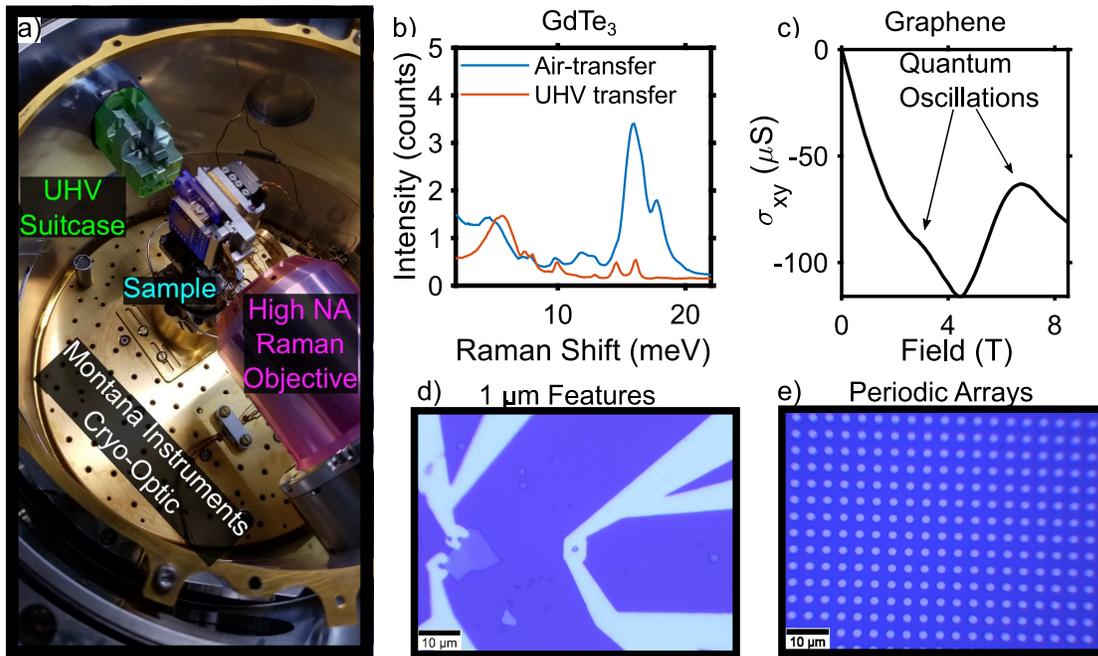


Figure 2.3: a) Photo taken when transferring a sample from the glovebox into the Low-temperature Raman system. Highlighted in green is the transfer arm from the UHV suitcase, in blue is the sample holder mounted onto the cryocooler, and in purple is the high NA Raman objective. b) Comparison of Raman spectra of GdTe₃ demonstrating the degradation of the sample when exposed to air for even a few minutes. c) Hall conductance versus Magnetic Field for a CVD grown graphene sample, fabricated into a hall bar geometry in the glovebox. Even at 7 K, the sample shows quantum oscillations (see arrows). d) Superconducting aluminum loops of 1 μm radius fabricated onto FeTe_{0.55}Se_{0.45} demonstrating the single micron resolution of the μ PG101 photolithography system. e) Periodic arrays of 1 μm gold pillars.

photoresists while the rest of the fabrication process remains exactly the same, including energy dosage and developing times. The areas of photoresist that are developed out also allow for the developer to come in contact with the alumina, removing it as well. Thus we are still able to make good electrical contact to the graphene while preventing contact with the photoresist and other potential dopants.

The deposition tool also opens to the outside allowing users to clean samples with argon plasma or thermal annealing before loading them into the glovebox. An example is our fabrication of CVD graphene devices for use in bio-sensing applications. The CVD graphene is grown on copper foil and thus must be transferred onto SiO₂/Si wafers via wet transfer.[55] In order to clean the graphene, we bake the samples in the deposition tool at 350 °C in 10⁻⁷ mBar pressure for nine hours before alumina deposition (described above) then subsequently transferring samples into the glovebox for patterning. The result of this is samples that are clean enough to not only see quantum oscillations at 8 K and 7 T shown in Fig. 2.3c, but are also able to be used as single-bacterium bio-detectors.[53]

2.4 Ultra High Vacuum Suitcase

After fabrication, samples typically must be taken out of the glovebox to be measured in more specialized pieces of equipment such as surface-sensitive (STM, APRES) or low-temperature transport and optical probes. Furthermore, many new materials and heterostructures are first created by MBE, requiring *in-situ* probes to determine their device characteristics.[56–58] This presents a chance for the samples to see air and degrade. Typically this is avoided by coating the samples with a “capping-layer” (e.g. alumina) or covering mesoscale samples with hBN. However, samples may interact with these materials in unexpected ways such as accidental electrical shorting if the alumina contains many pinholes or if the hBN induces strain into the samples. The addition of hBN to an exfoliated flake could cause additional complexities including

changing the dielectric environment or inducing Moire patterns that, while exciting, make reproducibility of devices quite difficult as both layers must be aligned in the same orientation for every device.[45, 59–65] Another exciting example of eliminating hBN from air-sensitive devices is the β -Fe_{1.1}Se crystal, where recent experiments have shown enhancements of T_c in monolayer films as compared to bulk samples but clean monolayer-devices have yet to be realized.[56, 57] This is in part due to the air-sensitivity of the system at low layer numbers but is also due to the crystal's sensitivity to strain.[66] Recent experiments have shown that the T_c of β -Fe_{1.1}Se thin films change as much as 10 K with 1% strain which demonstrates the problem in making hBN encapsulated devices.[67]

To expand the range of probes and fabrication capabilities of the cleanroom-in-a-glovebox, we designed and built a UHV chamber to couple to various vacuum suitcases (see Fig. 2.1d). The intermediate chamber has a block for attaching different kinds of sample holders allowing us to transfer materials into the glovebox from MBE and out to STM, low-temperature Raman, or electrical transport systems (e.g. see Fig. 2.3a). One measurement system of particular interest is the custom-designed Montana Instruments low-temperature Raman system. This system has been described in detail in other works[68] but has been adapted to be compatible with a UHV suitcase. All of the suitcases that are used follow typical transfer procedures with the addition of a connection to an inlet for Argon gas. Specifically, after the sample is brought into the intermediate space, the suitcase is valved off and Ar added to bring the chamber to match the glovebox pressure. Once matched the intermediate chamber is opened to the glovebox, where the sample holder is brought in using a second manipulator arm. When transferring devices out of the glovebox a baking step is added to the normal process after vacuuming where the entire chamber is heated to 120°C. This step helps remove any excess impurities introduced when exposing the intermediate chamber to the glovebox.

The merits of such work are shown in Fig. 2.3b, where we probe the Raman response of GdTe_3 , established to be highly air sensitive.[34] Two bulk crystals were prepared in the glovebox, then one was transferred into the low-temperature Raman system in air and freshly cleaved just before cool down. The second sample was transferred via the UHV suitcase. The crystal that was transferred in air clearly shows a large tellurium oxide peak around 17 meV that obscures phonon modes.[34, 69] However, the material transferred via vacuum suitcase revealed sharp phonon modes, with the exception of the CDW amplitude mode at low energies. In addition, we found the Raman response to be much more uniform across the sample surface.

2.5 Conclusions

Here we demonstrated the construction and operation of a cleanroom-in-a-glovebox. The system combines the inert environment of a glovebox with the fabrication and characterization facilities of a cleanroom. While modifications had to be made to existing equipment and procedures, the result is a fast and efficient fabrication facility that allows devices made from many air-sensitive systems that were previously unattainable. In addition, the far reduced cost, ease of use, and environmental requirements open the door to using this setup in a wider array of educational as well as research settings.

CHAPTER III

Topology in $\text{FeTe}_{0.55}\text{Se}_{0.45}$

3.1 Introduction

New particles can be a convincing signature of emergent phases of matter, from spinons in quantum spin liquids[70] to the Fermi arcs of Weyl semimetals[71, 72]. Beyond potentially indicating a broken symmetry or topological invariant, they can be put to use in future topological quantum computers[73]. Until recently it was believed the non-trivial topology of the bulk would lead to new states in one lower dimension at the boundary with a system of differing topology. However, higher order topological insulators (HOTI) have been realized[74–79], where the resulting boundary modes exist only at the intersection of two or more edges, producing 1D hinge or 0D bound states. One route to creating these higher order states is through the combination of a topological insulator and a superconductor with anisotropic pairing[80–83]. Usually, this is done by combining two separate materials and inducing superconductivity into the TI via proximity[84–88]. However, this method requires long coherence lengths and extremely clean interfaces, making experimental realization of devices quite difficult. For studying HOTI, as well as the combination of strong correlations and topology, the material $\text{FeTe}_{0.55}\text{Se}_{0.45}$ (FTS) may be ideal, as it is a bulk, high-temperature superconductor with anisotropic pairing that also hosts topologically non-trivial surface states[89–91].

FTS is part of the $\text{FeTe}_{1-x}\text{Se}_x$ family of Fe-based superconductors, which ranges from

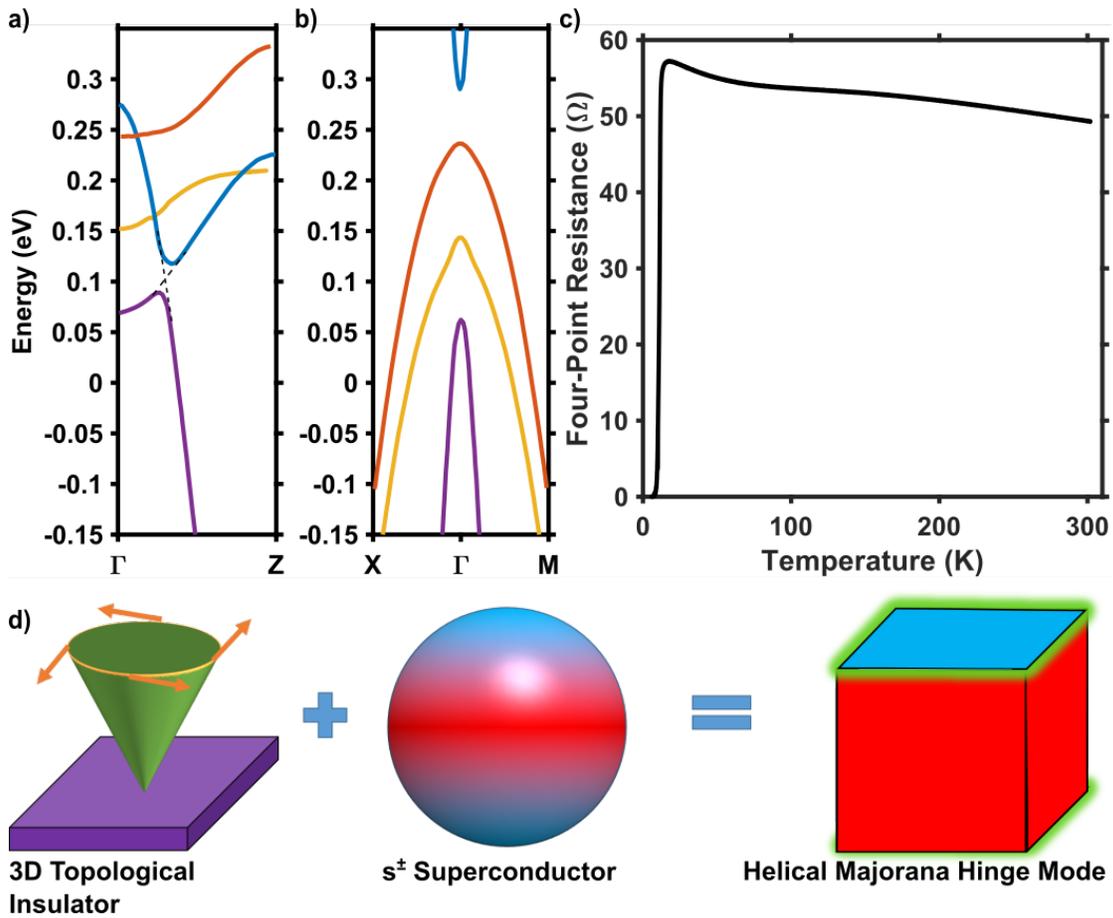


Figure 3.1: a) Theoretical band structure of FeTe_{0.55}Se_{0.45} along the Γ -Z and (b) the X- Γ -M cuts[90]. The p_z orbital of the chalcogenide is shown in blue, crossing the three d-orbitals, resulting in two Dirac points and topological, spin-orbit gap. c) Resistance vs. Temperature graph for an exfoliated flake of FTS, showing a clear superconducting transition around 10K. d) Diagram showing the ingredients needed for a Helical Majorana Hinge Mode

an antiferromagnet in FeTe to a bulk superconductor in FeSe[92]. These generally have the same Fermiology as the other Fe-based superconductors in that there are hole pockets at the Γ -point and electron pockets at the M-points[89, 93–96]. The relative strengths of the interband vs intraband scattering in principle should determine the superconducting symmetry, however, there is a complex interplay between the spin-fluctuation exchange, intraband Coulomb repulsion, and the doping level that all contribute to the symmetry of the superconducting order parameter[97, 98]. Indeed, experiments performed on FeTe_{0.55}Se_{0.45} find no evidence for a node with strong signatures of s^\pm order,[94, 95, 99] while experiments on other alloys suggest nodal s^\pm , anisotropic s-wave, and even p-wave[96, 100–103]. Interestingly, tuning away from FeSe leads to enhanced spin-orbit coupling and bandwidth. As a result, the p-orbital is shifted down in energy, crossing the d-orbitals with opposite parity along the Γ to Z direction (See Figure 3.1a and b). The first two crossings are protected by crystalline-symmetry resulting in bulk Dirac states above the Fermi energy. However, the lowest energy crossing is avoided resulting in a spin-orbit coupled gap, resembling those typically found in topological insulators[90, 104]. While the Fermi level falls into this gap, the original hole and electron Fermi surfaces at Γ and M , respectively, are retained[89, 90]. ARPES measurements have observed the resulting spin-momentum locked surface states, as well as their gapping out in the superconducting state[89, 105]. Additionally, there is evidence from STM that this results in apparent Majorana zero-modes inside magnetic vortices[91, 106, 107].

