Visualizing Quasiparticle Scattering of Nematicity in NaFeAs and of Topological Surface States in MoTe$_2$

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Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences

Columbia University

2018
Abstract

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Scanning tunneling microscopy has been a powerful tool in expanding our understanding in the study of condensed matter physics. Many of the exotic materials of interest exhibit rich phases of matter at different temperatures and pressures. In order to probe the rich array of phases we developed a novel technique of combining scanning tunneling microscopy with tunable temperature and tunable mechanical strain in ultra high vacuum conditions.

The mechanisms that give rise to high temperature superconductivity has been a long standing problem in physics. The discovered of iron-based high temperature superconductors (pnictides) have spurred much research into the mechanisms that give rise to the different exotic states observed in these new materials in hopes to better understand the underlying nature of unconventional superconductivity. Here we present a detailed study of the Nematic ordered phase in the prototypical iron-based high temperature superconductor, NaFeAs. Using our novel strain, temperature, scanning tunneling microscopy technique, we can attain an atomic-resolution view of the effects of the nematic phase on the local density of states along with the effects of anisotropic strain on the electronic structure. We further systematically study NaFeAs along both axes of the phase diagram, tuning temperature and Cu doping. We probe the material from the parent compound to beyond the superconducting dome with increased Cu doping and from superconducting temperatures to
well above the structural transition temperatures.

Using our novel strain, temperature, scanning tunneling microscopy technique we nanoscopically identified the region of long-range nematic order and the region of nematic fluctuations in the phase diagram and find that true long range nematic order sets in at the tetragonal to orthorhombic structural transition temperature but nematic fluctuations continue at higher temperatures and also into the overdoped regime, then seemingly disappearing at the edge of the superconducting dome. We further find that our applied stain increasing the amplitude of the nematic fluctuations showing strong nonlinear coupling between strain and electronic nematicity.

The power of our novel strain, temperature, scanning tunneling microscopy technique in probing quasiparticle interference proves ideal for studying the topological, Weyl semimetal 1T'-MoTe\(_2\). In it’s orthorombic phase the material has topologically nontrivial protected surface Fermi arcs. By measuring quasiparticle interference in this material at different temperatures we can probe both topologically nontrivial phase (orthorhombic phase) and the topologically trivial phase (monoclinic phase). In the topologically nontrivial phase we see quasiparticle interference measurements in good agreement with angular resolved photoemission spectroscopy and theoretical calculations. In the topologically trivial phase we see the lack of the quasiparticle interference coming from the trivial surface state.
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Acknowledgements

It has been quite the journey in my graduate career. There have been many people who have helped, pulled, and pushed me to its end.

Many thanks to Marcel Agüeros and Summer Ash for their unwavering support throughout my time in the Bridge Program. They pushed me to be a better academic and instilled a self-confidence throughout my time in the program. Thanks also to my former undergraduate advisor, Wendell Hill, who put me in contact with Marcel Agüeros. When I came to him in need of someone to talk to, not only did he listen to me but he went out of his way to help which led me to where I am today.

I would like to thank my advisor, Abhay Pasupathy, who gave me a chance when no one else would. He allowed me to grow into the scientist that I saw in myself and provided the support when needed. His type of management and insightful knowledge was the right combination I needed during my professional growth.

In my research group I cannot thank enough my three labmates who I grew very close to and who were instrumental in me getting as far as I have. Thanks to Ethan Rosenthal who took me under his wing and guided me in the lab and in research. Thanks to Carlos Argüello who helped immensely on class work and spent countless hours talking about our respective journeys. To Chris Gutiérrez for providing a role model on how a first generation Latino can become a successful physicist. Thanks to all three for the good times, the stressed out times, and the fun times! Without their
presence graduate school would have been insurmountable.

I also need to thank Georg Pohl, Tyler Evans, and Soumyo Mukherjee. They were the reason I survived quantum mechanics my first semester, and proved to be the friends who I could count on throughout graduate school. Although I didn’t interact with them on a daily basis, knowing I had people to count on whenever I needed it made this endeavor possible.

It was a bittersweet moment when I became the senior in the lab. As I gained more responsibility my core day in day out support group of Ethan, Carlos, and Chris all had graduated and moved on to bigger and better things. Fortunately Lior Embon, Alex Kerelsky, and Drew Edleberg kept me sane, both with their help in the lab and their friendship. They are the reason that I have been able to truly enjoy my last years in graduate school. I also need to thank Sky Cheung, Ali Dadgar, and Dennis Wang for lending an ear, and giving me their support whenever I needed it.

Thanks to my friends Steven Mohammed, Chris Medina, Angelo Esposito, and Nate Saffold. I met them at different times in my graduate years but they all have made my time at Columbia much more enjoyable. They have always been available to blow off steam or to commiserate over graduate school woes.

Thanks to my close childhood friends Mosi Forde, Ariel Rosales, and Alfredo Guevara. As we have grown older we have carved out our own lives, which unfortunately means we see each other much less than we used to. But even so, they are always a phone call away whenever I’ve needed. No matter how much time has passed between when we see each other, we always fall right back into our old usual ways in our friendships. The comfort of their friendships has kept me grounded, and I couldn’t think of a better group of people to always have on my side.

Many thanks to my loving parents, Fernando Andrade and Montserrat Andrade, who without them I wouldn’t be here today. They risked everything they knew to
come to a foreign land, escaping war, to better our future. To my father, who didn’t
know how to use a computer himself but who bought me my first computer at the
age of 15 not knowing how instrumental it would be in nurturing my technical and
scientific interest. To my loving mother who was incredibly tenacious at figuring out
the public school system, medical care, and government bureaucracy to give her family
the best opportunities she could. She has been the most loving and unconditionally
supportive person in my life. Thanks to my brothers, Ricardo Andrade and Sergio
Andrade, who have put up with all my antics throughout our lives and stuck with me
nonetheless, even though I know they didn’t have much of a choice! To the rest of
my family living in El Salvador and Montreal, even though I occasionally saw them
I know they are always there whenever I need them.

And lastly I have to thank my girlfriend, Kelsey Hendricks. She has been there for
me throughout this entire journey. She has seen my growth over the near decade that
I’ve known her. She has seen me at my worst and at my best and has loved me all
the same. Her support, her sense of humor, her sense of adventure, her mere presence
has not only made this graduate school journey so much brighter and happier but
has made my life’s journey incredibly joyful and full of charm. While the unknown
future can be a scary thought, I know life will be fine knowing she’ll be by my side.
Para Mis Padres
Chapter 1

Scanning Tunneling Microscopy

Theory

Scanning tunneling microscopy (STM) exploits the counterintuitive physical phenomena where particles have a non-zero probability to tunnel through a potential barrier. In order to achieve this in the lab, STM consists of having an atomically sharp tip at distances of angstroms from a sample. Under these conditions the probability of electrons tunneling between the sample and the tip and visa versa is quite small, but non-zero, and we are able to read a constant current of electrons that have tunneled between the sample and tip.

1.1 Tunneling

Particle tunneling is quite a strange physical phenomenon in the quantum regime but it nonetheless falls out of the wave-like, probabilistically description of particles from the Schroedinger equation 1.1. This is commonly taught at the undergraduate level in physics courses and is at times easy to forget how strange the quantum world really
is with the hindsight of having a fleshed out quantum theory 1.1 over many decades as well as exploiting such phenomena in our labs on a daily basis.

\[
\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} = (E - U_0)\Psi(x) \tag{1.1}
\]

The basic solution to the Schroedinger equation 1.1 is an exponential equation 1.2

\[
\Psi(x) \propto e^{-kx} \tag{1.2}
\]

\[
k = \sqrt{\frac{2m(E - U_0)}{-\hbar^2}} \tag{1.3}
\]

We can see that depending on whether \(E > U_0\) or \(E < U_0\) we either get a real or imaginary \(k\) from equation 1.3. Therefore when \(E > U_0\), we get imaginary exponential which corresponds to sinusoidal solutions to the Schroedinger equation. If instead, we have \(E < U_0\), and hence inside the potential barrier, we get an exponential decaying solution. In figure 1.1, we have a simple cartoon description of what this probabilistic wave solution looks like. Outside the potential barrier we have some probability amplitude of finding the particle, inside this probability amplitude decays exponentially, and then on the other side of the barrier we have a smaller, non-zero probability amplitude of finding the particle. This is the basic quantum tunneling phenomena exploited by STM and is used as the probing mechanism to study different materials.
1.2 Scanning Tunneling Microscopy

During actual experimental conditions where an STM functions, it is a bit different than the single particle tunneling picture described in the previous section. When we bring a sample and a tip atomically close to each other, both the sample and the tip contain a “sea” of electrons. The potential barrier can be approximated by the average work function $U$ equation 1.4 (i.e. the minimum amount of energy required to remove an electron from a solid) consisting of the work function between the tip and vacuum $U_{tip}$ and the work function between the sample and vacuum $U_{sample}$ figure 1.2a.

$$U = \frac{U_{sample} - U_{tip}}{2}$$  \hspace{1cm} (1.4)

In principle, tunneling occurs from either sample to the tip or the tip to the
sample. Therefore in order to create a current we create a small electric field by
applying a bias voltage between the sample and the tip ($V_{bias}$) that is much smaller
than the work function, figure 1.2b. The wave function therefore decays as equation
1.5.

$$\Psi(x) \propto e^{-x} \sqrt{\frac{2m}{\hbar^2}}$$  

(1.5)

$$I \propto \sum_{E_F - V_{bias}}^{E_F} |\Psi(d)|^2$$  

(1.6)

Here $x$ is the distance between the sample and the tip (i.e. the potential barrier
width). The probability of finding an electron a distance $d$ into the potential barrier
is the square of the wavefunction $|\Psi(d)|^2$ and therefore the current is the sum of all
these probabilities, equation 1.6, summed up to the Fermi level $E_F$.

![Figure 1.2: Cartoon of the work function between sample and tip (a) with no voltage
bias applied and (b) with a voltage bias applied between the sample and the tip.](image)

The current will therefore drop as $\propto e^{-d}$ and we can use this in order to probe
differences in height on the sample. We can create a feedback loop where we force the tip to maintain a constant current at all times by allowing the tip to either retract or extend in order to maintain the same current (i.e. the same distance \( x \)). The current will change as the tip moves over a bump or a hole and the feedback loop will move the tip away or towards the sample respectively. By scanning a surface and rasterizing the change in tip height, we can then create topography data sets of the surface of a sample. In figure 1.3a, we see a typical topographic data set of a gold crystal. We can clearly see ripples on the surface of gold caused by a surface reconstruction where certain atoms 'buckle' into pairs of lines called herringbone near the gold surface and vacuum interface in order to minimize it’s energy \([2][3]\). In figure 1.3b, we see the same topographic data set but represented in a 3-dimensional plot where we can clearly see the presence of steps of different heights on the surface of gold.