Recent theoretical work on FTS has suggested that the combination of an s^\pm order parameter and topological surface states could give rise to higher order topological superconductivity[81]. In short, the changing superconducting phase causes the surface states to gap out anisotropically. Depending on the relative strength of the isotropic versus the anisotropic term, this could lead to the [001] and the [100] or [010] face having superconducting order parameters with opposite phase. As shown in Figure 3.1d), this is predicted to produce a pair of 1D Helical Majorana Hinge Modes emerging

at the 1D interface of the top/side surfaces[81]. Whether or not the modes we observe are indeed Majorana modes, the appearance of HHZM requires both s^\pm superconductivity as well as strong 3D TI surface states. Thus observing Helical Hinge Zero Modes in FTS would provide strong evidence that it is an s^\pm topological superconductor.

To search for the HHZM it is tempting to rely on methods previously exploited to reveal the unconventional nature of the cuprates[108]. Specifically, normal-metal/superconductor junctions demonstrated Andreev Bound States resulting from the d-wave order only on [110] surfaces[88, 109–111]. In the case of FTS, this approach is more challenging as one must tunnel into the hinge between [001] and [010] and the modes are nominally charge neutral, thus requiring an Andreev process to be observed[112]. To achieve this, we created 2D atomic crystal heterostructures with thick hBN covering half of the FTS. By draping contacts over the side of the FTS or atop the hBN we can separately probe conductance into the hinge from the c -axis. As expected for modes protected from back-scattering, we find a cusp-like zero-bias peak only on the hinge contacts that is absent from the c -axis junctions. The mode is well-described by a Lorentzian, consistent with other studies on one-dimensional zero-energy bound states[113]. Confirmation that the mode does not result from our fabrication method or defect density is provided by soft-point contact measurements on facets of various bulk crystals (See Supplemental Fig S3). Taken together these data strongly suggest the presence of the HHZM in FTS resulting from its higher order topological nature and the presence of s^\pm superconductivity[88, 114]. The helical hinge zero mode in FTS should only exist in the superconducting state. As such we expect a sharp zero-bias conductance feature below T_c on the hinges between the [001] and side surfaces as compared to purely on the [001] face. Alternatively, Majorana zero modes on the hinge should give quantized conductance, revealed through nearly perfect Andreev reflection.[81] However, as discussed later, observing this quantized conductance may be challenging as the coherence length in FTS is $\approx 3nm$ [102, 103]. To test this we used 2D atomic crystal heterostructures

to simultaneously fabricate Normal Metal/Superconductor (NS) low-barrier junctions on various crystal facets (See Figure 3.2a and 3.2d). The first type of NS junction is a standard lithographically-defined contact that drapes over the edge of the exfoliated flake. This contact will form a junction with the [001] and [100] surfaces as well as the hinge between them. The second type of contact is fabricated by first transferring hexagonal Boron Nitride (hBN) over half of the FTS flake, insulating the side and edge from electrical contact. We then drape a contact over the side of the hBN, forming a junction primarily on the [001] face (See depiction of the side view in Fig 3.2d). The entire fabrication process, from exfoliation to device, is performed in an inert argon atmosphere or vacuum. Patterns for mesoscale contacts were defined using standard photolithography techniques and our Heidelberg μ PG101 direct-write lithography system. Contact areas are then cleaned with an argon plasma at high vacuum immediately before thermal deposition of 5nm of Cr then 45nm of Au. Full fabrication details can be found in the Supplementary.

3.2 Results and Discussion

We first established that our control contacts are only tunneling into the c-axis by studying their base temperature differential conductance. Specifically, we sourced current between a top contact (5 or 6 in Fig. 3.2a) to one of the current leads (#1 or #4), while measuring the resulting voltage between the same top contact and the other current contact. This three-point experiment ensures the conductance results primarily from the interface of the top contact. As shown in Fig 3.2b, we observe a small zero bias conductance peak that is $\approx 20\%$ higher than the background. The shape and height are consistent with previous point contact Andreev reflection measurements along the c-axis of $\text{FeTe}_{0.55}\text{Se}_{0.45}$, [115] and confirms the contacts are in the low-bias, Andreev regime. We note these previous works were performed at temperatures below our base temperature, and as such could resolve the rather small gap. At higher bias, we

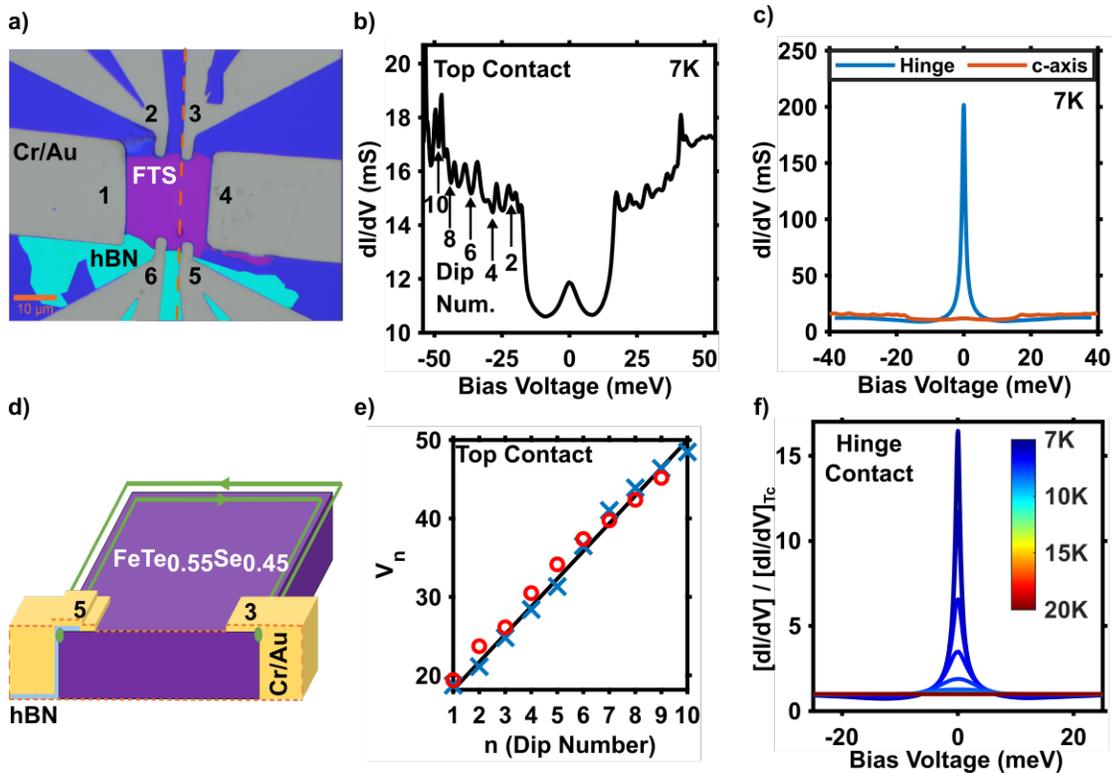


Figure 3.2: a) False color image of the exfoliated device; numbers denote contacts used. b) $\frac{dI}{dV}$ vs DC Bias voltage for contact 5 at 7 K. c) $\frac{dI}{dV}$ vs DC Bias voltage for contact 3 at 7 K. d) Depiction of contact geometry for top only (5) and hinge (3) contacts. e) Dip number vs. Voltage for c-axis only contacts. The black line is a fit to McMillan-Rowell Oscillations which follow the equation, $\Delta V = n \times \frac{h\nu_F}{4ed_s}$. Blue and red points are experimental data extracted from the positive and negative bias voltages respectively. f) Temperature dependence of differential conductance for various temperatures.

observe an enhancement in the conductance at $|V| \geq 20 \text{ meV}$, consistent with spin-orbit induced gap. Above this value, we observe a series of conductance dips that are fully consistent with McMillan-Rowell Oscillations (MRO)[116, 117]. These MRO result from Fabry-Perot like interference of quasiparticles in the normal layer undergoing AR at the interface and reflecting off the back surface of the metal. The MRO are linearly spaced by voltages[116] defined by the equation $\Delta(V) = n \cdot \frac{e v_F}{h d}$ where n is the dip number, v_F is the Fermi velocity at the contact, and d is the thickness of the metal which we set to 50 nm (See Figure 2e). From this fit, we extract a renormalized Fermi velocity of approximately $1.7 \times 10^5 \text{ m/s}$. We note that similar behavior was observed if the current/Voltage was reversed between contacts #1 & #4, we measure from contact #6, or measuring between contacts #6 and #5 exclusively (see Supplemental Fig S4a). This shows the robustness of these results and combined with the detailed spectra, confirm the contacts over the hBN are Andreev tunneling only into the c-axis.

Next, we turn to the spectra measured in an identical manner, but with the hinge contact (#3 in Fig. 3.2a). Since the normal-state and high bias resistance of the hinge contact is nearly identical to the control contact we expect the spectra to be similar. However, as shown in Fig. 3.2c the zero-bias conductance in the hinge contact is quite distinct from the response observed in the control contact and previous point contact experiments. Specifically, we observe a cusp-like zero-bias conductance peak (ZBCP) in the hinge contact that reaches a value 17-times higher than the high bias or $T \approx T_c$ conductance. This rather large enhancement is also likely responsible for the absence of a clear observation of the gap, which would be far smaller. These results provide strong evidence for a zero mode that only exists on the hinge. The "cusp-like" shape and magnitude of the peak could result from an Andreev Bound State (ABS)[108, 110, 111], however, this requires either a node in the superconducting gap or time-reversal symmetry breaking,[118, 119] neither of which has been detected in $\text{FeTe}_{0.55}\text{Se}_{0.45}$ [94–96, 99, 101–103]. As discussed later, direct evidence against the

ABS interpretation is provided by the dependence of the peak on temperature, and near independence on the contact's type (planar, point contact) or material (Ag, Au, Bi₂Te₂Se₁). Interestingly, this behavior is also inconsistent with previous observations of standard Andreev Reflection(AR)[109], Coherent Andreev Reflection (CAR)[120], the Kondo Effect[121, 122], and Joule heating[123].

To ensure the zero bias conductance peak emerges at T_c and is not the result of an ABS, we directly analyzed its temperature dependence by fitting the data with a Lorentzian line shape. This is based on recent theoretical studies on one-dimensional superconducting wires showing that both Majorana Zero Modes and ABS produce a Lorentzian differential conductance spectra[113]. While this may not be the correct model for our case, to the best of our knowledge there are no calculations for the conductance spectra expected from hinge modes in a higher order topological superconductor. Nonetheless, the differential conductance spectra are generally well described by a Lorentzian (see Fig 3.3a). The temperature dependence of the height and width of the peak determined by the fits for the data presented in Fig. 3.2f are shown in Fig. 3.3b & c, respectively. These data provide direct evidence for the connection to the bulk superconductivity, though are inconsistent with an ABS. Indeed, we find that as the temperature is raised, the height of the ZBCP decreases exponentially until it is completely quenched at T_c (see Fig3.2a and Fig3.3b), where we define T_c as the temperature for which $\frac{dR}{dT}$ passes through zero. While lower temperature data are required to determine the exact functional form, it is clear from Fig. 3.3b & c that the mode is substantially different from the $1/T$ behavior typically expected from an ABS. Furthermore, we found a similar shape and temperature dependence in contacts of various barrier height, also inconsistent with standard Andreev reflection.[88, 124, 125]

Similar to the height of the peak, we find the width of the zero bias conductance peak grows exponentially with temperature (see Fig. 3.3). Interestingly the energy scale governing the peak height ($E_H \approx 0.08 \text{ meV}$) and the width ($E_\Gamma \approx 0.1 \text{ meV}$) are quite