Figure 1.3: (a) A topographic image of a gold crystal. (b) A 3D plot of the same topographic image.
1.2.1 Bardeen’s Solution

What I’ve outlined so far is a simplified view on the tunneling actually occurring in experiment. Bardeen has a more complete solution for the tunneling between a sample and a tip [4][5]. He concluded the tunneling current \( I \) equation to be

\[
I = \frac{4\pi e}{\hbar} \int_0^{eV} \rho_{\text{sample}}(E_F - eV + \epsilon) \rho_{\text{tip}}(E_F + \epsilon)|M|^2 d\epsilon
\]  

(1.7)

In Bardeen’s solution, \( \rho \) is the density of states of material and \( M \) is the tunneling matrix that in principle can depend on many factors such as tip shape and the wavefunctions in the materials we use. In practice, we make certain assumptions to simplify our current equation 1.7. We assume plane waves along the direction of the tip and sample, the shape of the tip to be spherical, and that our applied bias to be much smaller than the work function. We further try to simplify the tunneling equation 1.7 by using a material for that tip that has a very flat density of states, therefore in the energy range that we probe samples, our tip’s density of state is more or less independent from energy. These assumptions and simplifications allow us to treat matrix element \( M \) as energy and space independent as well as treating \( \rho_{\text{tip}} \) as energy independent. With these simplifications, we can simplify the equation to

\[
I \approx \frac{4\pi e}{\hbar} \rho_{\text{tip}} |M|^2 \int_0^{eV} \rho_{\text{sample}}(E_F + \epsilon) d\epsilon
\]  

(1.8)

Since STM is a local probe we are probing the local density of states (LDOS) \( \rho(E, \vec{r}) \) and therefore

\[
I \propto \int_0^{eV} \rho_{\text{sample}}(E + \epsilon, \vec{r}) d\epsilon
\]  

(1.9)
1.3 Scanning Tunneling Spectroscopy

Another mode of data acquisition is to hold the tip at a certain distance above a sample, then ramp the bias voltage between two voltages, and we record how the tunneling current changes. This gives us a $I(V)$ curve. We can take the derivative of the $I(V)$ curve and get a $dI/dV$ curve that allows us to directly measure the LDOS, equation 1.10.

$$\frac{dI}{dV} \propto \rho_{\text{sample}}(E + \epsilon, \vec{r}) \quad (1.10)$$

Taking the numerical derivative of our $I(V)$ curve can result in a very noisy data set since a straight numerical derivative can amplify high frequency noise. A more robust method that we use in our lab is to use a lock-in amplifier where we add a small oscillation to the bias voltage [6][7]. This allows us to directly measure the $dI/dV$ from the oscillating current.

1.4 Spectroscopy Map

We can combine both modes of data acquisition that I have mentioned so far, topography and spectroscopy. We can stabilize a certain distance above the sample and take a spectra at a certain point over the sample. We can now move over by some predefined amount, stabilize at the same distance and take the sample spectra again. We can continue to do this and collect a spectroscopy map, where each pixel in the image corresponds to the spectra at that particular point. As it turns out, this data set contains very rich information about excitation modes and electric scattering within the sample.
Chapter 2

Scanning Tunneling Microscopy Technique

In principle, the STM is quite simple. Its probing mechanism consists of a nanoscopic gap between the sample and the tip which we then move the tip over the sample to acquire our desired data. In practice, a lot of instrumentation goes into actualizing this in the lab. Here I'll detail how we are able to achieve these conditions in the laboratory.

2.1 Piezoelectrics

Piezoelectrics are the work horse of an STM. Piezoelectricity is a phenomena where there is a linear relationship between the electronic state of the material and the physical shape of the material [8]. Therefore by applying stress to a material (such as pressure) the material exhibits an electric field due to this deformation. This process is also reversible, so that by applying an electric field on the sample it will deform itself. There are many different kinds of piezoelectric materials (often called piezos) but for
our purposes we use lead zirconate titanate (PZT) which is a ceramic piezoelectric that has the nice property of working in ultra-high vacuum (UHV) conditions, typically $10^{-10}-10^{-11}$ Torr. We used three main types of piezoelectrics: sheer piezos figure 2.1a, bending piezos figure 2.1b, and stretching piezos figure 2.1c.

2.1.1 Course Motion

Sheer piezos are mainly used for course motion. These are what we use to move the tip and the sample around. The mechanism used to perform this action is a move/slip motion that we repeat many thousand times as illustrated in figure 2.2. First we sandwich what we want to move between stacks of sheer piezos. We then apply a very high electric field across the piezos ($\sim 200$V) causing them to sheer along the direction we want to move our object. The object is now displaced by some very small amount ($\sim$microns). We then quickly ramp the voltage to 0V (or -200V) in order to cause the sheer piezos to quickly return to their original shape. If this is done fast enough, we can overcome the static friction between the piezo and the object causing the object to stay in place and returning the piezos to their original non-sheered position. We have now moved the object by a small amount and we can repeat the process again. In our actual STM we sandwich a small metal prism that
contains the tip and scanning mechanism in order to move the tip closer or farther away from the sample. We have a separate set of sandwiched plates that controls the samples lateral motion with respect to the tip.

Figure 2.2: Cartoon of a course motion using sheer piezoelectric materials

2.1.2 Scanning

We use bending piezos to perform the actual scanning of the sample surface. This is done by arranging four bending piezos in a 2x2 grid as shown in figure 2.3. In this arrangement, each piezo can bend inward or outward. We can exploit this by varying the different voltages applied to all the piezos such the we have the full range of motion along a small 2-dimensional surface at the end of this scanning tube.

2.2 Ultra High Vacuum

Because we are required to maintain such a small distance between the sample and the tip, there are many particles that can get in between this gap or we can get unwanted
particles sticking to the surface of the sample or tip. In order to mitigate this issue we perform our measurements in ultra-high vacuum conditions. This is defined as the pressure range between $10^{-10}$-$10^{-11}$ Torr. For comparison the atmospheric pressure outside of the international space station, which is about 400 km above sea level, is about $10^{-7}$ Torr. We actually operate at a much lower pressure than space. In order to achieve these conditions we employ a couple of cleaning techniques and pumps in successive order to come down to such pressures.

First we make use of sonication to clean the pieces that will function inside our UHV chambers. This consists of submerging our pieces in acetone, and using a device (a sonicator) to vibrate the piece at ultrasonic frequencies (tens of kilo-Hertz). This removes contaminates on the piece and the acetone is both water and oil soluble. We then submerge the piece in isopropanol and sonicate again to remove any acetone residue. We finish the cleaning process by heating the piece to $100^\circ$C for 10-20 minutes. In order to minimize contamination while handling our clean pieces we use latex gloves which only come into contact with other clean tools or pieces.

Our UHV chamber usually consists of welded circular stainless steel pieces with
circular openings called flanges. To close the flanges we use a copper gasket in between a stainless steel cover. After properly sealing the chamber, we first use a scroll pump to begin to bring down the pressure in the chamber. The scroll pump generally get the pressure inside the chamber to $10^{-3}$ Torr. Once we’re around these pressures we turn on a turbo pump. A turbo pump is essentially a fan or sets of fans that spin extremely fast (10 of thousands revolutions per minute). The turbo pump brings the pressure to about $10^{-8}$. If this is the first time pumping the system down after having the system open we then bake the system. This consists of heating up the chambers and pieces inside to 100°C for a couple days in order to remove any possible moisture left on the inner surfaces of the system. After baking, we then turn on an ion pump which will take the system to the UHV regime. If the chamber is too big for one ion pump to bring it down to UHV pressures we might use two. Once we cool the system to 4K the cold walls of the system will act as a cryogenic pump, making things stick to its cold walls. Ion pumps work by ionizing particles and then applying a high electric field that accelerate and capture the ionized particle. They have the added benefit of having no moving parts, which make them perfect for vibration sensitive environments which is crucial for STM measurements. We then turn off the turbo pump and the scroll pump and leave the ion pump on to maintain UHV conditions.

### 2.3 Cryogenics

Many of the materials we study exhibit many different phases of matter of interest. Of great interest is superconductivity because of the obvious applicability to our current technology, but there also exists a rich set of phases that are interesting in their own right and help elucidate deeper understanding of condensed matter physics. A lot of these phases arise or at different temperature ranges and in order to access
these phases we have a temperature 'knob' that we can set our desired temperature conditions to study these materials. The way we achieve this is by using a combination of liquid nitrogen and liquid helium, which are at 77K and 4K respectively.

In figure 2.4 we have a cartoon drawing of the cross section of the cryostat. It consists of two tanks where the inner one contains liquid helium and the outer concentric tank contains liquid nitrogen. The tanks are further thermally coupled to two shields that surround the STM which are in the same concentric orientation as the tanks. The liquid nitrogen tank/shield is mainly used as a radiation shield that absorbs room temperature radiation while surrounding the liquid helium tank with 77K radiation. This significantly decreases the boil off rate of the liquid helium.

Our temperature 'knob' is achieved with two mechanisms. First, we have a thermal 'switch' that thermally couples or decouples the liquid helium bath from the liquid helium shield/STM (labeled as 'I/O' in figure 2.4). When the switch is closed and making a good thermal connection, the STM reaches about 5K. When the switch is open, disconnecting the STM from the liquid helium tank, the temperature stabilizes at about 32K. In order to access temperatures in between 5K-32K we use the fact that the switch is a mechanical clamp and hence we can vary the contact pressure that’s providing the thermal connection. By varying the contact pressure in combination with a heater powered by a proportional–integral–derivative (PID) controller located bellow the thermal switch, we can access any temperature between 5K-32K. Above 32K, we then just use the heater with the PID controller to access temperatures from 32K-77K. For temperatures above 77K, we can fill the liquid helium tank with nitrogen and again use the heater with the PID controller.
2.4 Vibration Isolation

It is extremely important that we are able to have a stable junction between the tip and the sample. That is, we have to maintain a constant gap between the tip and the sample of just a couple of angstroms. It becomes extremely important that we have a form of vibration isolation from the outside world for the STM. In our lab, we have three points of vibration isolation as seen in figure 2.5. The entire system is inside a noise isolation room which minimizes vibration from outside the room. The UHV chambers that house the STM sit on an optical table that are floating on air cushions by the means of air pistons. And finally the STM itself hangs off springs as the last line of vibration isolation.
2.5 Tip Preparation Process

At times, some people will characterize using an STM is more of an art than a science which is mostly due to having to familiarize oneself with tip conditions. Originally tips where cut cross ways in the hope that the very tip is atomically sharp enough to get single localized tunneling current. Things have improved since then but it still requires quite a bit of trail and error.

2.5.1 Tip Etching

First we use tungsten metal wire because it provides a flat density of states around the Fermi level where we conduct most of our experiments. The etching technique is quite simple, we use a NaOH and distilled water solution where we partially submerge the tip such that part of the tip is in the solution and part of the tip is above the surface. We then apply a high DC voltage (∼10V) between the tungsten wire and the
solution. Quite quickly, the solution starts to etch the tungsten wire at the solution’s interface and the submerged part of the tungsten wire falls off. What we are left with, is a very sharp conical-like tungsten tip which we can then use in our STM.

2.5.2 Gold Preparation

We us a gold crystal with the 111 surface [2][3] oriented towards the tip. We further require that we have an atomically clean and pristine gold crystal. In order to achieve this we use a heater and an ion gun used to accelerate argon ion. We first anneal the gold by heating it to 700°C. After 25 minutes of initial annealing, we start to sputter ionized argon atoms onto the surface of the gold. The sputtering will continue for 15 minutes and then turn off. Another 20 minutes of the annealing session starts and this cycle continues anywhere from a couple of hours to three days, depending on the initial gold conditions.

After this annealing and sputtering cycle, we then have an ideal gold surface which we can use for tip preparation. As seen in figure 1.3, a good gold 111 surface consists of herringbone. This happens when atoms near the gold and vacuum interface ’buckle’ in order to minimize it’s energy [2][3].

2.5.3 Tip Preparation

While tip etching as described in section 2.5.1 produces quite a sharp tip, it is still not atomically sharp enough as required for our particular measurements. To further sharpen the tip, we continuously poke the tungsten tip into a gold crystal nanometers deep. This will coat the tungsten tip with gold atoms and as we pull out the tip, we get a mound of gold atoms connecting the tip and the surface of the gold crystal that gets thinner and thinner as we pull the tungsten tip away as seen in figure 2.6.
Eventually the gold atom chain will break and we’ll end up with an atomically sharp tip.

Figure 2.6: Pulling the tip away from the sample creates a string of gold atoms extruded from the surface of the gold. As the tip is continuously pulled away from the surface, the string breaks and the tip ideally is left with an atomically sharp end at the bottom of the tip.