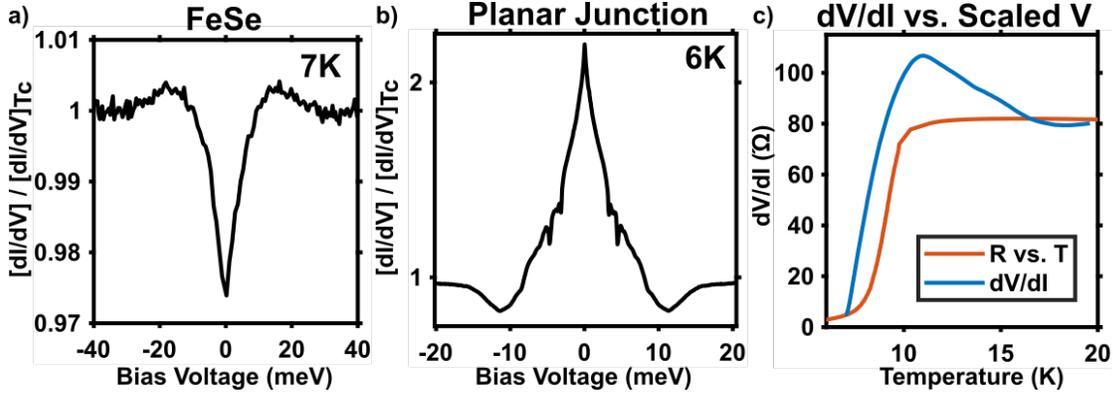


Figure 3.3: a) dI/dV versus voltage normalized to the spectra taken at T_c (solid line) with a Lorentzian fit (dashed line), for $T = 7K, 9K,$ and $15K$. b) and c) ZBCP heights and widths, respectively, extracted from the Lorentzian fit versus temperature. The exponential temperature dependence (orange lines) is at odds with a normal Andreev bound state that follows a $1/T$ dependence. The small energy scale of the exponential may result from the reduced superconducting gap on the side surfaces. While the rather small width at zero temperature is consistent with a topologically protected 1D mode.

close. We note that comparable results were obtained from other contacts revealing the hinge mode. Nonetheless, the energy scales governing the temperature dependence of the mode are far smaller than either the superconducting gap of the bulk or the surface states.[89] However, to the best of our knowledge, the size of the superconducting gap on the side surface has not been measured. As such we speculate this small apparent energy scale results from a much weaker proximity effect on the $[010]$ and $[100]$ surface states. Interestingly, extrapolating the width of the zero bias peak to zero temperature suggests an extremely narrow mode ($\approx 3.5 \mu eV$). While further studies at lower temperatures are required to confirm this extrapolation and the specific shape of the mode, if correct it points to the highly coherent nature of the excitation. As such the temperature dependence is consistent with our expectations for topologically protected 1D modes.

For additional confirmation that the ZBCP does not result from fabrication, exfoliation, impurities or the specific metal used in the contact, we performed a series of additional control experiments, summarized in Fig (3.4). First, the topological gap in

FTS closes with reduced tellurium levels, thus we expect the hinge mode is absent from FeSe. To confirm this as well as the irrelevance of contact type or normal metal used, we employed soft-point contact measurements. For FeSe we observe no evidence of an increase in conductance at zero bias below T_c (see Fig (3.4a)). However, performing the same soft-point contact spectroscopy across multiple different $\text{FeTe}_{0.55}\text{Se}_{0.45}$ crystals always produces an increase in conductance at zero-bias when cooled below T_c consistent with the data on contacts made via photolithography (see Supplemental Fig S3). The soft-point contacts revealed a smaller enhancement of the zero bias conductance in the superconducting state. However this is expected since the quasi-particle lifetime in the Ag paint contact is likely lower, which smears the spectra and reduces the height at zero bias. Similarly, we used planar junctions with $\text{Bi}_2\text{Te}_2\text{Se}_1$ via a method that has previously enabled spectroscopic studies with low barriers in van der Waals materials.[84] As shown in Fig. 3.4b, these junctions also resulted in nearly identical spectra near zero bias. Here the lower zero bias conductance is expected as it contains contributions from the normal material being in series with the contact. Another extrinsic explanation for the peak is the interstitial Fe-atoms known to be present in these materials. However, we excluded this explanation by measurements on annealed samples where the Fe impurity content is dramatically reduced (see Supplemental Fig S3a), though the topology and T_c are only mildly affected.

An alternate mechanism for producing a ZBCP is Joule heating at the contact. We took a number of steps to rule this out. First, similar results were obtained regardless of the exact contact configuration (e.g. swapping contacts employed for current versus voltage in point contact or three-point measurements). In addition, we compared the voltage and temperature data by inverting the $\frac{dI}{dV}$ spectra and comparing it to the resistance versus temperature data taken on the same contact configuration (see Fig 3.4c). To align the two curves, we translate the $\frac{dV}{dI}$ curve such that zero voltage coincides with the temperature at which it was recorded (7 K). Next, we assume the voltage where the

maximum resistance is measured is equivalent to heating to T_C , as this is the temperature where a peak in resistance is typically observed (see Fig 3.1d). While the exact voltage dependence due to heating could be more complex, it is clear the $\frac{dV}{dI}$ versus voltage spectra are far in excess of the resistance measured at T_C , though at high bias they do return to the value measured at T_C . This further excludes voltage induced heating as the origin of the zero bias conductance peak. In addition, the background conductances in the c-axis, hinge, and point contacts are nearly identical. Therefore the heating across all of them should be approximately the same. However, they reveal quite distinct spectra (i.e. strong ZBCP in the hinge contact vs. nearly none in the c-axis) which, combined with the emergence of the zero-bias conductance peak (ZBCP) at T_C in numerous contacts (see Figure 3.2 and Supplemental Figure S2), eliminates heating.

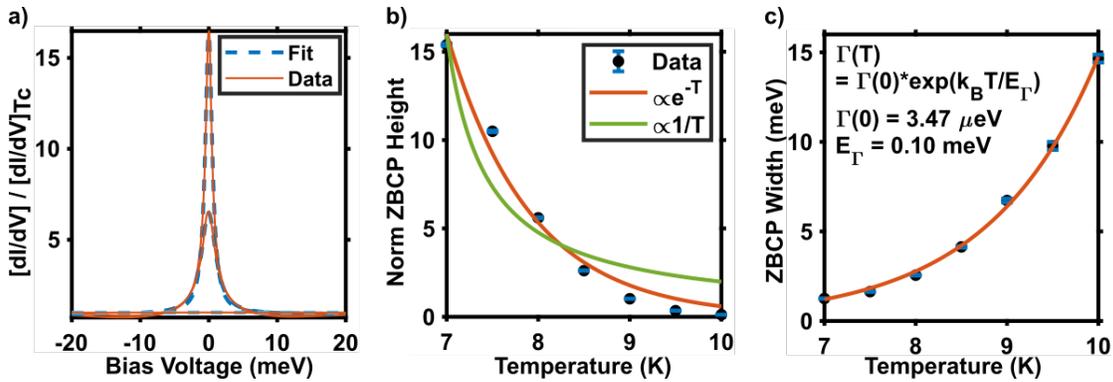


Figure 3.4: a) Soft-point contact on a bulk crystal of FeSe normalized to the critical temperature. b) Differential conductance using a planar junction, revealing a similar zero-bias peak. The smaller height results from the normal resistance of the $\text{Bi}_2\text{Te}_2\text{Se}_1$ that is in series with the tunnel contact. c) Differential resistance versus scaled voltage (blue) plotted along with the resistance versus temperature curve (orange). The strong overshoot of the voltage-dependent resistance and its return at high-bias to the normal state resistance confirms the spectra and zero bias conductance peak are not a result of heating.

3.3 Conclusions

In summary, via a variety of contact methods, we reveal helical hinge zero modes in the topological superconductor $\text{FeTe}_{0.55}\text{Se}_{0.45}$. Specifically, contacts to the [001] surface made using hBN reveal standard Andreev reflection, while those draped over the hinge contain a cusp-like, zero-energy feature in the differential conductance. By combining with measurements using soft-point contacts on various crystals, we further confirm the intrinsic nature of this new mode. Furthermore, the appearance of an HHZM in FTS helps to establish both the topological and s^\pm nature of the superconductivity. An important question raised by these results is the large size and the temperature dependence of the HHZM. It is possible that the large ratio of contact area to coherence length at the measured temperature ($\approx 1000\xi$), makes the measurement essentially many point-like contacts in parallel, leading to an apparently large conductance. The contact size may also play a role in the temperature dependence, as could the unknown size of the superconducting gap on the side surface. Thus future theoretical and experimental efforts must be made to better separate out the contact effects from the intrinsic response of the hinge mode we observe.

CHAPTER IV

New Results in $\text{FeTe}_{0.55}\text{Se}_{0.45}$

4.1 Introduction

Recent works have called into question the exact topological nature of FTS claiming the crystal is not a topological insulator but rather a topological semi-metal with buried Dirac nodes[126]. These works describe how the current DFT-derived band structure of FTS predicts a Fermi energy that is 200 meV below what is observed in ARPES experiments. Furthermore, theoretical efforts to simply raise doping levels within the material reveal a completely different band structure with no topological gap around the Fermi energy. In light of this it is crucial to obtain evidence with more experimental techniques to better understand the nature of the topology in the FTS system. Indeed, the underlying physics which predicts the helical hinge mode also predicts the same mode to manifest as a bias-independent conductance plateau in a differential conductance measurement rather than the previously observed zero-bias conductance peak[52, 81]. In the theoretical work, this helical hinge zero mode should be robust against local perturbations due to the topological protection provided by the anisotropic superconductivity discussed in the last section, however this work reveals . Namely, we find that when tunneling measurements are performed across pristine, high-symmetry crystalline edges bias-independent conductance plateaus consistent with Perfect Andreev Reflection (PAR) are consistently observed below bias voltages of 6 meV. When performing the same experiment across

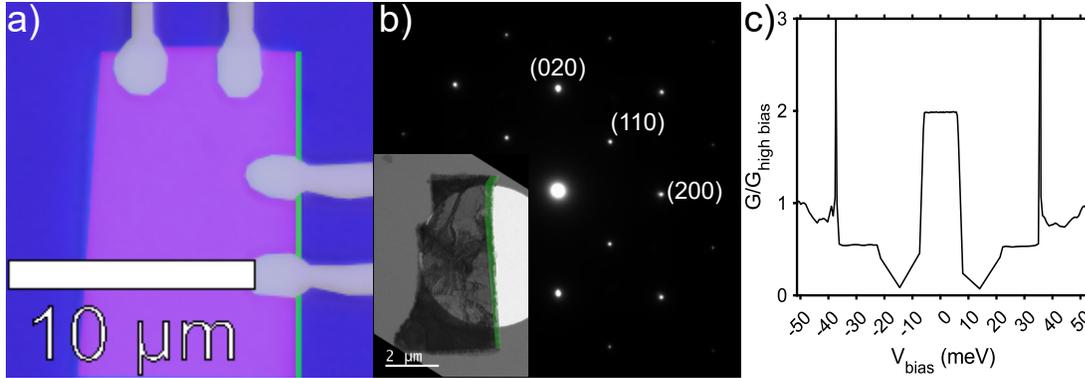


Figure 4.1: a) False color optical image of a representative device with a straight (100) edge highlighted in green. b) TEM diffraction pattern demonstrating the (100) edge. Inset shows the flake measured as well as the diffraction aperture. c) Base temperature differential conductance curve.

“rough” edges such plateaus are not observed. PAR requires the strength of the potential barrier at the interface to be exactly zero. There are many factors that contribute to the magnitude of the potential barrier (Z) including: The difference in Fermi velocity between the two materials, the tunneling barrier, temperature, and electron scattering at the disordered crystal lattice at the contact interface[123]. Thus, observing PAR at 7K for multiple device suggests that there is an underlying mechanism which is allowing the incoming carriers to ignore the potential barrier entirely such as symmetry-forbidden backscattering.[127]

4.2 Observation of Bias-Independent Conductance Plateau

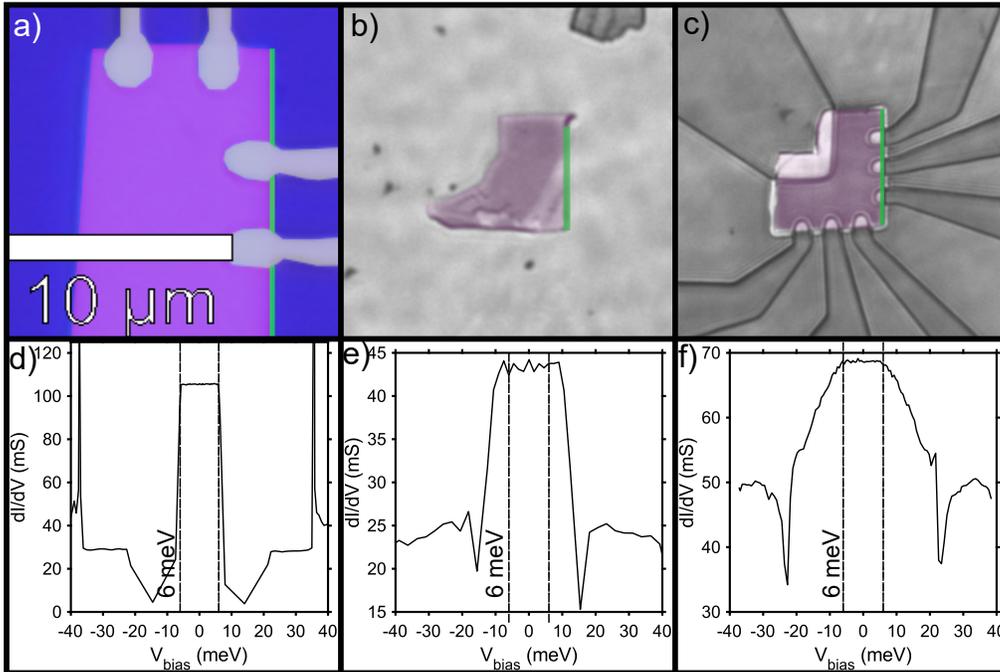
The tunneling conductance of a normal-metal/superconductor interface can be modeled by assuming an delta-function potential barrier at the interface characterized by a strength parameter Z , i.e., the BTK model. An in-depth discussion and pseudo code for performing these simulations can be found in Appendix A], however we will take some of the main results of these calculations for discussions here. The BTK model on a standard Bardeen-Cooper-Schrieffer (BCS) s-wave superconductor predicts a bias-independent conductance plateau only when the strength of the potential barrier

between the normal-metal and superconductor is exactly zero and only at temperatures lower than $0.2T_c$. Even slight deviations from a zero-strength barrier result in significant dips around zero-bias, thus observing PAR is exceedingly rare and typically only occurs only in extremely clean materials [127, 128]. Therefore when PAR is observed in a system it is usually due to an underlying mechanism which causes the incoming carriers to ignore the barrier completely, such as forbidden backscattering due to topological spin-momentum locked bands[127, 129]. PAR has three unique identifiers in a differential conductance spectrum: a perfectly flat plateau, the plateau is at twice the conductance of the normal state, and the plateau extends out to the superconducting energy gap.

To study the effect of edge quality on the differential conductance, we fabricated contacts on flakes which has long straight edges (Fig 4.1a). Using TEM, these edges were shown to be high-symmetry [100] faces indicating a pristine crystal edge (Fig 4.1b). Strikingly, these pristine crystal edges showed a bias-independent conductance plateau at low bias energies. These plateaus are perfectly flat and are exactly twice the normal-state conductance (measured using the conductance values at high-bias). The plateaus extend out to 6 meV in applied bias voltage which is fairly large when compared with the energies measured in the literature however these values have a large range themselves from 1.7 and 2.5 meV in STM and ARPES measurements[89, 130] all the way up to 4.5 meV in other point contact measurements[131]. Both the outer peaks and the plateau shoulders follow a BCS-like temperature dependence (the white dotted lines in Fig 4.4d are drawn using the equation $\Delta(T) = -1.74\Delta_0(1 - \frac{T}{T_c})^{1/2}$ which is valid for $T \approx T_c$) and both quench at T_c , as measured by the sudden drop in resistance seen in Fig 4.4a. Furthermore, this plateau saturates at $2G_n$ as the temperature drops which indicates that this effect is not due to Joule heating due to poor contacts, as discussed in Chapter III see (Fig 3.4 and S. Das, *et al.*[132]).

This bias-independent conductance plateau is observed in multiple devices with straight edges, however when performing tunneling experiments on “rough” edges (i.e.

Straight Edges (Green)



Rough Edges (Red)

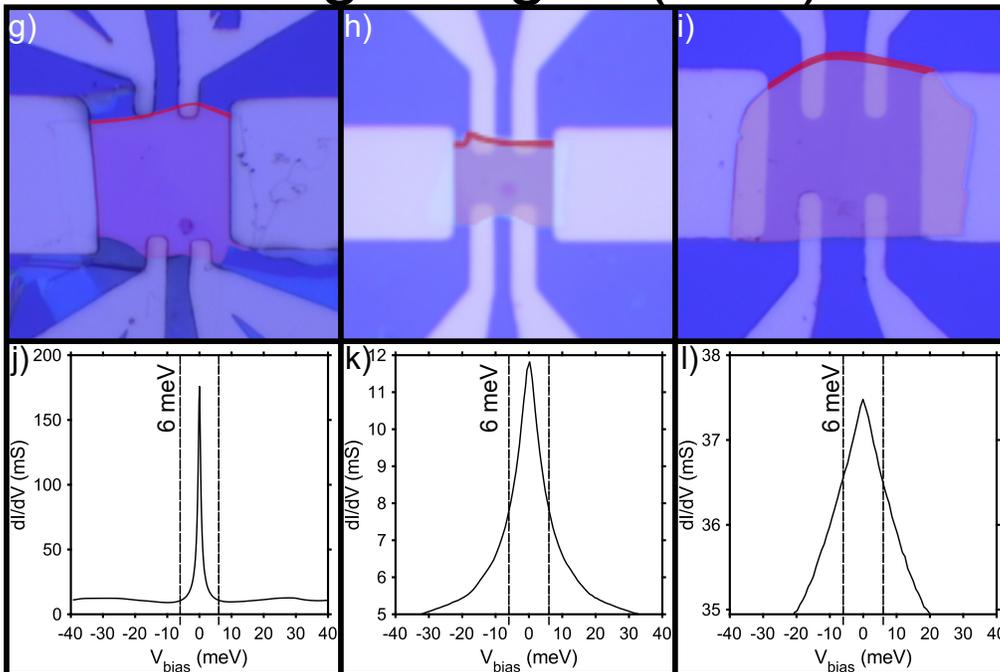


Figure 4.2: Optical photos and associated conductance measurements of straight edges (a-f) versus rough edges (g-l). Measured edges are highlighted in either green or red. The dashed lines in the conductance graphs denote $\pm 6\ \text{meV}$.

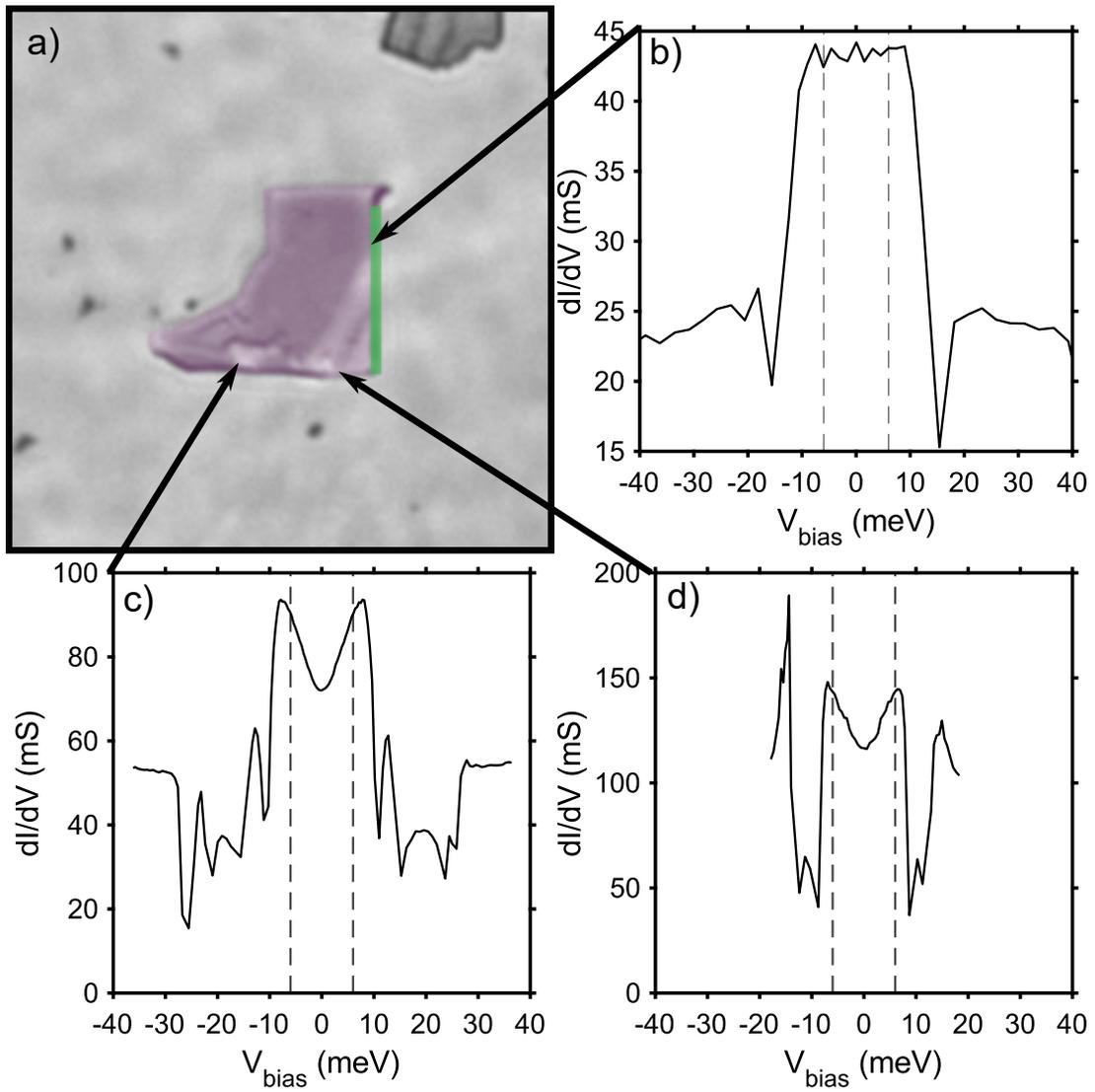


Figure 4.3: Measuring straight versus rough edges on the same device. a,b) Same data as seen in Fig 4.2. c,d) Differential conductance measured across the rough edge of the device in two different points.

edges that are not straight) the differential conductance does not show a plateau at low-biases (Fig 4.2). This pattern follows even when measuring different edges on the same flake as seen in Fig 4.3. In this device, the contact fabricated on the straight edge (highlighted in green) demonstrated a plateau below 6 meV of bias voltage. In contrast, the two contacts fabricated on the rough edges of the same flake both show spectra that are consistent with Andreev Reflection (AR) but with a non-zero barrier strength. This suggests that either the PAR in this system is sensitive to the local contact conditions or the contact to the bulk superconductivity is greatly increased with rough contacts. In the first case, the topological nature of FTS would be immediately called into question as the topology should not be affected by local crystal symmetry breaking. Indeed, this would seem to indicate that FTS would be something closer to a Topological Crystalline Insulator. In the latter case, the PAR is not affected by the local contact conditions but the signal is drowned out among a much larger supercurrent when better contact is made to the superconducting bulk. This better contact might be attributed to multiple contacts points being made by the Cr/Au on the rough edges.

There is a striking difference when comparing the conductance at zero-bias to the BTK model. Indeed, while a BTK calculation with $Z = 0$ displays a zero-bias conductance saturating around $T = 0.2T_c$ the measured zero-bias conductance in FTS saturates at a far higher temperature around $T = 0.75T_c$. This provides further evidence that the PAR is not simply caused by lucky, perfect contacts as it seems the mechanism is only limited by the magnitude of the superconducting gap not by temperature.

4.3 Magnetic Field Dependence

The Dirac surfaces states that are a key signature of a topological bulk are protected via time-reversal symmetry. It follows that if time-reversal symmetry is lifted via a magnetic field, any Dirac nodes that are aligned (the plane perpendicular to the spin-momentum locking determines the “direction” of the cone) along the magnetic field

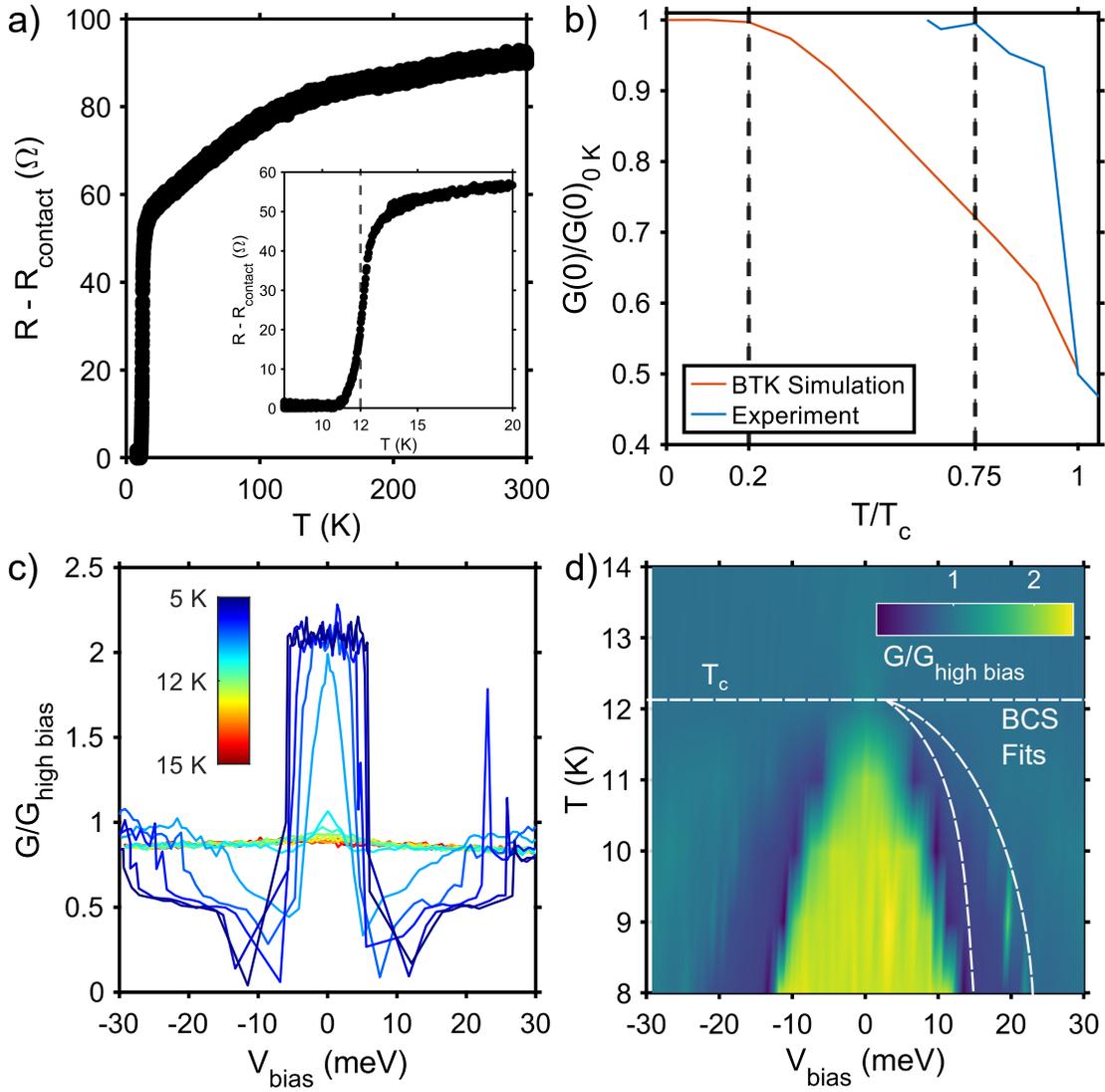


Figure 4.4: a) Two-point resistance with contact resistance subtracted out. b) Comparison of zero-bias conductance for the standard s-wave BTK simulation and our PAR data. c) Differential conductance as a function of temperature. d) Colormap of differential conductance versus a current bias and temperature.