2.6 Sample Preperations

Sample preparation is an important part of STM technique. Different samples require different methods to prepare them before insertion into the vacuum chamber and once they are inside the vacuum chamber. For most of our samples that we have we use the same method of preparation but the environment it’s performed in might change (i.e. doing it in the lab in open air or in an argon rich environment such as in a glove box). Looking at figure 2.7a we have a cross section of what a completely prepared sample looks like. The sample is first glued to a sample holder (which fits into the STM) using H20E Epo-tech, colloquially called silver epoxy. This special type of epoxy is conducting, allowing for us to apply our bias voltage $V_{bias}$ to the sample through the
sample holder. We then cure the sample with the silver epoxy on the sample holder at 100°C for 1 hour. Afterwards this allows us to apply Loctite 1C Hysol epoxy on the top surface of the sample (which we call white epoxy). We then use a small aluminum wire cut to about half a centimeter to glue on top of the white epoxy. We again cure the entire stack at 100°C for 1 hour. This cures both epoxies and we move the sample into the STM chamber through the load lock chamber. If we prepared the sample in air this just consists of moving the sample from the heater (an oven or heating plate) into the load lock chamber. If we are using a glove box, we first place the sample in an air tight container inside the glove box, moving the container to the STM room, and then briefly and quickly place the sample in the load lock chamber.

![Diagram of sample preparation](image)

Figure 2.7: (a) A cartoon cross section showing the different layers of a prepared sample ready for cleaving inside the STM chamber. (b) By applying a small amount of force at the top of the aluminum post, a fresh surface is exposed inside the STM chamber.

Once the sample is in the load lock chamber we start pumping down the load lock using the scroll pump and then after some time we turn on the turbo pump to get the chamber down to about $10^{-8}$ Torr. Once it’s at this pressure we can open the gate separating the load lock chamber from the preparation chamber and quickly move the sample in. The gate is then closed and the scroll pump and rough pump
are turned off due to their high vibration. The sample can now be moved to the STM chamber which is where we cleave our sample (see section 3.4 and figure 3.7 to see a photograph and description of the STM chambers). This consists of hitting the aluminum post on a ledge inside the STM chamber. This, ideally, peels a layer away from the sample leaving a freshly exposed surface, see figure 2.7b, which has only been in UHV conditions.

Sometimes when cleaving a sample is not possible, such as graphene or other 2D materials, we can use the annealer used for gold preparation to head up the sample to evaporate contaminants on the surface of the sample.
Chapter 3

Scanning Tunneling Microscopy Implementation

After a brief overview of STM theory in chapter 1 and STM technique in chapter 2, I now like to discuss our actual functioning STM which we use to realize what I have described in the previous chapters. While again, the principles remain fairly simple, achieving these conditions with picometer precision requires quite a bit of state of the art instrumentation.

3.1 Microscope Head

When dealing with piezoelectric materials, the amount that the material actually deforms is a very small amount of about .1% of its original dimensions. Since we use a move/slip motion to perform course motions, we ideally want a longer amount that we move before we try to quickly move the piezos back to achieve a slip (see figure 2.2). Also, the longer you displace the object we want to move, the more length we give ourselves to quickly move the shear piezos back in order to cause a slip. In order
to increase the amount that a piezo deforms, we build piezo stacks. Looking at figure 3.1, we have an image of a shear piezo stack (figure 3.1a). Looking at the cross section (figure 3.1b) we see how this shear piezo stack works. The technique used is to stack one piezo on top of the other. If we were to stack a piezo one of top of the other, with the electrode on the bottom of the piezo being positive and the top electrode being negative, we would then have to introduce a insulating layer between piezos to avoid short circuiting the stack. This entails an extra step of having an insulating layer in between each piezo which adds more steps in stack construction. When working at these tiny scales, it’s better to reduce the number of assembly steps if possible. What we do is we stack a new piezo on top of another one, we flip the piezo upside down with respect to the bottom piezo. The benefit of this methods is that we only need one electrode sandwiched between piezos without the need of an insulating layer. We wire the electrodes such that the polarity interchanges between piezos layers.

Figure 3.1: (Left) A photograph of a piezo stack consisting of 4 shear piezos. (Right) A cartoon of the crossection of piezo stack.

Scanning heads are quite difficult to make and we therefore, in our lab, tend to purchase scanning heads from a manufacturer. The scanning tube works as described in section 2.1.2 and in figure 2.3. In figure 3.2 we have an example of the type of scan tube that we use.
In order to move the tip into position we use the stacks to move the scan tube as described in section 2.1.2. This same principle (move/slip technique) is also used to move the stage where the sample sits in a 2D plane perpendicular to the tip position. In figure 3.3 we see the stage mechanism. It consists of two stages where one stage moves the device along one direction using the move/slip piezo mechanism described above. Then there is another stage mover that moves the device along the perpendicular direction to the previous one, again using the move/slip piezo mechanism. This allows for complete movement on a 2D plane within some limited range (typically a 1 cm$^2$ area).

In figure 3.4 you can see an assembled microscope. The z mover is located at the bottom, with the scan tube moving up and down. The scan tube has a collet at the top end in order to hold the tungsten tip that we use. Directly above the scan tube is the stage where the sample is placed. The stage is the bottom end of the xy movers located directly above the stage. This moves the stage, and therefore whatever sample on it, on a 2D plane perpendicular to the scan tube. In this con-
The stage mechanism consisting of 2 tracks perpendicular to each other that allows the stage to move on a 2D plane using move/slip piezo mechanism.

The sample surface that will be scanned is facing downward and the tip approaches the sample from below. This essentially is the heart of the STM, the rest of the instrumentation is to minimize noise or to allow operation in certain conditions (i.e. different temperatures or pressure). In figure 3.4 you can also see the springs that the microscope hangs off of as illustrated in the cartoon in figure 2.5 in order to minimize physical vibration that introduces noise while scanning. Furthermore, you can also see the magnetic dampening mechanism to aid in the dampening of any vibration that propagate to the microscope. The magnets are structurally attached to the microscope head, if the microscope head moves then the magnets move accordingly. As the magnet moves (from the microscope vibrating), it creates eddy currents in the copper housing surrounding the magnets. These eddy currents in turn create an opposing magnetic field leading to the dampening of the magnets, causing the cooper to heat up slightly. The amount of heat energy transferred to the copper is proportional to the kinetic energy loss of the moving magnet. While a vibrating microscope head will eventually stop moving from kinetic energy loss due to friction, the magnetic dampening mechanism accelerates the loss of it’s kinetic energy. Magnetic
dampening is more effective at lower, cryogenic temperature which we work in which leads to a very stable microscope head.

![Photo of the microscope head attached below the spring and magnetic dampening mechanism.](image)

Figure 3.4: Photo of the microscope head attached below the spring and magnetic dampening mechanism.

### 3.2 Cryostat

The cryostat is the main device that provides the cooling power to our microscope. The cryostat consists of two concentric reservoirs with the inner reservoir holding liquid helium at 4K and the outer reservoir holding liquid nitrogen at 77K as described in section 2.3. Our cryostat was constructed by Cryo Industries and is shown in figure 3.5a. A cartoon cross-section of the basic layout of the cryostat is shown in figure 2.4. At the bottom of the cryostat is a rod (see figure 3.5b) called the cold finger. The cold
finger is thermally connected through a "switch" to another rod that is in contact with the liquid helium bath. The switch consists of a clamp that grasps/releases the cold finger from the rod directly in contact with the helium bath. The microscope is attached to the bottom of the cold finger (see figure 3.5c). The microscope, along with the liquid helium shield, is thermally connected to the cold finger and the liquid nitrogen shield is not. While the liquid nitrogen shield cannot be completely thermally isolated from the helium bath due to having to maintain the structural integrity of the cryostat, certain solutions were implemented to minimize the thermal contact such as using stainless steel stilts in locations where the liquid nitrogen shield has to be attached to something in thermal contact with the liquid helium bath.

Figure 3.5: (a-c) Images of our cryostat which is attached above the microscope in different stages of disassembly.

### 3.3 Gold Preperation

As explained in section 2.5.2, preparing the gold crystal consists of alternating between sputtering the surface of the gold for 15 minutes and then turning the sputtering off for 25 minutes all while maintaining the gold at 700°C. This is done for a couple
of hours to a couple of days depending on the condition of the gold. In figure 3.6a we have a photograph of the gold crystal in the process of being annealed at 700°C. This is done by running a current of 7 Amps at 14V through two tungsten coils in parallel located right underneath the gold. Due to the high temperature, we get a nice reddish/orange glow from black body radiation for these materials. In figure 3.6b we can see the area of the gold crystal that has been sputtered successfully by the discoloration of the gold where the sputtering beam was concentrated. Figure 3.6c is an example of properly prepared gold on the microscope stage, being approached by a tungsten tip.

Figure 3.6: (a) A gold crystal (111) in the process of being annealed and sputtered. (b) After annealing and sputtering the gold crystal (111). (c) Tip approaching prepared gold (111).
3.4 Complete STM

Finally, putting all the pieces together we get a working STM that I have used for the acquisition of our data through my graduate years. Looking at figure 3.7, the biggest part is the cryostat that sits atop the STM chamber (which houses the STM) and below the STM chamber sits an ion pump. To the left of the STM chamber is the preparation chamber which houses the annealer and the ion gun, used in gold preparation as described in section 2.5.2 and sample heating. There is another ion pump below the preparation chamber. To the left of the preparation chamber is the load lock chamber which provides a door to the inside of the chamber used for sample loading and unloading. Connected to the load lock chamber is a turbo pump and connected to that is a scroll pump (see section 2.2). It all sits on top of a heavy floating optical table which itself is in an acoustic isolation room. As I have just listed, this comprises the main supporting components of our STM along with the actual STM head residing inside the STM chamber.
Figure 3.7: Our completed STM.
Chapter 4

STM Data Interpretation

STM is a powerful technique for probing local electronic properties of conducting materials as described in section 1.2. While topographic data sets are a powerful technique for identifying local features, such as molecules on a sample, adatoms, defects, or vacancies, we can get a deeper understating from directly probing the local density of states along with spacial information of the sample.

4.1 Dispersion Relation

The dispersion relation is a description of how momentum is related to the energy of a particle for a particular system. Let’s take the simplest of scenarios and consider a particle in a 1 dimensional box of size $a$. In this scenario $U_0 = 0$ inside the box and infinite outside the box, essentially bounding the particle in the box. From Schroedinger equation (equation 1.1) we get

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} = E \Psi(x) \quad \text{for} \quad 0 < x < a \quad (4.1)\]

and similarly from equation 1.3 we get
\[ k = \sqrt{\frac{2mE}{-\hbar^2}} \]  

Therefore the dispersion relation for the particle in the box is simply

\[ E = \frac{\hbar}{2m} k^2 \]  

For the particle in the box, we get a parabolic relationship between the wavenumber \( k \) and the particle's energy \( E \).

### 4.2 Band Theory

One of physics' most popular tools for describing the underlying physics of different materials is band theory. Band theory is a powerful tool to understand many phenomena such as our understanding of semiconductor physics which powers our modern digital world. While band theory is quite deep and complex, I'd like to briefly give an overview which underlies our interpretation of our STM measurements.