will lose their time-reversal symmetry protection. In contrast, if the Dirac node is perpendicular to the magnetic field, the node will simply shift up or down in energy but the node will keep its topological protection. In this manner, if the PAR is caused by forbidden backscattering due to topological bands we expect highly anisotropic responses to different directions of applied magnetic field. What is observed in the experiment is that when applying a magnetic field parallel with the hinge being measured (the *a*-axis of the material), the PAR remains completely unaffected up to $5T$ (shown in Fig 4.5). Furthermore, when the field is rotated to the *c*-axis of the crystal the PAR seems to collapse quite rapidly which would give credence to a topological origin as discussed earlier. Therefore, while the dependence of the PAR on magnetic field seems to corroborate a topological origin, we must be careful to differentiate the response of the PAR from that of the bulk superconductor. Even though the upper critical field of FTS is around $35T$ [133] the bulk superconducting response of FTS flakes is quite anisotropic, even below $9T$ [134]. Similar to the temperature dependence, this apparent quenching of the PAR might also be attributed to the bulk superconducting gap closing more quickly when the magnetic field is parallel to the *c*-axis of the crystal[134]. Additionally, magnetic fields cause screening currents close to the surface of the superconductor, giving rise to the Doppler effect wherein incoming carriers must match the increased momentum of the superfluid[84]. Therefore, more work must be done in order to attribute the magnetic field response to an underlying topological origin.

4.4 Conclusion

In this work, we extended the scope of our electronic spectroscopy of FTS to uncover exciting underlying physics. Specifically, we used cleaner crystals and lower temperatures to observe Perfect Andreev Reflection in FTS indicating an underlying topological mechanism that allows tunneling carriers to ignore the potential barrier. Interestingly, the PAR only manifests along clean, straight edges not along “rough”

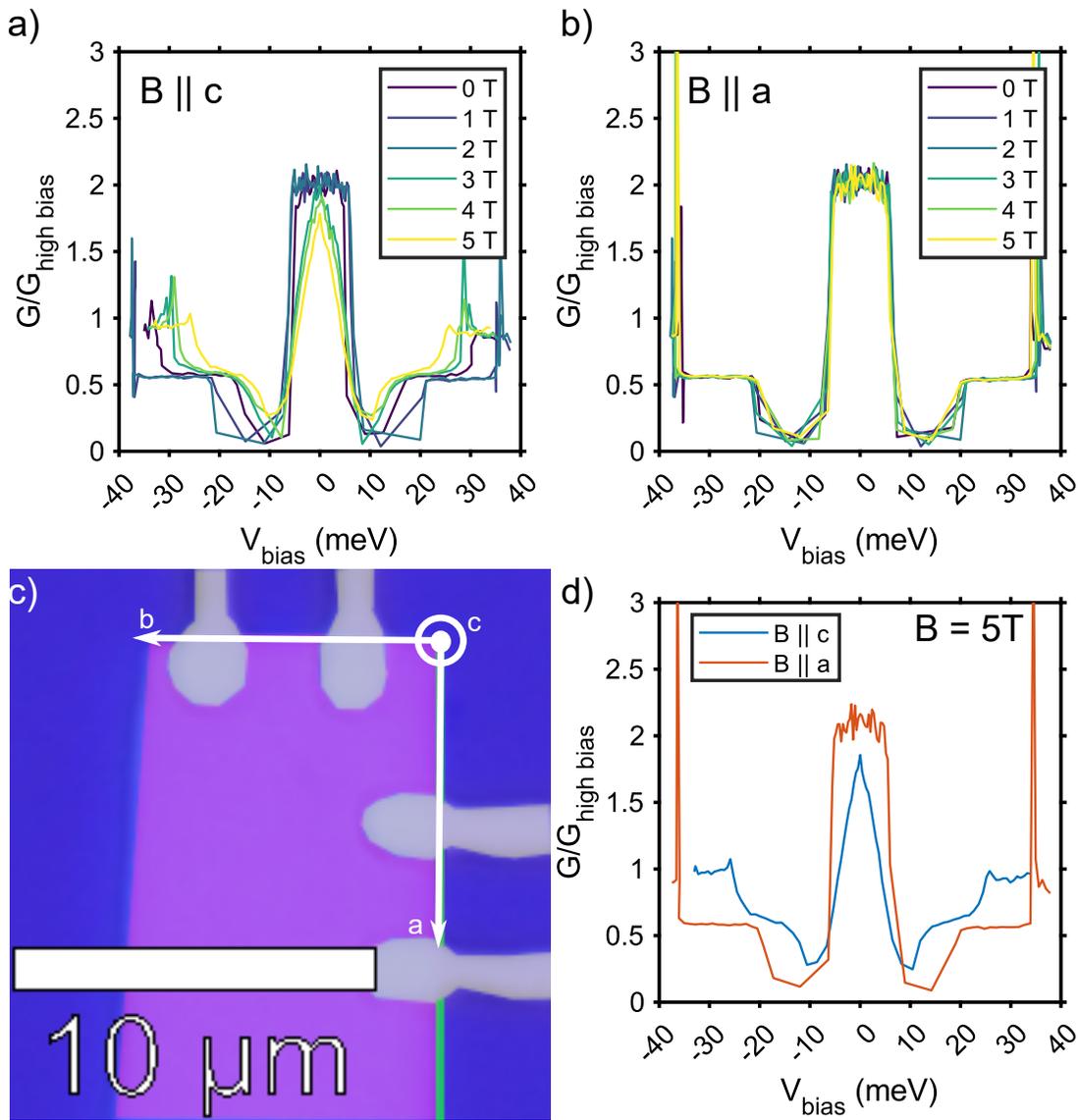


Figure 4.5: Differential conductance as a function of magnetic field for a) a magnetic field that is parallel to the edge being measured and b) a magnetic field that is perpendicular to the magnetic field being measured. d) Comparison of conductance spectra at 5T for both magnetic field cases.

edges indicating that this mechanism is either very sensitive to local conditions or its signal drowned out due to better contact to the superconducting bulk. To further investigate if this mechanism is topological in nature, we explored the response of the PAR to external magnetic fields parallel to the a and c -axis. We found that while the PAR is quenched far quicker in a c -axis magnetic field than an a -axis magnetic field, it is not out of reach to attribute this to the bulk superconducting gap becoming quite small in a c -axis field, rather than the magnetic field affecting the PAR-causing mechanism directly. Further measurements still need to be done to determine if a b -axis field affects the PAR differently from an a -axis field. If it does, then we may be able to use the superconducting Doppler effect to determine where the tunnel junction is and if it is due to a 1D mode along the hinge or a 2D surface along the side of the material.

CHAPTER V

Conclusion

5.1 Summary

In this dissertation we have presented numerous works investigating the topological nature of iron-based superconductor $\text{FeTe}_{0.55}\text{Se}_{0.45}$. To accomplish this, we required a fabrication environment that consistently left the surfaces and edges of the crystals in pristine condition. With this in mind, in Chapter II we discussed the concept, development, and optimization of the “Cleanroom-in-a-Glovebox”. This glovebox takes the workflow from a standard cleanroom photolithography process and condenses it into an inert argon environment. The merits of such works were demonstrated by comparing the Raman signals of various air-sensitive materials before and after exposure to air (Fig 2.3). Furthermore, these materials were subsequently fabricated into electronic devices using photolithography and shown to have high quality Raman signals, demonstrating the power of the glovebox fabrication process. The linear layout of the fabrication workflow was optimized to maximize the number of available machines as well as minimize the time between fabrication steps. We also demonstrated that in addition to its powerful fabrication and characterization abilities, the glovebox is also a perfect tool for training the next generation quantum workforce. The simple interfaces of the fabrication facilities provide a low-stress situation for scientists to learn nanofabrication without fear of breaking the equipment. The conveyor-belt layout of the glovebox

takes the mental load off of the student-scientists so they can focus on the creative and fun aspects of creating mesoscopic devices. Such considerations have already produced fantastic publications and collaborations from scientists of all experiences including summer scientists who were able to make significant contributions to ongoing lab work[52, 53, 135] and collaborators who used the system to great effect answering fascinating questions[34, 51, 69, 136, 137].

In Chapter III we presented strong evidence for a normal mode that exists purely on the hinge or the side of the FTS crystal in the superconducting state. Recent theoretical work has suggested that such a mode could be the result of the combination of an exotic s^\pm order parameter and a topological surface state. In short, the anisotropy of the superconducting phase gaps out adjacent faces of the Topological Insulator (TI) causing a normal mode at zero energy to appear at the hinge between the top and side surfaces. To observe this we fabricated a normal-metal / superconductor junction along the hinge of the material along with a built-in control junction which only contacts the c-axis of the material with the intent to investigate the Density of States (DoS) of the hinge. When performing differential conductance measurements across the control junction a normal Andreev spectrum is observed that is consistent with point-contact measurements made on thin films of FTS. In stark contrast, when the differential conductance measurements were made on the hinge contact an enormous zero-bias conductance peak emerges right below the critical temperature and does not seem to saturate as the temperature is lowered. This is strong evidence of a normal state emerging along either the hinge or side of the material that is not present along the c-axis of the material.

Finally, in Chapter IV we extended the scope of our electronic spectroscopy of FTS to uncover exciting underlying physics. Specifically, we used cleaner crystals and lower temperatures to observe Perfect Andreev Reflection in FTS indicating an underlying topological mechanism that allows tunneling carriers to ignore the potential barrier. Interestingly, the PAR only manifests along clean, straight edges not along “rough”

edges indicating that this mechanism is either very sensitive to local conditions or its signal drowned out due to better contact to the superconducting bulk. To further investigate if this mechanism is topological in nature, we explored the response of the PAR to external magnetic fields parallel to the a and c -axis. We found that while the PAR is quenched far quicker in a c -axis magnetic field than an a -axis magnetic field, it is not out of reach to attribute this to the bulk superconducting gap becoming quite small in a c -axis field, rather than the magnetic field affecting the PAR-causing mechanism directly. Further measurements still need to be done to determine if a b -axis field affects the PAR differently from an a -axis field. If it does, then we may be able to use the superconducting Doppler effect to determine where the tunnel junction is and if it is due to a 1D mode along the hinge or a 2D surface along the side of the material.

5.2 Future Work

Beyond finishing the work put forth in Chapter IV, there is a clear and exciting road forward for FTS and other topological superconductors. Here I lay out some experiments I believe would provide interesting insight into the fundamental physics of FTS.

5.2.1 FeTeSe

In Chapter IV we touched on the concept of symmetries protecting the topology of a crystal. This work provided evidence that there may be an important symmetry on the [100] face of the FTS crystal but it would be useful to elucidate whether this is actually due to the c_4 symmetry, if the contact to the superconducting bulk is better along rough edges, or if it's simply a matter of crystal quality. Here I suggest performing a series of three-point measurements (as shown in Chapters III and IV) on a variety of crystal facets: specifically on the [100], [110], and [010] facets as these would provide the strongest implication of the c_4 symmetry. To accomplish this, one would naturally also need a new fabrication process to cut the exfoliated crystal into pristine edges. Here

we suggest either RIE (in the fashion of graphene heterostructure devices), FIB (such as the beautiful devices shown in the work of G. B. Osterhoudt[138]), or shadow-mask techniques while growing MBE thin-films. Furthermore, if the crystal facet is found to be an essential ingredient to produce PAR then an important next step would be to determine if the PAR also evolves with crystal thickness as this would be a perfect test for topology. In principle, if the topological surface states on opposing faces are not well-separated then these states will hybridize and open a gap. Therefore there should be a clear transition with decreasing thickness, e.g., going from observing PAR to not observing PAR on similar edges.

Along the same line of thought, it would be quite useful to be able to gate these normal modes in and out of the Dirac cone. In principle, if one tracks the normalized conductance as a function of gate voltage, the conductance should plateau at $2G_N$ (where G_N is the conductance across the same contacts but at high bias) while the chemical potential is in the Dirac cone and then start to vary outside of the cone. This would be a direct test of the topology of the band structure put forth in Chapter II. This is of course a heavily idealized prediction of the experiment as there are many bulk bands that cross the Fermi energy that may complicate the data, but to first order I would hope that the normalization process takes care of that. In addition, many preliminary experiments need to be done before this type of device can be realized. The most pertinent of which is to use graphene to contact FTS to see if the PAR is still observed and to make sure the graphene itself doesn't contribute interesting physics to the tunneling phenomena. One would also need to make sure the gating doesn't affect the superconductivity. In principle, the superconductivity should perfectly screen the gate but given the inhomogeneous nature of FTS it would be good to check that gating doesn't destroy the superconductivity by pinching off superconducting paths.

Another interesting parameter to tune would be the Te-doping level of FTS. The hypothesis is that this will produce a similar result to the thickness experiment mentioned

above, i.e., a topological transition as one dopes from FeSe down to FeTe. Much of the explanation given for the topological nature is the widening of the bandwidth when FTS is doped with tellurium, thus there should be a clear transition in the PAR response when measuring different dopings.

Lastly, experiments that delve deeper into the band structure of FTS are of great importance as the underlying topology won't be truly understood until the band structure is understood. While electrical gating allows us to probe the band structure locally, it is not strong enough to delve deeply into the bulk bands. Along this line, I see two paths for LASE to probe the preported Dirac crossings far above the Fermi level. The first would be to dope the material using the powerful technique developed by Yiping Wang, *et al.* wherein the authors demonstrated remarkable doping levels in graphene using proximity to α -RuCl₃[136]. The second would be to excite carriers from the Fermi level up to these buried Dirac crossings using a laser with the appropriate wavelength. However there are many questions with this experiment and there is little theoretical work about this type of experiment on FTS.

5.2.2 Fe-Based Superconductivity

Finally, performing similar experiments beyond FTS is of the utmost importance for myriad reasons. First, while FTS is a fantastic material it is not stoichiometric and thus the exact doping ratio of tellurium to selenium can vary not only from crystal to crystal, but also from flake to flake. As discussed previously, the topology of FTS is expected to depend heavily on the Te/Se ratio therefore even small deviations from the (55,45) ratio can have devastating consequences on experiments. Second, following from the first point, the topology and superconductivity of FTS seems to be quite fragile and thus observations of phenomena which are a direct result of the topology and/or superconductivity pose a problem for the repeatability of such experiments. As an example, a recent high-profile paper observed "nearly-quantized" zero-bias peaks in

vortices of FTS consistent with MZM, however such zero-bias peaks were only observed in 1 out of every 60 vortices[130, 139].

An interesting material to start off these “beyond FTS measurements” with would be LiFeAs as it is also an iron-based superconductor with hole and electron pockets at Γ and M respectively, it is topological, has a high T_c (18 K) and H_{c2} (80 T), and it is stoichiometric[140–142]. In addition, its air-sensitivity should not be a problem for LASE due to the cleanroom-in-a-glovebox, thus LASE is perfectly suited for measurements of this material.

APPENDICES

APPENDIX A

Pseudocode for Andreev Reflection fitting

As mentioned in the main text, Andreev Reflection is the process by which an electron is reflected as a hole at the interface between a normal-metal / superconductor interface. By modeling and fitting our data to this model we are able to extract useful quantities such as the superconducting gap size (at a specific temperature), the transparency of the interface, and the thermal broadening of our spectra from our junction size. Thus, here I layout a condensed version of the BTK calculation for differential conductance across a normal-metal / superconducting interface then I go through pseudo-code on how to fit this calculation to our data.

A.1 BTK Theory

In 1964, Alexander F. Andreev published a paper describing a process by which an electron incident upon a superconductor forms a cooper pair in the superconductor and retro-reflects a hole[143]. This phenomena was originally used to describe the thermal conductivity properties observed in superconductors in the intermediate state where there are many normal sections in direct contact with superconducting sections. It wasn't until 1982 that Blonder, Tinkham, and Klapwijk used the phenomena to calculate the differential conductance spectra across a normal metal/superconductor junction[124].

A.1.1 The BdG Formalism

The key innovation in the BTK model is the use of the BdG equations to match the wavefunctions of the quasi-particles excitations at the interface[124]. Here I will closely follow the explanation of the BdG equations shown in Chapter 14 of "Topological Insulators and Topological Superconductivity" by Bernevig and Hughes[21]. First we start with the Hamiltonian for a single-particle in a simple metal.

$$H = \left(\frac{p^2}{2m} - \mu \right) I_{2 \times 2} \quad (\text{A.1})$$

Where μ is the chemical potential and $I_{2 \times 2}$ is the identity matrix in the spin variables. The second-quantized Hamiltonian is given by:

$$H = \sum_{\mathbf{p}, \sigma} c_{\mathbf{p}\sigma}^\dagger \left(\frac{p^2}{2m} - \mu \right) c_{\mathbf{p}, \sigma} \quad (\text{A.2})$$

Where c^\dagger and c are the quasi-particles creation and annihilation operators respectively. Using the anti-commutativity relation of fermions, $\{c_{\mathbf{p}\sigma}^\dagger, c_{\mathbf{p}'\sigma'}\} = \delta_{\sigma\sigma'} \delta_{\mathbf{p}\mathbf{p}'}$, we can rewrite the Hamiltonian above as,

$$H = \frac{1}{2} \sum_{\mathbf{p}\sigma} \left[c_{\mathbf{p}\sigma}^\dagger \epsilon(p) c_{\mathbf{p}\sigma} - c_{-\mathbf{p}\sigma} \epsilon(-p) c_{-\mathbf{p}\sigma}^\dagger \right] + \frac{1}{2} \sum_p \epsilon(p) \quad (\text{A.3})$$

Where $\epsilon(p) \equiv \left(\frac{p^2}{2m} - \mu \right)$ and we have relabeled the sum index \mathbf{p} in the second term to $-\mathbf{p}$. Here we introduce a new spinor to explicitly label the energy eigenvalues for both spins of both ϵ_p and ϵ_{-p} . E.g., we define $\Psi_{\mathbf{p}} \equiv \left(c_{\mathbf{p}\uparrow} c_{\mathbf{p}\downarrow} c_{-\mathbf{p}\uparrow}^\dagger c_{-\mathbf{p}\downarrow}^\dagger \right)$, then we can rewrite

the above Hamiltonian as,

$$H = \sum_{\mathbf{p}} \Psi_{\mathbf{p}}^{\dagger} H_{BdG}(\mathbf{p}) \Psi_{\mathbf{p}} + \text{constant} \quad (\text{A.4})$$

$$H_{BdG}(\mathbf{p}) = \frac{1}{2} \begin{pmatrix} \epsilon(p) & 0 & 0 & 0 \\ 0 & \epsilon(p) & 0 & 0 \\ 0 & 0 & -\epsilon(-p) & 0 \\ 0 & 0 & 0 & -\epsilon(-p) \end{pmatrix} \quad (\text{A.5})$$

The point of this formalism becomes immediately apparent when we introduce a superconducting pairing potential.

$$H_{\Delta} = \Delta c_{\mathbf{p}\uparrow}^{\dagger} c_{-\mathbf{p}\downarrow}^{\dagger} + \Delta^* c_{-\mathbf{p}\downarrow} c_{\mathbf{p}\uparrow} \quad (\text{A.6})$$

$$= \frac{1}{2} \left[\Delta \left(c_{\mathbf{p}\uparrow}^{\dagger} c_{-\mathbf{p}\downarrow}^{\dagger} - c_{-\mathbf{p}\downarrow}^{\dagger} c_{\mathbf{p}\uparrow}^{\dagger} \right) + \Delta^* \left(c_{-\mathbf{p}\downarrow} c_{\mathbf{p}\uparrow} - c_{\mathbf{p}\uparrow} c_{-\mathbf{p}\downarrow} \right) \right] \quad (\text{A.7})$$

$$\therefore H + H_{\Delta} = \sum_{\mathbf{p}} \Psi_{\mathbf{p}}^{\dagger} H_{BdG}(\mathbf{p}, \Delta) \Psi_{\mathbf{p}} \quad (\text{A.8})$$

$$H_{BdG}(\mathbf{p}, \Delta) = \frac{1}{2} \begin{pmatrix} \epsilon(p) & 0 & 0 & \Delta \\ 0 & \epsilon(p) & -\Delta & 0 \\ 0 & -\Delta^* & -\epsilon(-p) & 0 \\ \Delta^* & 0 & 0 & -\epsilon(-p) \end{pmatrix} \quad (\text{A.9})$$

Using this formalism, we can see that the pairing potential simply couples the upper and lower blocks of the H_{BdG} for the simple metal Hamiltonian. From here we can diagonalize H_{BdG} to obtain the energy eigenvalues.

$$E_{\pm} = \pm \sqrt{\epsilon(\mathbf{p})^2 + |\Delta|^2} \quad (\text{A.10})$$

The quasi-particles dispersion relations for the normal metal ($|\Delta| = 0$) and the superconductor ($|\Delta| = 0.1m$) are plotted in Fig A.1 which also conveniently serves as a perfect

starting point for the discussion of the BTK calculation.

A.1.2 The BTK calculation

First, we consider a normal metal in contact with a superconductor. The dispersion relations for the two are as calculated in the previous section and the barrier in the interface is modeled by a Dirac-delta function with magnitude Z . BTK considers a plane-wave electron incident from the normal metal on the left side of the junction thus when the electron encounters the barrier there are four possibilities (shown in Fig A.1):

- A) The electron is Andreev reflected as a left-moving hole and a right-moving Cooper-Pair transmits into the superconducting fluid.
- B) The electron is specularly reflected as a left-moving electron.
- C) The electron is transmitted as a right-moving electron-like quasiparticle.
- D) The electron is transmitted as a right-moving hole-like quasiparticle.

To solve for the probabilities of each process occurring we first define the momenta in the normal metal and superconductor respectively as,

$$k^\pm = \sqrt{\frac{2m_N}{\hbar^2}} \sqrt{E_{FN} \pm E} \quad (\text{A.11})$$

$$q^\pm = \sqrt{\frac{2m_{SC}}{\hbar^2}} \sqrt{E_{FSC} \pm \sqrt{E^2 - \Delta^2}} \quad (\text{A.12})$$

Then we simply match the boundary conditions, i.e., the wavefunctions and their derivatives are the same at the boundary. Starting with the wavefunctions,

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{ik^+x_0} + C \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-ik^+x_0} + D \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{ik^-x_0} = A \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} e^{iq^+x_0} + B \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} e^{-iq^-x_0} \quad (\text{A.13})$$

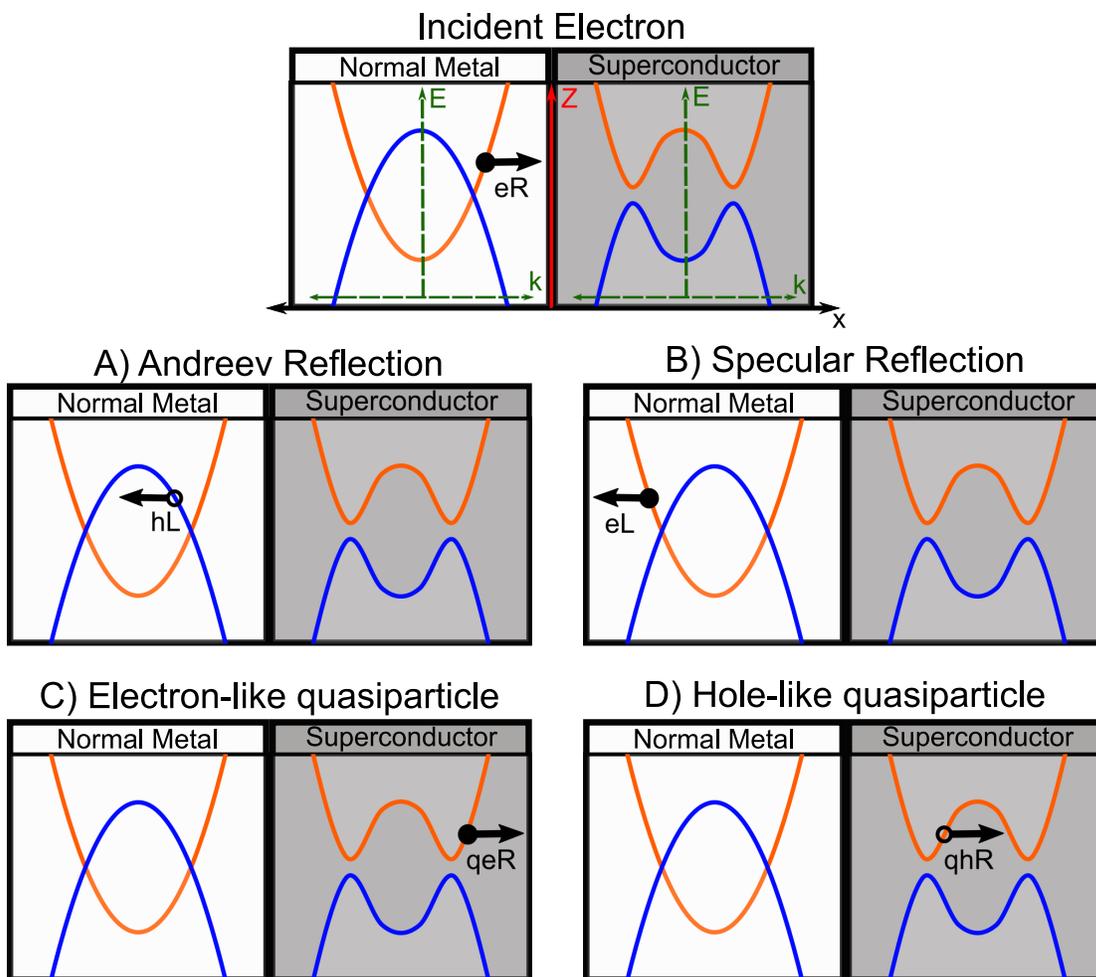


Figure A.1: Dispersion relations for a normal metal and superconductor in physical contact with one another. The red axis denotes the real-space position of the two materials with a potential barrier at their interface. The subset green, dashed axes denote the dispersion relations within the respective materials. A right-moving incident electron (top) can take one of four paths once it hits the NM/SC barrier: A) Andreev reflect as a left-moving hole, B) Normally reflect as a left-moving electron, C) Transmit as a right-moving electron-like quasi-particles, or D) Transmit as a right-moving hole-like quasi-particles.