#### 4.2.1 Block's Theorem

Bloch's theorem corresponds to the description of a system with a periodic potential. In a crystal, this periodic potential arises naturally from the very nature of the periodic crystal structure. Considering a simple one dimensionality crystal with spacial periodicity \( a \), we therefore have a potential \( U \) where

\[ U(x) = U(x + a) \]  

(4.4)
Inserting this periodic potential in our Schroedinger equation (equation 1.1), Bloch’s theorem states that the solution for the wavefunction $\Psi(x)$ can be written as

$$\Psi(x) = e^{ikx}u_k(x) \quad (4.5)$$

where $u_k(x)$ has the periodicity of the crystal (the periodic potential) [9]

$$u_k(x) = u_k(x + a) \quad (4.6)$$

This applies for any solution to the Schroedinger equation with a periodic potential. From equation 4.5 and equation 4.6 we can then show

$$\Psi_k(x + a) = e^{ik(x+a)}u_k(x + a)$$

$$\Psi_k(x + a) = e^ika e^{ikx}u_k(x) \quad (4.7)$$

$$\Psi_k(x + a) = e^{ika}\Psi(x)$$

This tells us that a translation of the order of the crystal periodicity $a$ corresponds to a phase factor to the original wavefunction [9]. Furthermore letting $k' = k + g$ where $g$ is the reciprocal vector of the crystal periodicity $a$

$$\Psi_{k'-g}(x) = e^{i(k'-g)x}u_{k'-g}(x)$$

$$\Psi_{k'-g}(x) = e^{ik'x}e^{-igx}u_{k'-g}(x) \quad (4.8)$$

$$\Psi_{k'-g}(x) = e^{ik'x}u_{k'}(x) = \Psi_{k'}(x)$$
4.3 Nearly Free Particle

It’s useful to look at the system where we have a periodic potential with a periodicity of $a$ in one dimension but with an extremely weak periodic potential. Under these conditions the energy of the a particle is that of a free particle

$$E = \frac{\hbar}{2m} k^2$$  \hspace{1cm} (4.9)

But we know from Bloch’s theorem that the solution to the Schroedinger equation is of the form of equation 4.5. Therefore we know that adding a reciprocal lattice vector $g$ to the wave number $k$ we get the same wavefunction as shown in equation 4.8. Therefore the energies are the same

$$E(k) = \frac{\hbar}{2m} k^2 = \frac{\hbar}{2m} (k + g)^2 = E(k + g)$$  \hspace{1cm} (4.10)

This gives us an infinite number of wave vectors $k$ with the same energy at intervals of the reciprocal vector $g$, figure 4.1a. In a sense, this gives us many bands that represent the allowed energies of the particle in the nearly free particle model. Figure 4.1a is called the extended representation because we’ve plotted the wave number $k$ at higher $k$ than the Brillouin zone. We can go further and plot the wave number $k$ only in the first Brillouin zone (figure 4.1b), folding in the larger wave numbers, without loss of generality. These are what we call the bands of crystal (see reference [9]).

As it turns out, the presence of a potential has the effect of splitting the bands where we have degenerate energy states. As we have done in undergraduate physics, we get a splitting of the allowed energies for a degenerate systems in the presence of a potential (like the hyperfine splitting) [1]. Using 1st order perturbation theory we
can show that the degenerate unperturbed energies at $(k - G)^2$ and $k^2$ is split under a weak potential.

We have two degenerate states, $(\vec{k} - \vec{g})^2$ and $\vec{k}^2$, where the unperturbed energies are the same and therefore the 1st order non-degenerate perturbation correction to the energies blow up. We therefore must use 1st order degenerate perturbation theory

$$E_{\vec{k}} \rightarrow E_{\vec{k}}^{\pm}$$  

(4.11)
\begin{align*}
E_{\vec{k}}^\pm &= \begin{bmatrix}
\langle \psi_{\vec{k}}^{(0)} | H' | \psi_{\vec{k}}^{(0)} \rangle & \langle \psi_{\vec{g}-\vec{k}}^{(0)} | H' | \psi_{\vec{g}-\vec{k}}^{(0)} \rangle \\
\langle \psi_{\vec{g}-\vec{k}}^{(0)} | H' | \psi_{\vec{k}}^{(0)} \rangle & \langle \psi_{\vec{g}-\vec{k}}^{(0)} | H' | \psi_{\vec{g}-\vec{k}}^{(0)} \rangle
\end{bmatrix} \\
&= \begin{bmatrix}
\langle \psi_{\vec{k}}^{(0)} | H' | \psi_{\vec{k}}^{(0)} \rangle & \tilde{V}_{\vec{g}} \\
\tilde{V}_{\vec{g}}^* & \langle \psi_{\vec{g}-\vec{k}}^{(0)} | H' | \psi_{\vec{g}-\vec{k}}^{(0)} \rangle
\end{bmatrix} \\
&= \begin{bmatrix}
E_{\vec{k}}^{(1)} & \tilde{V}_{\vec{g}} \\
\tilde{V}_{\vec{g}}^* & E_{\vec{g}-\vec{k}}^{(1)}
\end{bmatrix} \\
0 &= \begin{bmatrix}
E_{\vec{k}}^{(1)} & \tilde{V}_{\vec{g}} \\
\tilde{V}_{\vec{g}}^* & E_{\vec{g}-\vec{k}}^{(1)}
\end{bmatrix} - \|E_{\vec{k}}^\pm\| \\
&= \begin{bmatrix}
E_{\vec{k}}^{(1)} - E_{\vec{k}}^\pm & \tilde{V}_{\vec{g}} \\
\tilde{V}_{\vec{g}}^* & E_{\vec{g}-\vec{k}}^{(1)} - E_{\vec{k}}^\pm
\end{bmatrix}
\end{align*}

\begin{align*}
0 &= [E_{\vec{k}}^{(1)} - E_{\vec{k}}^\pm][E_{\vec{g}-\vec{k}}^{(1)} - E_{\vec{k}}^\pm] - |\tilde{V}_{\vec{g}}|^2 \\
&= E_{\vec{k}}^{(1)} E_{\vec{g}-\vec{k}}^{(1)} - E_{\vec{k}}^\pm E_{\vec{k}}^\pm E_{\vec{g}-\vec{k}}^\pm + |E_{\vec{k}}^\pm|^2 - |\tilde{V}_{\vec{g}}|^2 \\
&= |E_{\vec{k}}^\pm|^2 - E_{\vec{k}}^\pm [E_{\vec{k}}^{(1)} + E_{\vec{g}-\vec{k}}^{(1)}] + E_{\vec{k}}^{(1)} E_{\vec{g}-\vec{k}}^{(1)} - |\tilde{V}_{\vec{g}}|^2
\end{align*}

Then by using the quadratic formula

\[ E_{\vec{k}}^\pm = -\frac{[E_{\vec{k}}^{(1)} + E_{\vec{g}-\vec{k}}^{(1)}]}{2} \pm \sqrt{[E_{\vec{k}}^{(1)} + E_{\vec{g}-\vec{k}}^{(1)}]^2 - 4[E_{\vec{k}}^{(1)} E_{\vec{g}-\vec{k}}^{(1)} - |\tilde{V}_{\vec{g}}|^2]} \]

We see that when \( E_{\vec{k}} = E_{\vec{g}-\vec{k}} \), at the Brillouin zone boundary, we open up a gap the size of \( 2\tilde{V}_{\vec{g}} \) which is plotted in figure 4.2.
4.4 Simple Quasiparticle Interference Picture

The main data acquired by our cryogenics STM is measurements of quasi-particle interference (QPI). The underlying mathematical model for QPI is beyond the scoop of this thesis but we can nevertheless proceed with a qualitative and quantitative picture. If we take our description of our weak periodic crystal as described in section 4.3 above, we can image that we end up with a band structure in the 1st Brillouin zone which is shown in figure 4.2.

Let's take the upper-most band in figure 4.2 which I have plotted in figure 4.3a. Now imagine we have an electron with a specific wavenumber $k$. We'll assume elastic scattering (i.e. no loss of energy). At this particular energy, let's call it $E_3$, we only have two available states that the electron can exist. that is $k_3$ and $-k_3$. The electron
Figure 4.3: (a) Upper band from weak periodic potential. (b) QPI for band. (c) Energy slices in 1 dimension.

will only be able to scatter to either of these two states. We can define a scattering vector \( q = k_3 - (-k_3) \) which gives up \( q = 2k_3 \). We can plot these scattering vectors for all possible energies in this one band in 1 dimension which is shown in figure 4.3b as a green line. This scattering band is a bit broader than the momentum band (dotted blue line) but it’s dispersion is nevertheless related to the original momentum band. We can furthermore take a contour of constant energy, meaning a cross section of this scattering band at a constant energy, and plot it as shown in figure 4.3c. Here I have plotted three such constant energy contours for three different energies. We see two points on the this 1 dimensional momentum space plot corresponding the allowed scattering vectors \( q \) corresponding to that energy. What is important to notice is the dispersion, or the “movement” of points as we change energy. This is the telltale sign of a QPI signal from our data sets since these points position in momentum space are correlated to the change in energy indicating scattering of electrons in the momentum bands. This is exactly what we are probing when we take spectroscopy maps as described in section 1.4 except that we probe 2 dimensional momentum space as opposed to 1 dimensional momentum space as described in this example.

Generalizing our QPI description in 1 dimension that we have thus far outlined to 2 dimension, we have a very similar picture. In figure 4.4a we have a 2 dimensional
energy band dispersion for a nearly free particle, which turns out to be a 2 dimensional paraboloid as one might expect in extending our 1 dimensional example from section 4.3. In STM, when we take spectroscopy maps we have a discrete energy resolution. In practice the number of energy sliced that we usually probe for a 128px map is about 100 energy slices. For this particular example, if we were to take a single energy slice (or contour of constant energy) we would see a circle in 2 dimensional momentum space, figure 4.4b. As before, a QPI plot would produce all the possible scattering vectors. While in the 1 dimensional QPI for a single energy slice (figure 4.3c) we only have 2 possible scattering vectors corresponding to backscattering and hence 2 points in q-space (which is just the scattering vectors \( q \) plotted in momentum space), in the 2 dimensional case we have an infinite number of states that an electron can scatter to, the scattering doesn’t have to just be backscattering (e.g. the scattering doesn’t have to just occur across the entire diameter of the circle). We therefore expect more of a Gaussian disk from this simple example indicating that there are more short scattering vectors possible for an electron than longer scattering vectors, figure 4.4c.

As it turns out looking at simple metals such as copper crystals (111), people have
seen these circular contours of constant energy, figure 4.5. People have used a technique called angle resolved emission spectroscopy (ARPES) to image these circular contours of constant energy, figure 4.5a [10]. The technique consists of shooting a sample with a laser at certain energies. This energy knocks out electrons with the initial energy of the incoming photons minus the work function of the sample-vacuum boundary. The electrons will scatter at different angles from the surface corresponding to their kinetic energy and momentum in the sample. Using this technique we can directly probe the electronic structures of many materials and it’s a powerful technique used in conjunction with STM scattering measurement. In figure 4.5b [11], we see an STM QPI measurement of a copper crystal (111) where they have found that the measure QPI has a radius correspoing to the 2 times the radius of the contour of constant energy at the same energy. While the images in figure 4.4 are from 2 separate experiments [10][11], it nonetheless illustrates the power of STM measurements in probing underlying electronic structure and it is often very useful to combine STM measurements with ARPES experiments.
4.5 STM Quasiparticle Scattering Measurement

Now that we have briefly discussed the origins of QPI scattering when talking about a materials band structure we can now show how this is actually realized in an STM measurements. As described in section 1.3 and section 1.4, the STM can take spectroscopy maps. This consists of holding the tip at a certain distance above a sample, and then ramping the bias voltage between an initial voltage and final voltage, and recording the change in tunneling current. This give use a tunneling current vs voltage measurement. By using a lock-in amplifier, we can directly measure the derivative of this relationship giving us what we call a $dI/dV$ map. This map consisted of a 3 dimensional data set where 2 axes are the real space position where the spectra was taken, and the third dimension is the $dI/dV$ data. Recalling equation 1.10, what the $dI/dV$ map actually corresponds to is the real space image of the local density of states (LDOS) at different energies. If no scatterers existed in the material the LDOS in real space would be a flat image because the particles are traveling at different phases corresponding to their energy and wavenumber $k$. But if we were to have a scatterer, then standing waves are created from particles scattering off of the impurity corresponding to the particles energy and wavenumber $k$ called Friedel oscillations [12]. By taking the Fourier transform (FT) of the real space image, we can get the momentum space representation of these scattering vectors [13][11]. Therefore, the FT of the real space $dI/dV$ map at different energies will produce a dispersing QPI scattering images in momentum space. This dispersion is then directly related to the specific band structure of the material as described in section 4.4 above.

In order to get a good idea of what this looks like in actual data, figure 4.6 shows a $dI/dV$ map at three different energies, -70meV, -210meV, and -350meV. In figure 4.6a-c we have the real space images at these different energies. Due to impurities
scattering quasiparticles as well as the steps located on the upper left of the images, we get ripples in the LDOS which directly correspond to the scattering vector at each respective energy. In figure 4.6d-f we have the FT of the real space images at the same energies (-70meV, -210meV, and -350meV). Remarkably, we clearly see a circular shape which clearly grows as we go up in energy. This is directly coming from quasiparticles scattering in the parabolic band of gold at these energies. This remarkable measurement is what allows us to directly probe not only the LDOS but the quasiparticle scatterings in materials.

Hopefully these first initial chapters have illustrated a tangible overview of the STM technique and what types of measurements one can perform. Obviously there is quite a bit more detail to what I have gone over but it should help in grasping the measurements and conclusion I have come to during my research of NbSe$_2$, high temperature superconductors LiFeAs, NaFeAs, NaFeCuAs, NaFe$_2$As$_2$, and Wyel semimetal MoTe$_2$ as I touch on a couples of these materials in the following chapters.
Figure 4.6: (a-c) Real space spectroscopic map at 3 different energies, -70meV, -210meV, -350meV respectively. (d-f) The respective Fourier transform of (a-c) clearly showing a parabolic dispersion from QPI scattering.
Chapter 5

Phases in NaFeAs

The discovery of iron based high temperature superconductors (pnictides) in 2006 by Japanese scientists [14][15] has led to quite bit of interest in high temperature superconductors. Magnetism tends to destroy superconductivity in classical and copper based high temperature superconductors (cuprates) [16]. It has been a very widespread idea that magnetism and superconductivity compete and therefore one can’t coexist in the presence of the other. With the finding of this new class of superconductors that have iron (Fe) as a building block, which has a magnetic moment, has led to interesting theories on the emergence of superconductivity which include the presence of magnetic states. It becomes important to fundamentally understand the underlying physical phenomena that leads to the rich states these exotic material exhibit in order to understand the interplay of these states with one another. I have focused my primary work in graduate school in understanding different phases of the pnictides which seem to preclude superconductivity in these materials.
5.1 NaFeAs/Pnictides Crystal Structure

The pnictides are layered crystals with weak van der waals forces holding the layers together. Along the layered plane however the bonds in the crystal are much strong making it a perfect material for cleaving as described in section 2.6. The common crystal structure in pnictides is the iron (Fe) and arsenic (As) structure. It consists of a single atomic layer of Fe which is sandwiched between 2 arsenic layer as shown in figure 5.1a. The Fe atoms are bonded to the the top and bottom arsenic atoms such that the bottom bonds are 90° with respect to the top bonds. This is the common structure in the pnictides. The unit cell will either contain one of these Fe-As layers or more and any number of other atoms. In NaFeAs, the Fe-As layer is itself sandwiched between a layer of sodium (Na) atoms, figure 5.1b. This structure is the basic structure of NaFeAs which is repeated throughout the crystal.

![Figure 5.1: (Left) Fe-As layer in iron based high temperature superconductors. (Right) Crystal structure of NaFeAs with outline of unit cell.](image)

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5.2 NaFeAs/Pnictides Phases

NaFeAs has a rich number of phases that it undergoes depending on temperature and doping (exchanging atoms with isovalent atoms thereby adding or removing electrons). NaFeAs can exhibit a couple of different phases. It has a paramagnetic/orthorhombic phase, a spin density wave/tetragonal phase, and a superconducting phase at different temperatures and low doping, figure 5.2. At room temperature the crystal is in the paramagnetic/tetragonal phase consist of a square lattice where the crystallographic direction $a$ and $b$ are equal. The spins at each lattice site are randomly oriented with no particular pattern. At round 54K in the parent compound (zero doping), the crystal transitions into the an orthorhombic crystal structure where crystallographic directions $a$ and $b$ are no longer equal [17]. The crystal elongates along $a$ and shrinks along $b$. At around 41K, again in the parent compound, the spins align themselves in a spin density wave (SDW) configurations where we have the spins aligning themselves in an anti-ferromagnetic configuration (alternating spin orientation) along the longer $a$ crystallographic direction while on the orthogonal, $b$ direction the spins align themselves in a ferromagnetic configuration (the spins are aligned in the same direction). And finally NaFeAs has a superconducting phase around 18K for the optimally doped compound. While this phase description is specific to NaFeAs, most of the phase diagrams for the pnictides look remarkably similar although with different transition temperatures for the different phases. But it’s important to note the existence of the SDW phase which precluded (and might even coexist) superconductivity [18][19]. Understanding the nature of this magnetism in this material (as well as other pnictides) becomes very important in the fundamental understanding of high temperature superconductivity.
Figure 5.2: Cartoon representation of NaFeAs phase diagram showing the onset of different phases depending on temperature and doping content along with Fe-As crystal layer in the paramagnetic/tetragonal phase, the paramagnetic/orthorhombic phase, and the spin density wave/orthorhombic phase.

5.2.1 Nematicity

Nematic effects are observed in many quantum materials including 2D quantum hall states [20][21], ruthenates [22], cuprates [23][24][25][26][27][28] and the pnictides [29][30][31][32][33][34][35][36]. Strong electronic nematicity is seen across the 122 [29][30][37][31][33] [38][39][40][41][42], 111 [34][36][43], 1111 [41] and 11 [44][45][46] types of pnictides. There have been a couple measurements that showed an inconsistency with the NaFeAs phase diagram, figure 5.2. There have been measurements
that show inequivalent measurements along both the $a/b$ directions in the paramagnetic/tetragonal phase, in transport [29][30][42][47], in nuclear magnetic resonance [48], in optical data [49], and STM [34]. This is not expected given the crystal has 4-fold (C4) symmetry and thus the band structure should exhibit the same symmetry. This indicates an underlying pattern/phase in the crystal. It has been proposed that there exist a nematic phase where the spins semi-align themselves in a certain pattern such that translational symmetry is retained but rotational symmetry is broken. The terminology comes from liquid crystals. In a liquid crystal, you have a lot of molecules in a random orientation and position, figure 5.3a. This is the configuration that one would expect from a fluid. But under certain conditions, such as a polarizing electric field, the molecules can be orientated along a specific direction, figure 5.3b. The molecules in the liquid crystal now have a specific direction which they are oriented, thereby minimizing its rotation symmetry (in figure 5.3b the symmetry becomes C2 yet the liquid crystal retains its translational symmetry because the molecules are still positioned randomly in the liquid crystal.

![Figure 5.3: (a) Cartoon of liquid crystal molecules with no specific orientation and no periodicity. (b) Cartoon of liquid crystal in a nematic phase where the molecules have a specific orientation but no periodicity.](image)

In pnictides, nematicity is similar to the liquid crystal description with some
caveats. Looking at the 2 dimensional square lattice in the tetragonal phase, the crystal has a square periodicity and a C4 rotational symmetry. Considering the spin directions of at the atomic lattice sites, we have a random orientation for their directions, figure 5.4a. In this phase, much like in the liquid crystal example, the orientation of the spins don’t have specific direction and the crystal retains both translational symmetry of the 2D lattice and C4 rotational symmetry. In the onset of the nematic phase however, the spins tend to favor a certain orientation (while still fluctuating) but they haven’t arranged themselves into a true, new periodicity in the crystal, figure 5.4b. The spins have started to coalesce into what will eventually turn into a SDW but it has yet to fully set in. It should be noted that in the SDW phase the material is still a nematic phase and is sometimes called as such since it still holds true that we have translational symmetry but reduced rotational symmetry. To the same extend the orthorhombic phase is also considered to be nematic since the $a$ and $b$ crystallographic directions become inequivalent. But to reiterate, the SDW phase transition is at 41K and the orthorhombic phase transition is at 54K, above these temperature, we have the tetragonal phase with this fluctuating nematic phase. In this configuration, you still have a new translation symmetry due to the anti-ferromagnetic orientation of the spins along one direction and the rotational symmetry is reduced to a C2 symmetry. In such a case, it would be expected to see inequivalent directions between the 2 crystallographic directions even in the square lattice of the tetragonal crystal configuration. The spin orientation [45][50] isn’t necessarily the only mechanism to achieve this nematicity, it has also been hypothesized that orbital orientation [51][52][53] is the main mechanism in nematicity. In the following chapter (chapter 6), I will show the strong link between spin and nematicity in my our experiments.
Figure 5.4: (a) Cartoon of a square lattice crystal with the spins at the atomic sites have no specific orientation and no periodicity (besides the crystals periodicity). (b) Cartoon of a square crystal in a nematic phase where the spins at the atomic sites have a preferred orientation.
Chapter 6

QPI and NaFeAs Nematicity

Most of my studies on pnictides have been on the NaFeAs single crystal compound. NaFeAs is an interesting pnictide to study due to the separation between when the crystal goes from a tetragonal/paramagnetic phase into an orthogonal/paramagnetic phase at 54K and when the crystal transitions into the SDW phase at 41K (see figure 5.2). In other pnictides the onset of SDW phase and orthogonal structural change occurs at the same or relatively the same temperature making it difficult to study the mechanisms underlaying the cause of these different phases.

6.1 Parent Compound and Nematicity

First we study the non-doped, parent compound of NaFeAs across the temperature axis on the phase diagram. Looking at figure 5.2 we see the crystal goes from tetragonal/paramagnetic to orthorhombic/paramagnetic at 54K. We expected in the tetragonal phase the $a$ and $b$ cryptographic directions should be equivalent and therefore we should see C4 rotational symmetry, while in the orthorhombic phase, the $a$ and $b$ crystallographic directions are inequivalent and can manifest inequivalent elec-
tronic features along the crystallographic direction of an STM measurement. Looking at NaFeAs at 26K, well within the SDW phase in figure 6.1a, we have an energy slice at 10mV from a spectroscopy map. We see unidirectional electronic features as we might expect given that the $a$ and $b$ crystallographic directions are no longer equivalent, $a$ is longer than $b$, and we have the spins aligned in an anti-ferromagnetic orientation along the $a$ direction, and in the ferromagnetic orientation along the $b$ axis. Now we continue to measure the sample as we increase the temperature. In figure 6.1a-f we can see the evolution of the real space electronic features at 10mV from 26K to 75K in rough increments of about 10K. We can clearly see the persistence of this unidirectional electronic features well into the tetragonal/paramagnetic phase above 54K. While this is surprising given the crystal’s C4 rotational symmetry in this phase, it matches what others have observed[29][30][47] showing the inequivalent directions in the tetragonal/paramagnetic phase.

Figure 6.1: (a-f) Evolution of the real space STM spectroscopy scans of NaFeAs from 26K, up to 75K. (a-c,e) Settings are: $V_{set} = -100mV$ and $I = 300pA$. (d,f) Settings are: $V_{set} = -50mV$ and $I = 300pA$ (Figure from reference [34]).
This unexpected unidirectionality, the breaking on C4 symmetry to C2 symmetry, is what we described as the nematic phase. In order to better understand the underlying physics of these electronic features in the spectroscopic scans, we can study these scans in momentum space by taking the Fourier transfer (FT) of the real space spectroscopic images, figure 6.2a-d. We can see the evolution in momentum space of the spectroscopic map. We clearly see dispersing features at low energies around the Fermi level, strongly indicating QPI scattering in our measurements. We can therefore try to understand our QPI scattering by looking at the band structure of NaFeAs from previous ARPES measurement[36] and producing the expected QPI scattering around the Fermi level.