then the derivatives.

$$\frac{\hbar^2}{2m_N} \left\{ ik^+ \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{ik^+x_0} - ik^+ C \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{-ik^+x_0} + ik^- D \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{ik^-x_0} \right\} \quad (\text{A.14})$$

$$= \frac{\hbar^2}{2m_{SC}} \left\{ iq^+ A \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} e^{iq^+x_0} - iq^- B \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} e^{-iq^-x_0} \right\} \quad (\text{A.15})$$

$$+ \left\{ A \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} e^{iq^+x_0} + B \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} e^{-iq^-x_0} \right\} \quad (\text{A.16})$$

where x_0 is the position of the barrier (it is typically set to zero) and u_0, v_0 are the electron-weight and hole-weight of the quasiparticles, respectively. Thus the transmission coefficients are given by:

$$\begin{aligned} a &= \left(|A|^2 * \left(u_0^2 - v_0^2 \right) \right) \frac{q_{SC}^+}{k_N^+} & b &= |B|^2 * \left(u_0^2 - v_0^2 \right) \frac{q_{SC}}{k_N^-} \\ c &= |C|^2 & d &= |D|^2 * \frac{k_N^-}{k_N^+} \end{aligned} \quad (\text{A.17})$$

Before plugging in the momentum values there are some quick simplification we can make here to improve readability. Using, $v_F^{SC} = \hbar k_{FSC} / m_{SC}$ and $v_{FN} = \hbar k_{FN} / m_N$, we define $Z_0 \equiv H / \hbar \sqrt{v_{FN} * v_{SC}}$. Now we can define the Z parameter that will characterize the potential barrier as:

$$Z^2 \equiv Z_0^2 + \frac{(1 - r_v^2)}{4r_v} \quad (\text{A.18})$$

$$r_v \equiv \frac{v_{FN}}{v_{FSC}} = \sqrt{\frac{E_{FN} m_{SC}}{E_{FSC} m_N}} \quad (\text{A.19})$$

so that we can set $E_{FN} = E_{FSC}$ and $m_N = m_{SC}$. Next, we set $\gamma = u_0^2 + (u_0^2 - v_0^2) Z^2$. Finally, we note that the solution is vastly different in the two scenarios where $E < \Delta$

and $E > \Delta$ thus it behooves us to write them as a piece-wise function.

$$\begin{aligned}
 a(E) &= \begin{cases} 0 & E < \Delta \\ \frac{(u_0^2 - v_0^2)u_0^2(1+Z^2)}{\gamma^2} & E \geq \Delta \end{cases} & b(E) &= \begin{cases} 0 & E < \Delta \\ \frac{(u_0^2 - v_0^2)v_0^2 Z^2}{\gamma^2} & E \geq \Delta \end{cases} \\
 c(E) &= \begin{cases} \frac{4Z^2(1+Z^2)(\Delta^2 - E^2)}{E^2 + (\Delta^2 - E^2)(1+2Z^2)^2} & E < \Delta \\ \frac{(u_0^2 - v_0^2)Z^2(1+Z^2)}{\gamma^2} & E \geq \Delta \end{cases} & d(E) &= \begin{cases} \frac{\Delta^2}{E^2 + (\Delta^2 - E^2)(1+2Z^2)^2} & E < \Delta \\ \frac{u_0^2 v_0^2}{\gamma^2} & E \geq \Delta \end{cases}
 \end{aligned} \tag{A.20}$$

Thus we can simply read-off the differential conductance across the junction as:

$$\sigma_n = 2 * d(E) + a(E) + b(E) \tag{A.21}$$

The plots for various potential barrier strengths (Z) are shown in Fig A.2 along with some other corrections in the next section.

A.2 Pseudo-Code for fitting spectra

Tunneling in a normal metal/superconductor interface can produce wildly different spectra depending on the various parameters such as temperature, barrier height, disorder, and more (see Fig A.2 for a few simple examples). This pseudo-code was written to characterize such superconducting tunneling spectra via the 1D BTK model and extract information such as the superconducting gap. The results of running each individual algorithm are shown in Fig A.2 to show how each parameters affects a tunneling spectrum, however in most cases one will need to use two or more of these algorithms in concert to obtain a good fit for a spectrum. For a full extension of the model to 2D, 3D, and unconventional superconductivity please read the in-depth topical reviews by D. Daghero & R. S. Gonnelli[144] and Kashiwaya & Tanaka[145].

First we write a function (Algorithm 1) that calculates the BTK conductance spectra at zero temperature. The inputs to this functions are: the measured voltage vector in

millivolts (meV), the barrier height (Z), the superconducting energy gap (Δ_{SC}), and the thermal broadening parameter (Γ). This code is useful for understanding what the

Algorithm 1 Single Gap BTK conductance

```

1: function BTK1G(meV, Z,  $\Delta_{SC}$ ,  $\Gamma$ )                                ▶ Returns conductance vector.
2:    $N_q = \left| \frac{meV+i\Gamma}{\sqrt{(meV+i\Gamma)^2-\Delta_{SC}^2}} \right|$                                 ▶ quasi-particles DoS
3:    $N_p = \frac{\Delta_{SC}}{\sqrt{(meV+i\Gamma)^2-\Delta_{SC}^2}}$                                 ▶ Pair DoS
4:    $\tau_n = \frac{1}{1+Z^2}$                                 ▶ Define the transparency
5:    $\gamma = \frac{N_q-1}{N_p}$                                 ▶ Define  $\gamma$  function. Not  $\Gamma$ !
6:    $G = \frac{1+\tau_n|\gamma|^2+(\tau_n-1)|\gamma^2|^2}{|1+(\tau_n-1)\gamma^2|^2}$                                 ▶ G will be a vector.
7:   return G,  $\tau_n$                                 ▶ We return  $\tau_n$  in preparation for the next function.
8: end function

```

conductance looks like at various Z-values, Gap-sizes. The broadening term can be used (or fit) to simulate a finite temperature since (as the name suggests) it is basically a term that broadens the spectral peaks out.

If we want to incorporate the temperature in a more rigorous way we can take the outputs of the previous function then integrate the convolution of their product with the Fermi function (Algorithm 2). I've used an anonymous function since these codes were

Algorithm 2 BTK at finite temperature

```

1: G,  $\tau_n = BTK1g(meV, Z, \Delta_{SC}, \Gamma)$ 
2: for V in meV do
3:    $f_C = G\tau_n \left( \frac{1}{e^{(e-V)/k_bT}} - \frac{1}{e^{E/k_bT+1}} \right)$                                 ▶ Convolution. Outputs a function.
4:    $I_{ns}(V) = \int_{-\infty}^{\infty} f_C dE$                                 ▶ Integrate function over all energies.
5: end for
6:  $\frac{dI}{dV} = |\nabla(I_{NS})|$ 

```

originally written in MatLab however the same task can be accomplished in Python with a lambda function instead. Alternatively, one could also skip the for-loop by implementing the numpy function `numpy.convolve(vector1,vector2)`. Algorithm 3 is a simple extension that allows us to model the conductance with two superconducting gaps.

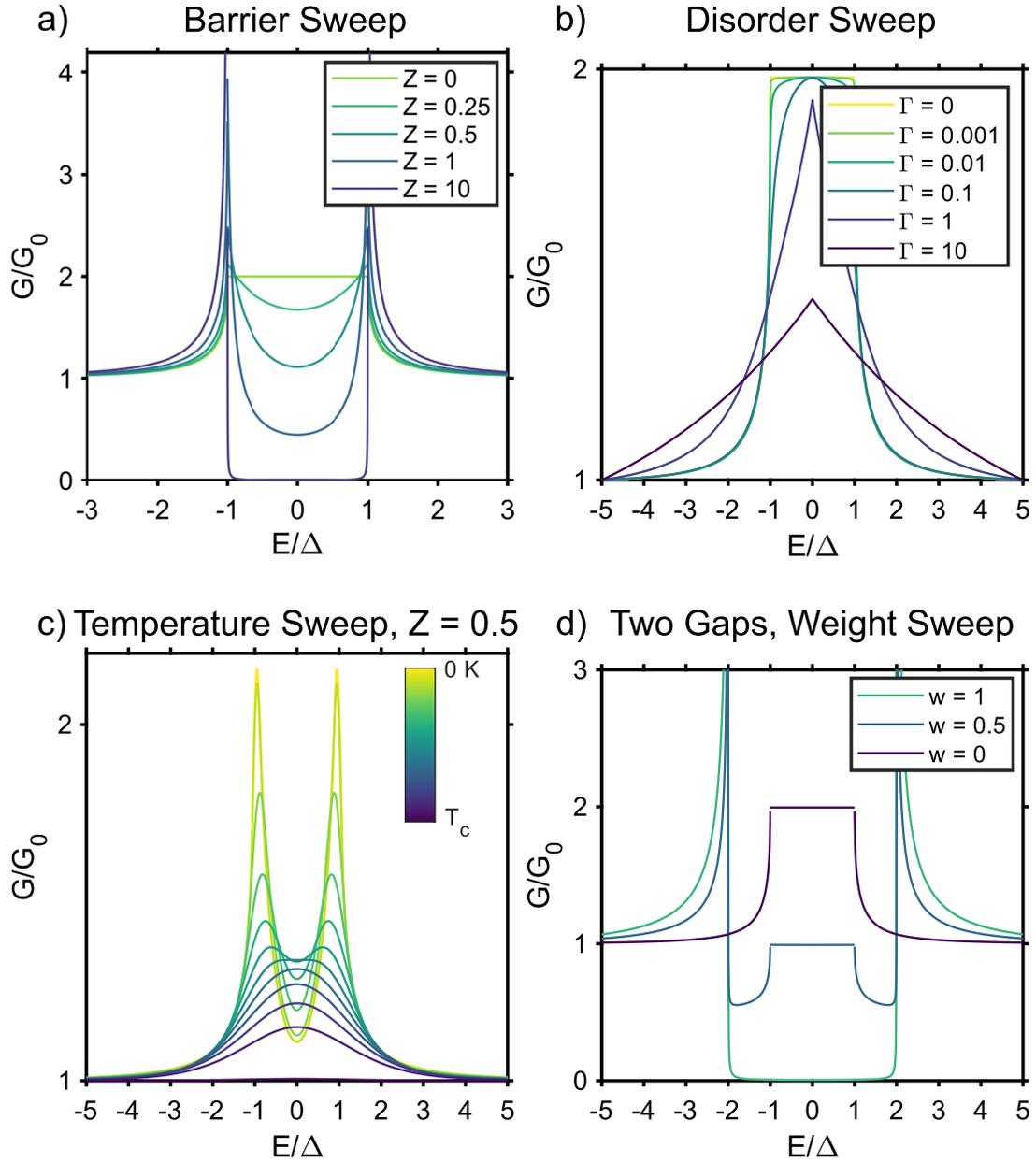


Figure A.2: Various demonstrations of the differential conductance calculated using the algorithms described in A.2. a) Single gap, zero Kelvin sweep of the potential barrier strength Z . b) Single gap, zero Kelvin, zero barrier sweep of the thermal broadening parameter Γ . c) Single gap, half-strength barrier, temperature sweep. d) Two superconducting gaps where the second gap is twice as large as the first demonstrating the w parameter in action.