![Figure 6.2](image)

Figure 6.2: (a-d) FT of a conductance map from -55meV to +55meV showing the dependence of momentum space features on energy. (Figure from reference [34])

We use ARPES measurement across the different phases that have been performed on this material[36]. In figure 6.3 (from reference [36]) we see the schematics from the ARPES measurements on NaFeAs across 3 main phase: the tetragonal/paramagnetic phase (T>54K), the orthorhombic phase/paramagnetic phase (41K<T<54K), and the tetragonal/SDW phase (T<41K). Here we see the evolution of the energy bands of NaFeAs. In the tetragonal/paramagnetic phase we have C4 rotational symmetry as one would expect from the equivalent a/b crystallographic directions, figure 6.3a. It’s important to note that from this particular measurement no obvious nematicity can be seen in this phase as what we have seen in the more local measurements.
of STM, figure 6.1. At the transition temperature $T_S$ where NaFeAs goes into the orthogonal/paramagnetic phase, we lose C4 rotational symmetry and retain C2 rotational symmetry due to the inequivalent $a/b$ crystallographic directions, figure 6.3b. Crossing into the orthorhombic/SDW phase a couple of things happen. Along the ferromagnetic spin aligned direction, the periodicity remains the same, while along the anti-ferromagnetic direction the periodicity doubles leading to 2-fold increase of the real space unit cell. This corresponds to a halving of the Brillouin zone in reciprocal space leading to band folding as seen in 6.3c, and causing gaps to open up (not shown) where we get bands crossing (similar to the nearly free particle example in section 4.3). The contour of constant energy near the Fermi level in the orthogonal/SDW phase from the APRES measurements is shown in figure 6.4a. From here you can make a cartoon model of the measurements as shown in figure 6.4b.

Figure 6.3: ARPES band measurements of NaFeAs in the (a) tetragonal/paramagnetic phase, (b) orthorhombic/paramagnetic phase, (c) orthorhombic/SDW phase. (Figure from reference [36])

A cartoon model of the contour of constant energy near the Fermi level for all three phases from ARPES measurements is plotted in figure 6.5a-c. From these bands it is possible to calculate the expected QPI from each band structure in each phase (similar to the previous example of the nearly free particle in figure 4.4a). These are plotted in figure 6.5d-f. We notice a couple features in the QPI structure in momentum space for the different phases. In the SDW phase, we get a very rich structure that has C2 rotational symmetry along with strong off axis peaks of strong
QPI intensity, figure 6.5d. In the orthogonal/paramagnetic phase, we also see C2 rotational symmetry but the QPI intensity is mainly concentrated in the center of an oval-like shape in momentum space, figure 6.5e. For the tetragonal/paramagnetic phase we have C4 rotational symmetry, again with the QPI intensity mainly in the center or a circular shape in momentum space, figure 6.5f. Next, we compare our predicted QPI calculation to the STM QPI data.

In figure 6.6a we have the expected QPI from the folded band structure in the SDW phase. Figure 6.6b-d shows the FT of the measured real space energy slices in the orthorhombic/SWD phase, the orthorhombic/paramagnetic phase, and the tetragonal/paramagnetic phase respectively near the Fermi level. We get a nice qualitative/quantitative match in the orthorhombic/SDW phase from QPI measurements and the QPI expected from ARPES band measurements. We get C2 rotational symmetry along with strong intensity off axis QPI peaks. However, more interestingly, the measured QPI from STM in the orthorhombic/paramagnetic phase and the tetragonal/paramagnetic phase also match the QPI calculated from the orthorhombic/SDW
phase with the folded bands. This hints to spin dynamics at play in the origin of the C4 rotational symmetry breaking in the tetragonal/paramagnetic phase since the measured QPI matches the expect QPI in the orthorombic/SDW phase from ARPES measurements. The proposed hypothesis to explain our C4 rotational symmetry breaking is the existence of an external strain field in the sample, possibly arising from sample mounting. We hypothesize strong coupling between strain and spin fluctuations in NaFeAs. When the sample is in the paramagnetic phase, we have random spin fluctuations at the atomic sights. If one were to introduce an external strain field, the fluctuations start to favor a certain orientation. Given the time scale of STM measurements, we only see the time average of these fluctuations. This is also motivated by measurements of the strain dependence of DC transport[29][30][54][55] and
optical conductivity[56][37]. In order to test this hypothesis we introduce a tunable strain "knob" into our measurements.

Figure 6.6: (a) QPI calculated from ARPES measurements in the orthorhombic/SDW phase. (b-d) QPI measurements form STM in the orthorhombic/SDW phase, orthorhombic/paramagnetic phase, tetragonal/paramagnetic phase respectively. (Figure from reference [34])

6.2 STM In Situ Strain

In order to probe the relationship between mechanical strain and microscopic electronic nematicity, we designed an apparatus by which anisotropic mechanical strain can be continuously applied to a sample while atomically-resolved STM and STS measurements are performed on the same area. We term the new technique Elasto-Scanning Tunneling Spectroscopy (or E-STS). The chief technical problems to overcome are the incorporation of the strain-producing apparatus within the available sample space of a few millimeters typical for high-resolution cryogenic STMs; the design of the experiment to allow the same nanoscopic area of the sample to be traced while varying the strain; and the typical issues associated with multilayer piezoelectrics including drift, creep and noise, especially at high temperature. Our design is shown in figure 6.7 and consists of a multilayer piezo actuator that expands/contracts along one axis (figure 2.1c) by up to ±0.1% (which is the typical orthorhombic distortion of parent pnictide compounds) upon application of voltages
strain) of ±250 V. The single crystal sample is glued to the top face of the piezo actuator, which also serves as one of the electrical contacts to the piezo. The crystal sample is maintained at the sample bias voltage \( V_{\text{bias}} \), while the other end of the piezo actuator is maintained at the voltage \( V_{\text{bias}} + V_{\text{strain}} \) via a low-noise floating voltage supply. STM imaging is performed on an in-situ cleaved crystal, where the tunneling current is measured from the tip as usual. The strain is independently measured using a resistive strain gauge as well by interferometry. E-STS as implemented is broadly applicable to crystal as well as film samples.

![Device used to strain samples while STM is being performed on them.](image)

**Figure 6.7**: Device used to strain samples while STM is being performed on them.

### 6.3 Strain in the Orthorhombic/Tetragonal Phase (<41K)

We first discuss E-STS measurements performed on NaFeAs at low temperature (T=6K). In this regime the material has both long-range magnetic (stripe SDW) and structural (orthorhombic) order. Global constraints on the strain state, presum-
ably arising from the details of sample mounting, mean that the orthorhombic order is not uniform across the sample. Instead, micron sized domains with near atomically sharp domain boundaries appear. The domain size presumably is set by the competition of domain wall and strain energies, and boundaries between domains have been previously visualized in STS imaging measurements\[31][34][35] (see also figure 6.19).

Figure 6.8: STM images of NaFeAs at T=6K at various values of applied strain, obtained on the exact same area of the sample (white bar represents 10nm). Nematic order can be visualized as yellow, unidirectional streaks in the image. At this temperature, nematic domains exist, with the domain boundaries showing up as dark lines in the image. As the applied strain (proportional to the voltage $V_{\text{strain}}$ shown in the bottom of the panels) is changed in the sample, the domain walls move and reduce the area of one of the domains at the expense of the other. Imaging conditions $V=+10\text{mV}, I=100\text{pA}$.

In figure 6.8a-e we show images of the exact same region of our NaFeAs sample taken at a temperature of 6K for different values of the external strain, as indicated by the piezo voltage $V_{\text{strain}}$. We tune the strain by changing the voltage applied to the strain piezo from +250V (maximal compression, figure 6.8a) to -250V (maximum tension, figure 6.8e), and measure the response of the material via STM. Imaging is performed at identical conditions at the same energy for each value of applied strain. For each new value of strain, the crystal undergoes a translational shift under the STM tip, providing an independent, in-situ measurement of applied strain. To zero out this shift we re-center the tip at each value of strain. In figure 6.8a two sharp domain walls are seen separating domains in which the direction of the longer $a$ axis changes by 90 degrees. On either side of the domain boundary, LDOS patterns that have C2
rotational symmetry can be seen in the vicinity of defects. These patterns also rotate by 90 degrees across the domain boundary in accord with the structural distortion. Comparison to figure 6.8b-e shows that the domain walls move as a function of applied strain so that as the magnitude of the compressive strain is decreased, the area of the domains with long axis aligned parallel to the strain direction increases and the area of the domains with long axis perpendicular to the strain direction decreases. For each value of strain, we can calculate the ratio of the domain areas of the two orientations. We plot this ratio as a function of strain in figure 6.9a. This figure shows the presence of significant hysteresis as well as irregular motion as a function of strain, reminiscent of Barkhausen[57] noise in the motion of domain boundaries from magnetization at the atomic scale.

Figure 6.9: (a) Plot of the ratio of the size of each of the domains in the field of view in images in figure 6.8a-e as a function of applied strain. It is clearly seen that the motion of the domains exhibit hysteresis and domain pinning. (b) Intensity of the nematic anisotropy parameter as a function of the applied strain. Within experimental error the intensity is independent of strain.
6.3.1 Quantifying Anisotropy

In STS scans where the defect density is low (such as those in figure 6.8) and the real space positions of the defects can be clearly identified, it is easy to directly identify the real space QPI signal corresponding to a single defect. To do this, we first identify the positions of each one of the defects in real space. We crop a small <10nm square region around each identified defect and average all of the cropped regions together to produce an average real space QPI signal associated with a single defect. To quantify the anisotropy in this average image, we rotate the image by 90 degrees (r → ˜r) and subtract it from itself, to generate a real space “difference plot”. Any non-zero value in the difference plot comes from $C_4$ symmetry breaking in the original image. We then obtain the anisotropy parameter $\eta$ by summing the absolute value of each pixel in the difference plot and normalizing by the sum of absolute values in the original image before rotation and subtraction. Mathematically,

$$\eta(w) = \frac{\sum_r |\delta \eta(r, w) - \delta \eta(\bar{r}, w)|}{\sum_r |\delta \eta(r, w) + \delta \eta(\bar{r}, w)|} \quad (6.1)$$

where $\bar{r}$ is the 90 degree rotation of $r$ about the $z$ direction and the prime indicates the sum over the smaller region of the average defect.

In the presence of large numbers of defects where individual defects cannot be identified with certainty, as well as cases where the QPI signal is weak relative to other spectroscopic features present in the sample, we cannot directly identify the anisotropic signature due to a single defect experimentally without additional modeling. This is the case in NaFeAs at high temperature in the presence of strain (Fig. 2 of the main text). In this situation, we work in Fourier space and consider the FT of an entire STS image $\delta \tilde{\eta}(q, w)$ To calculate the anisotropy in such an image, we rotate the image by 90 degrees ($q \rightarrow \bar{q}$) and subtract it from itself to generate a Fourier space
difference plot. We discuss the relationship between these experimentally calculated measures of anisotropy and theory in section 6.4.1.

Using the prescribed technique in equation 6.1, we can directly quantify the magnitude of electronic $C_4$ symmetry breaking as a function of strain from figure 6.8a-e. We take advantage of the fact that individual defect signatures can be easily identified in these images. We proceed by cropping a region centered on each defect and averaging all these cropped images together, thus generating an average spectroscopic signature for each value of strain. This average defect structure is then subtracted from the same image rotated by 90 degrees. The intensity in the resultant subtracted image is due to breaking of $C_4$ symmetry in the local electronic structure, and we can sum up all the intensity in the subtracted image to obtain a measure of the uniaxial electronic anisotropy at each value of strain. Since the images at different values of strain are obtained under the same tunneling conditions, we can directly compare the magnitudes of the anisotropy obtained by this process at different strain values. The resultant anisotropy is plotted as a function of strain in figure 6.9b. We see that within experimental error, the magnitude of the anisotropy is independent of applied strain at the low temperature at which this measurement was performed.

The data in figure 6.8 demonstrate the power of the E-STS technique to reveal the interplay between strain and electronic anisotropy. For an Ising-nematic ($C_4-C_2$ symmetry breaking)[57], the ground state contains domains of differently oriented orders. In the presence of uniaxial strain, one orthorhombic domain is favored over the other[58]. Our measurements of domain wall motion and anisotropy strength visualized in figure 6.8 rule out several competing scenarios for how electronic anisotropy and domain walls could evolve under strain. For instance, a competing scenario to that seen in experiment would be one where the domain walls are pinned (by disorder or collectively) while the magnitude of the electronic anisotropy is modified.
within each domain as a function of strain. Instead, our experiments indicate that nematic domains behave similarly to Ising ferromagnets, where an applied magnetic field changes the domain structure but does not affect the saturation magnitude of the magnetization within a domain.

6.4 Strain in the Tetragonal/Paramagnetic Phase (>54K)

We now turn to E-STS measurements at 54K, above $T_S$. Shown in figure 6.10 is a sequence of STS images taken over the same region of the parent NaFeAs sample at different values of the applied strain at 54K. The strain is varied starting from -200V going up to +200V and then reversing back to -200V. STS images are shown at three biases: +10mV, +20mV, and +30mV. All images are obtained under the same tunneling conditions ($V_{set}=-50$mV, $I=-100$pA). Anisotropy in the images shows up as white streaks in the images that are oriented nearly vertically. The overall magnitude of the anisotropy is strongly reduced from its low temperature value in all the images. Considering figures 6.10a-e taken at a bias voltage of +10 mV, it is seen that the anisotropy is maximal at a strain voltage of +200V (figure 6.10c) while it is nearly absent at -200V (figure 6.10a and e). The anisotropy is seen to be a continuous function of strain with no domains appearing at any strain value. The images also show no evidence for hysteresis. Similar behavior is seen in the +20mV STS scans (figure 6.10f-j) and +30mV STS scans (figure 6.10k-o). The overall magnitude of the anisotropy is small below -10mV and above +30 mV.

We now look at the extreme ends of our applied strain in order to compare to theory. Figure 6.11a and figure 6.11b compare the STS images for our most posi-
tive (figure 6.11a) and most negative (figure 6.11b) strain voltages. Both images are obtained at the same tunneling conditions. A strong anisotropy (identified by vertical yellow streaks) is visible in the +200V image (figure 6.11a) while in the -200V image (figure 6.11b) the anisotropy has completely disappeared from the entire field of view. This behavior is also confirmed in the Fourier transforms (FT) of the STS data presented in figure 6.12a and 6.12b. The FT of the +200V data (figure 6.12a) shows strong $C_4$ symmetry breaking, with a pronounced three-peak structure. As previously reported, the three-peak structure is a signature of Fermi surface reconstruction, whose presence at temperatures $T > T_{SDW}$ we interpret as evidence for large-amplitude SDW fluctuations[59][60]. In contrast, the FT for the -200V data (figure 6.12b) shows a strongly diminished intensity overall along with weak (if any) $C_4$ symmetry breaking.

Figure 6.10: (a-e), Real space, 10mV E-STS scans at 54K progressing from maximal applied compressive strain at -200V to maximal applied tensile strain at +200V and back to maximum applied compressive strain at -200V. (f-j), 20 mV E-STS scans for same conditions as (a-e). (k-o), 30mV E-STS scans for same conditions as (a-e).
Figure 6.11: STM spectroscopy images of NaFeAs at $T=54K > T_S$ over the same area of the sample at (a) $+200V$ (white bar represents 20nm) and (b) $-200V$. Spectroscopy is performed at $V=+20$ mV and $I=100$ pA. It is seen that the rotational anisotropy is small at $-200V$ and largest at $+200V$.

To interpret the high temperature E-STS data we first observe that experimental samples experience built-in strain, arising from sample growth, from the process of incorporation into the device, and from differential thermal contraction when cooled to low temperature. To reach a zero strain situation, external strain must be applied to counteract the built-in strain[30]. The fact that the electronic anisotropy is nearly destroyed at $V_{\text{strain}} = -200V$ indicates that at this voltage the built-in strain is canceled by the externally applied strain. In general, we find that different samples require different applied voltages $V_{\text{strain}}$ to eliminate the anisotropy, indicating differing values of built-in strain. We have thus established that at temperatures $T < T_S$ the physics is strongly affected by local strain, which in our apparatus can be continuously dialed to zero.

At high temperature we observe neither the hysteresis nor the nematic domains (see figure 6.15 for the temperature evolution of domain walls and figure 6.10 for measurements at high temperatures) that were characteristic of the response in the long-range ordered state for $T < T_{SDW}$. In the low $T$ state, strain only affects the
Figure 6.12: (a-b) Absolute value of smoothed Fourier transform (FT) of the STS images with applied strain +200V and -200V respectively. (c-d) Show difference plot obtained by rotating the FT in (a-b) by 90 degrees and subtracting them from the unrotated FT (a-b). Non-zero values indicate $C_4$ symmetry breaking. (e-f) Difference plot obtained from theoretical modeling of the QPI arising from unidirectional SDW fluctuations.

relative areas of the different domains, but not the locally determined magnitude of the anisotropy. In sharp contrast, at high $T$ above $T_S$ there is no evidence of domains and the local value of the anisotropy depends on the applied strain. The fact that for a certain value of applied strain the electronic anisotropy can be reduced to a nearly vanishing value at every point in a wide field of view is conclusive evidence that the electronic structure above $T_S$ does not exhibit long-range nematic order. This implies that the anisotropic data shown in figure 6.10 and 6.11 can be interpreted as a paranematic response of the electronic structure to applied strain: the strength of the electronic anisotropy observed is dependent on the net strain applied to the field of
view studied in the experiment.

Our observation that the magnitude of the anisotropy can be controlled by strain at high temperature is a key new insight that E-STS provides. We will show below that the intensity of the electronic anisotropy seen in STM is directly related to the amplitude of the nematic fluctuations. Thus our data show that the amplitude of the nematic fluctuations themselves are set by the strain applied to the system. Such a strong nonlinear coupling between the structure and electronic nematicity has not previously been anticipated, and indicates the importance of properly accounting for the structural degrees of freedom in any description of the electronic properties of the pnictides.

6.4.1 QPI Comparison with Theory

The experimental QPI signal can be determined in one of two ways – it can either be determined from the FT of a single defect, or from the FT of a large area map that includes many defects. While the two procedures give similar results, they differ in some important respects. Figure 6.13 illustrates this difference. Shown in area map of NaFeAs at taken at 10meV conditions at 26K. This image is chosen since individual defects can be clearly distinguished from each other. Thus, it is relatively simple to crop around each defect and average together the QPI signal from all the cropped areas to generate the QPI signal associated with a single defect. The result of this procedure is shown in the inset of figure 6.13a. The corresponding Fourier transforms (FT) of figure 6.13a and inset 6.13a are shown in figures 6.13b and 6.13c respectively. The FTs have been cropped to half of the 1 Fe BZ of NaFeAs. As can be seen, the FTs have many similarities, but there are also several differences in the two FTs. In particular, the central “stripe” seen in the FT of the full real space image
looks different in the FT of the average defect, where it shows up as two separated regions of intensity. The difference in the two procedures is largely due to the fact that when the FT is taken of an entire image with several defects, one is in effect adding together signals from defects that are distributed in space, each of which gives rise to a phase factor from the location of the defect. The sum of these phases is in general a strong k-dependent function that depends on the distribution of defects in space. In practice, this factor is mostly (but not fully) spherically symmetric. Thus, Fourier space difference plots of the QPI signal extracted in these two different ways are quite similar to each other (but not identical) as shown in figure inset 6.13b and inset 6.13c.

To present the anisotropy in a form that can be compared more directly to theory we subtracted the FT image from its rotation by 90 degrees (see section 6.3.1) to create difference plots (figure 6.12c and 6.12d). In a $C_4$ symmetric situation the result would be zero up to noise, and indeed for the most negative strain voltage (figure 6.12d) little anisotropy is visible; however for the highly strained case (figure 6.12c) a strong $C_4$ symmetry breaking is visible. We have modeled the STS data theoretically along
the lines of our previous work[34] by computing the density of states modifications arising from unidirectional (stripe) SDW fluctuations at $T > T_{SDW}$ (see section 6.5.2). The calculations depend on three parameters: the amplitude of the incoherent SDW fluctuations denoted $\Delta_{LRA}$, the correlation length $\xi$ and the size of the Fermi pockets. Comparisons of figure 6.12e-f to 6.12c-d reveal a nice qualitative and quantitative agreement. Modeling the change from figure 6.12c to 6.12d (or figure 6.12e to 6.12f) requires a substantial change in $\Delta_{LRA}$, as a decrease in the correlation length is not enough. In other words the amplitude of the incoherent SDW fluctuations in the paramagnetic/para-nematic state is itself a strong function of strain.

Figure 6.14: (a) Theoretical QPI calculation from $-\pi/2a_0$ to $\pi/2a_0$ with inset showing the resulting difference plot. (b) Fourier transform of average defect image in inset a from $-\pi/2a_0$ to $\pi/2a_0$ with inset showing the resulting difference plot.

The theory for QPI that we (and others) use refers to the scattering pattern in k-space (or real space) generated by a single impurity, and thus the true comparison should be made to the average defect FT. Indeed, the low temperature QPI from theory (figure 6.14a) matches quite well with the single-defect experimental QPI pattern (figure 6.14b). The theory calculation is performed for a model as described in section 6.5.2 with parameters $\xi^{-1} = 0$ and $\Delta_{LRA} = 0.1$. The bright points along the
\( q_y \) directions (green arrows in figure 6.14a-b) as well as the outer features that run parallel to the center bright points (purple arrow in figure 6.14a-b) are both reproduced in theory. The center bright points along the \( q_y \) direction (green arrow figure 6.14a-b) have a slightly different scattering vectors lengths with the experiment having a smaller vector length when compared to theory, falling within a \(.03\pi/a_0 \) range of each other. The outer features (purple arrow figure 6.14a-b) are farther from the center in \( q_x \) then what is seen in experiment, falling within a \(.1\pi/a_0 \) range. While theory doesn’t capture all the details seen in experimental QPI, it indeed captures the import scattering vectors from the band structure near the Fermi level as discussed in greater detail in reference [34].

6.5 Strain in the Same Area Across Phases

Having established the role of strain in the electronic anisotropy observed in STS, we present a quantitative measure of the electronic anisotropy as a function of temperature. To do this, we track a constant area of the sample as a function of temperature while keeping the externally applied strain to zero. Shown in figure 6.15a-f are a sequence of STS images taken over the same area of the sample as a function of temperature starting from \( T = 28K < T_{SDW} \), through \( T = 52K > T_S \). These images are all taken under identical tunneling conditions, and each temperature is stabilized for approximately a day before the measurement is performed. The differential thermal expansion between the sample and substrate over this range of temperature is estimated to be <0.01% and can thus be neglected. The images show several interesting features. First, we note the presence of domain boundaries (visible as light stripes, marked with arrows for clarity) in figure 6.15a-e (there is no domain wall visible in panel f). It is seen that as the temperature is raised, the position of the domain
walls changes in such a way that the area of the minority domain decreases and the image contrast that defines the domain wall decreases. Exactly at $T_S$, domain walls completely disappear from the image (figure 6.15f).

Figure 6.15: (a-f) STM spectroscopy images of NaFeAs at various temperatures over the same area of the sample (white bar represents 20nm). Spectroscopy is performed at $V=+10$ mV and $I=100$ pA. At low temperature, nematic domains are seen in the sample as straight lines, and the orientation of the nematic order rotates by 90 degrees across the domain boundary as is also seen in the Fourier images of each side of the domain (inset to (a)). As the temperature is raised, the domains move and eventually vanish at the structural phase transition $T_S=52$ K.