Algorithm 3 Two Gap BTK Fit

- 1: $G_1, \tau_1 = \text{BTK_at_finite_temperature}(meV, Z_1, \Delta_{SC,1}, \Gamma_1)$
 - 2: $G_2, \tau_2 = \text{BTK_at_finite_temperature}(meV, Z_2, \Delta_{SC,2}, \Gamma_2)$
 - 3: $G = w * G_1 + (w - 1) * G_2$ ▷ w ranges between 0 and 1.
-

Algorithm 4 is another simple function to either fit the temperature-dependence of the gaps to what's predicted via BCS theory or use this function to generate a series of gap sizes for our BTK versus temperature function later. I've presented this as a function so that it's easier to fit with, but this can be defined as an anonymous function (MatLab) or lambda function (Python) to reduce file complexity. Finally Algorithm 5 denotes the

Algorithm 4 BCS Gap

```

1: function BCSGAP( $T, \Delta_0, T_c, \alpha$ )                                ▶ SC gap at temperature T.
2:    $\Delta(T) = \left| 1.74k_b T_c \left( 1 - \left( \frac{T}{T_c} \right) \right)^\alpha \right|$ 
3:   return  $\Delta(T)$ 
4: end function

```

whole script for modelling and plotting a range of temperatures to both single gap and two-gap BTK models using the above functions. Fitting the function varies by platform a bit but the pseudo-code is to define the "BTK and finite temperature" file as the model as use the built-in fit functions.

Algorithm 5 BTK Temperature Fit

BTKTempFit

```

1:  $Temps, dataCell = loadData(folder)$                                 ▶ "load_data" is a script written by G.
   Osterhoudt.
2:  $fig = figure(1)$                                                 ▶ Can use plt.subplot in Python
3:  $G_0 = zeros(length(Temps))$                                        ▶ Will populate with normalization.
4:  $j = 0$                                                             ▶ Iteration variable
5: for T in Temps do
6:    $\Delta_{SC} = BCSGap(T, \Delta_0, T_c, \alpha)$ 
7:    $G = BTK\_at\_finite\_temperature(meV, Z, \Delta_{SC}, \Gamma)$ 
8:   Smooth
9:    $G_0(j) = G(end)$ 
10:   $j+ = 1$ 
11:   $plot(meV, G/G_0)$ 
12: end for

```

APPENDIX B

Model of the differential conductance circuit

As discussed in Chapter III, we are interested in measuring the differential conductance of samples versus a DC bias voltage. This is because the differential conductance of a normal sample is directly proportional to the DoS of a material. To see this, let's start off by considering the contribution of a single carrier tunneling from our contact to the sample, we also must consider carriers tunneling from the sample to the contact:

$$i_{sample \rightarrow contact} = -2e \frac{2\pi}{\hbar} |M|^2 (\rho_s(\varepsilon) \cdot f(\varepsilon)) \cdot (\rho_c(\varepsilon - eV) \cdot [1 - f(\varepsilon - eV)]) \quad (\text{B.1})$$

$$i_{contact \rightarrow sample} = -2e \frac{2\pi}{\hbar} |M|^2 (\rho_c(\varepsilon - eV) \cdot f(\varepsilon - eV)) \cdot (\rho_s(\varepsilon) \cdot [1 \cdot f(\varepsilon)]) \quad (\text{B.2})$$

Where $|M|^2$ is the tunneling matrix element which describes the specifics of the junction (for an excellent breakdown of how this matrix function corresponds to different junction types see Berthod (2011)[146]), $\rho_{s,c}$ is the DoS of the sample and contact respectively, and $f(\varepsilon)$ is the Fermi function. To get the total current across this junction we sum the

contribution from both directions and integrate over all energies.

$$I = -\frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} |M|^2 \rho_s(\varepsilon) \rho_c(\varepsilon - eV) [f(\varepsilon) \cdot [1 - f(\varepsilon - eV)] - f(\varepsilon - eV) \cdot [1 - f(\varepsilon)]] d\varepsilon \quad (\text{B.3})$$

Here we take the derivative with respect to ε to get:

$$\frac{dI}{d\varepsilon} = -\frac{4\pi e}{\hbar} |M|^2 \rho_s(\varepsilon) \rho_c(\varepsilon - eV) [f(\varepsilon) \cdot [1 - f(\varepsilon - eV)] - f(\varepsilon - eV) \cdot [1 - f(\varepsilon)]] \quad (\text{B.4})$$

Thus at a given bias voltage (eV) and temperature the differential conductance is proportional to the product of the densities of states of the sample and contact. Therefore if the contact has a constant DoS in energy, the differential conductance is directly proportional to the DoS of the sample.

When probing a sample in the superconducting state, the differential conductance can be used to probe the superconducting characteristics of the system. As an example, the BTK theory discussed in Appendix A demonstrates how to use the differential conductance versus bias voltage curve to determine the magnitude of the superconducting energy gap.

B.1 Measuring differential conductance

One method of measuring the differential conductance is to measure the current-voltage characteristics and then take a numerical derivative. This can be time-consuming to get enough data to ensure a low-noise $\frac{dI}{dV}$ curve and can lead to resolution limitations. An alternate method is to add a small AC voltage on top of the DC voltage then measure the resulting AC current. In this case, we can express the current response as a Taylor

series:

$$I(V + v \cos(\omega t)) = I(V) + \frac{dI}{dV} v \cos(\omega t) + \frac{1}{2} \frac{d^2 I}{dV^2} v^2 \cos^2(\omega t) + \dots \quad (\text{B.5})$$

Thus the signal measured at frequency ω will be proportional to the first derivative of the current-voltage characteristics. We can therefore use a Lock-In Amplifier (LIA) to directly measure the differential conductance without any numerical processing. Then we can probe the DoS for a range of the band structure by sweeping the bias voltage and measuring the $\frac{dI}{dV}$ at every point.

B.2 Circuit construction

Now let's see how this model is executed in the lab by examining the AC + DC adder circuit in more detail. The circuit as of May 2021 is shown in B.1. As we are interested in measuring the bias voltage across the junction (rather than the bias current) we start by sending in a DC voltage (point A) with a BK Precision 1785b. Given that this power supply only has 10 mV resolution and that the spectroscopic features we are searching for are of order 1 mV, we need to use a voltage divider (point B). This voltage divider introduces some problems that will be discussed in the next section. The AC voltage is then added to the DC voltage via a one-to-one transformer (point C) which has the added benefits of isolating the AC signal from the rest of the circuit. The AC signal can be sent through an attenuating circuit first if the current is too large. To find the current going through the sample we either insert a resistor in series with the sample or use a current pre-amplifier (pre-amp) but in both cases, the AC and DC voltages over the resistor (or output from the pre-amp) are measured in parallel (point E). The current going through the sample is then simply the measured voltage divided by the resistor (or 1/sensitivity if using the pre-amp). We also measure the AC and DC voltages at the sample so that we do not need to assume the voltages we output are actually what is placed across the

sample (point D).

B.2.1 Circuit troubles and solutions

The SR-570 Low Noise Current Preamplifier was found to send out a large voltage spike ($\sim 1\text{V}$!) across the circuit when switching sensitivities, which often damaged or destroyed the device. For this reason we switched to using the resistor method. For higher resistance devices in which a pre-amp is needed to measure a much smaller current it is recommended that the user ground the device, disconnect the pre-amp, make the gain and sensitivity adjustments, then reconnect and unground the device. This is a slow process but it will ensure the pre-amp voltage spike does not damage the device under test.

The governing physics behind the voltage divider is shown in the equation,

$$V_{out} = V_{in} * \frac{R_2}{R_1 + R_2} \quad (\text{B.6})$$

however this model assumes that the output voltage is over an open circuit meaning that the resistance of the sample is large compared to R_2 . When samples have a small resistance, the output voltage can change drastically from the expected value. This is especially concerning when the resistance of a sample changes drastically over a single measurement as can be the case when measuring superconducting tunneling. One solution is to use commercial voltage regulators to ensure a steady voltage is maintained even at high currents. However, most of these commercial voltage regulators have a minimum voltage output around 1.2 V which is three orders of magnitude larger than our 1 mV resolution requirement. Another solution is to switch to current-biased measurements when dealing with low-resistance samples however converting back to bias voltage can be quite tricky as will be discussed in the next section. Lastly would be to simply use a commercial high-resolution DC voltage source such as the DC205 DC

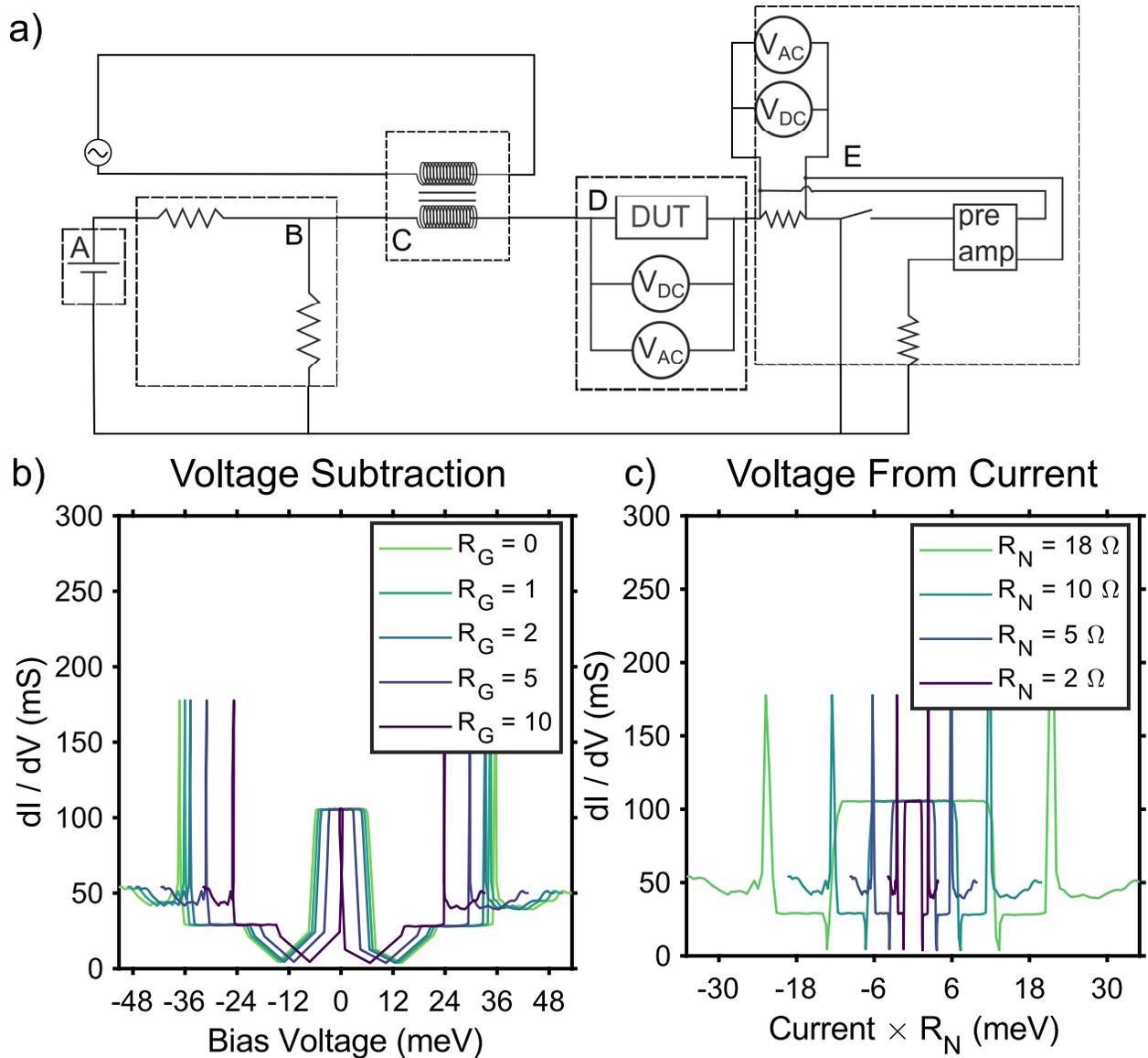


Figure B.1: a) Circuit diagram to add AC and DC voltages then measure differential conductance as a function of applied DC bias. b) Voltage correction of data in Chapter IV via subtraction of extra measured voltage due to the system resistances along the way. c) Voltage correction of the same data by measuring the resulting current and multiplying it by the normal resistance.

Voltage Source from SRS in order to eliminate the voltage divider completely. These sources can be quite expensive but offer resolutions down to the μV level.

B.3 Three-point measurements

Lastly, I would like to discuss some peculiarities with the three-point measurements used in Chapters III & IV. In particular, since we use the measured voltage across the junction as our bias voltage (independent axis) we need to carefully consider what voltage is actually being applied across the relevant part of the junction. To illustrate, the reason a four-probe (Kelvin) measurement is preferred when determining a sample's resistivity is the Kelvin resistance does not include contact resistance[147]. However in our measurement the quantity that we are measuring *is* the contact resistance thus we want to be sure we don't split that resistance out of our measurement. This presents an issue as the resistance of the chrome/gold contacts will also stay in the measurement and add additional voltage to our bias voltage reading. There are two ways to correct for this: 1) Use the resistivity of a control chrome/gold device to subtract out the resistance (and voltage) or 2) convert the measured current back to a voltage by multiplying by the normal state resistance of the junction. The results of both corrections are shown below for varying values of gold resistance.

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