To confirm that domains disappear in a much larger field of view than that presented in figure 6.15, we have tracked large areas > 500nm x 500nm areas of the sample across the structural transition temperature, which is at the limit of our STM scan range while keeping atomic registry with temperature. A subset of these images
is shown in figure 6.16. The images in figure 6.16a-b show effectively the same area of the sample at 45K and 49K (below $T_S$). We can clearly see domain boundaries (>20) appear as lines on these images, and we also see interesting domain wall motion as a function of temperature just below $T_S$ (which is not seen at very low temperature). The image shown in figure 6.16c is taken above $T_S$ and it is clear that there are no domain walls in the figure. This extends the statistics of figure 6.15 to a much larger number of domain walls, and we indeed see that all the domain walls are absent above $T_S$. To get even better statistics on the presence of domain walls, we scan multiple areas of the sample at each temperature. The fine scan limit of our STM is between 1-1.5 $\mu$m (depending on temperature) and we can further move around macroscopically on the sample to different locations with coarse motors. We have scanned (conservative estimate) about 80 $\mu$m$^2$ on the parent compound of NaFeAs across tens of samples at temperatures just below (temperatures that range from 3-7K below $T_S$) and above (temperatures that range from 1-7K above $T_S$) $T_S$. From our measurements just below $T_S$ we find that the average size of the domain is about 0.05 square microns. On the other hand, we have never seen any domains above $T_S$ in all of our measurements. If we assume a Poisson distribution of the density of domain walls, our observation of no domain walls implies that the probability that domain walls exist above $T_S$ (but we have missed them in all our measurements so far) is $< 10^{-6}$.

Our temperature dependent data for domain walls together with the strain dependence of the anisotropy provide definitive microscopic evidence that the true nematic transition is at the structural transition temperature $T_S$ and that there is a strong nematic susceptibility above $T_S$. While a similar conclusion has previously been reached by transport measurements and has been conjectured by some of us, the new data provide microscopic and spectroscopic evidence that rules out scenarios where a true
Figure 6.16: (a-c) STM images at below (a,b) and above (c) $T_S$ showing the evolution of domain walls with temperature. Below $T_S$, numerous (>20) domain walls are observed, which are visualized as curved lines on these images. Domains are observed to shrink or grow depending on the orientation of their anisotropy. No domain walls are observed above $T_S$.

nematic transition occurs above $T_S$.

6.5.1 Quantifying Temperature-Domain Anisotropy

We next use the temperature-dependent dataset in figure 6.15 to quantify the anisotropy seen in STM as a function of temperature. For each temperature, we determine the magnitude of $C_4$ symmetry breaking as in the analysis of section 6.3.1 for the domain that survives across $T_S$. We plot the resultant magnitude of the anisotropy as a function of temperature as the red dots in figure 6.17. In NaFeAs the spin density wave transition temperature $T_{SDW}$ (41K) is clearly separated from the structural transition temperature $T_S$ (52K) allowing us to distinguish the effects of the different orderings on the nematic order parameter. The most significant feature of this plot is the presence of a clear kink in the data just below the bulk $T_{SDW}$ at 40K. Several measures have been taken to minimize statistical and systematic sources of error in this plot. While the number of points on the curve is limited by the total data acquisition time (several months), each data point represents an average over
several hundred defects in the field of view and thus has virtually no statistical error. Independent data sets have also been obtained during heating and cooling experiments with identical results. The number of temperature data points we are able to obtain is constrained by the probability of tip changes at the elevated temperatures, and we optimize the experimental run time to keep the tip and sample conditions identical in the important temperature range of 25-55K, eliminating matrix element changes as a source of error. Thus, the observed kink is a true feature of the data set. The observed sharp decrease near $T_{\text{SDW}}$ rather than $T_S$ is direct evidence that the electronic nematicity observed in the electronic structure is primarily driven by spin fluctuations in this iron-based compound. We note that a close examination of the experimentally determined anisotropy parameter shows that the kink occurs a few Kelvin below the bulk $T_{\text{SDW}}$. Potential reasons for this include a slightly different surface $T_{\text{SDW}}$ and disorder-induced inhomogeneity in the locally measured $T_{\text{SDW}}$.

To understand the consequences of these measurements, we have developed a theoretical model to compute the QPI signal resulting from a Fermi surface reconstruction arising from either long-ranged stripe SDW order (at $T < T_{\text{SDW}}$) or stripe SDW fluctuations (at $T > T_{\text{SDW}}$) or a combination of the two. The model involves a gap parameter $\Delta_{\text{SDW}}$ parameterizing the amplitude of the fully coherent SDW order that sets in below $T_{\text{SDW}}$, a gap parameter $\Delta_{\text{LRA}}$ parameterizing incoherent SDW amplitude fluctuations (nematic fluctuations) at $T > T_{\text{SDW}}$ and the correlation length $\xi$ introduced in section 6.4.1. The results, shown in figure 6.17, confirm that a single model based on unidirectional SDW order and fluctuations can fully account for the experimentally observed anisotropy across different temperatures. To pinpoint whether the change observed at $T_{\text{SDW}}$ arises from the onset of coherent long ranged order or from a change in the amplitude of the (fluctuating plus coherent) gap we show two alternative calculations. In the first scenario, which highlights the impact
Figure 6.17: Nematic anisotropy measured as a function of temperature (red dots, note that the data are averaged over defects as described in section 6.3.1) and calculated from theory as described in text (solid curves). It is seen that a sharp kink exists at the magnetic transition temperature $T_{SDW} = 41\,K$, and most of the intensity in the nematic signal picks up only below the magnetic transition temperature. The key ingredient in the optimum theoretical fit (blue line) is the increase in the total SDW gap (i.e. both coherent and incoherent contributions) below $T_{SDW}$, as opposed to the appearance of coherent factors only (green curve). Note that removing the coherence factors (orange curve) barely changes the behavior of the blue curve.

of coherence factors, the magnitude of the total gap $\Delta^2 = \Delta^2_{SDW} + \Delta^2_{LRA}$ remains constant below $T_{SDW}$ but there is a transfer of incoherent spectral weight to coherent spectral weight as temperature is lowered, i.e. $\Delta_{SDW}$ increases at the same rate as $\Delta_{LRA}$ decreases. Then, the only change below $T_{SDW}$ is the appearance of coherence factors (via the anomalous, momentum off-diagonal Green’s function). In the second scenario, which highlights the effects of fluctuations, the fluctuating gap $\Delta^2$ increases as temperature is lowered due to an increasing $\Delta_{SDW}$ and a constant $\Delta_{LRA}$. The modeling clearly demonstrates that the main cause of the rapid increase in the anisotropy parameter below $T_{SDW}$ is an increase in the magnitude of the total fluctuating gap $\Delta^2 = \Delta^2_{SDW} + \Delta^2_{LRA}$, whereas the coherence factor effects arising from
long-range SDW order play a minor role. We have also modeled the strain dependence at $T > T_{SDW}$ by varying the fluctuating gap and the correlation length.

6.5.2 Theoretical Model

The relevant experimental quantity is the derivative with respect to bias voltage $V_{BIAS}$ of the sample-tip tunneling current $I$ ($\frac{dI}{dV}$), measured as a function of position $r$ on the surface of the sample. In an ideal sample the measured quantity would have the full translational and rotational symmetry of the lattice, but in the presence of defects at positions $R_i$ the measured quantity varies with position in a manner which is believed to be proportional to the defect-induced change $\delta \eta(r, w)$ in the local electronic density of states (LDOS) at position $r$ and energy $w = eV_{bias}$. The LDOS in turn is related to the defect scattering potentials $V_i$ by an electronic susceptibility $\chi$ that encodes information about the electronic physics and is discussed in more detail below:

$$\delta \eta(r, w) = \sum_i (r - R_i, w) V(R_i)$$  \hspace{1cm} (6.2)

Here we have assumed (as is the case in the experiment) that the resolution is on the scale of the unit cell size or greater so we may take the susceptibility to be translation-invariant and neglect local field corrections. For simplicity we also assume, following standard practice in the STS field, that each defect is point-like and gives rise to the same scattering potential and that the scattering is weak enough that a linear-response ansatz for the electronic response suffices.

The physical information is carried by the response function $\chi$, which describes the electronic standing waves created around each defect. The interference of the standing waves from different randomly positioned defects creates complicated patterns. We have found by modeling situations with different densities that if the pattern as-
associated with an individual defect cannot be isolated, the procedure of smoothing as described in section I above and then computing the difference of the image and its 90 degree rotation provides the best way to extract information about $\chi$.

Model: We use a four-band model of the pnictide Fermi surface with two zone-center hole-like Fermi pockets, labeled by $\gamma_1$ and $\gamma_2$, and two elliptical electron pockets, labeled by $X$ and $Y$. In the Brillouin zone appropriate to the single-Fe unit cell, the two electron pockets are centered at the $Q_x = (\pi, 0)$ and $Q_y = (0, \pi)$ points.

The band dispersions of the two hole pockets are given in terms of a function $h(\alpha_\gamma) = -\mu_\gamma + b(2\alpha_\gamma(1 - \cos k_x) + \frac{2}{\alpha_\gamma}(1 - \cos k_y))$ as

$$\varepsilon_{\gamma_1 \mathbf{k}} = \frac{1}{2} \left( h(\alpha_\gamma) + h\left(\frac{1}{\alpha_\gamma}\right) \right) + \frac{1}{2} \sqrt{\left( h(\alpha_\gamma) - h\left(\frac{1}{\alpha_\gamma}\right) \right)^2 + W^2} \quad (6.3)$$

$$\varepsilon_{\gamma_2 \mathbf{k}} = \frac{1}{2} \left( h(\alpha_\gamma) + h\left(\frac{1}{\alpha_\gamma}\right) \right) - \frac{1}{2} \sqrt{\left( h(\alpha_\gamma) - h\left(\frac{1}{\alpha_\gamma}\right) \right)^2 + W^2} \quad (6.4)$$

while the band dispersions of the electron pockets are

$$\varepsilon_{X \mathbf{k} + Q_x} = -\mu_e + b \left( 2\alpha_e(1 - \cos k_x) + \frac{2}{\alpha_e}(1 - \cos k_y) \right) \quad (6.5)$$

$$\varepsilon_{Y \mathbf{k} + Q_y} = -\mu_e + b \left( \frac{2}{\alpha_e}(1 - \cos k_x) + 2\alpha_e(1 - \cos k_y) \right) \quad (6.6)$$

The parameters $b = 4, \mu_\gamma = -0.17, \alpha = -2, W = 0.12, \mu_e = 0.32$ and $\alpha_e = 0.4$ are chosen so that the resulting Fermi surface resembles the Fermi surface of NaFeAs measured by ARPES[61]. The Fermi surface is shown in figure 6.18. Here, all energy scales are measured in units of $\varepsilon_0 \approx 1/3eV$, such that the bottom of the electron band is about 100meV below the Fermi level.

To compute the effect of SDW order and fluctuations on this Fermi surface we
Figure 6.18: Fermi surface for the four-band model, paramagnetic phase.

follow references [34][62]. We allow for the possibility of long-range stripe-like spin density wave order with a single ordering vector. For definiteness we choose the ordering wave-vector to be $Q_x = (\pi, 0)$. SDW order is characterized by an order parameter $\langle \Delta(\mathbf{r}) \rangle = \Delta_{SDW}$. A non-zero $\Delta_{SDW}$ couples the wave-vector $\mathbf{k}$ to $\mathbf{k} + Q_x$, in particular mixing the X electron band to the two hole bands (for simplicity we include only the coupling to the band $\gamma_1$ with the larger Fermi surface) and opening a gap, thereby changing the dispersion. We also allow for the possibility that long-range order is destroyed by phase fluctuations, $\langle \Delta(\mathbf{r}) \rangle \to 0$, so that there is no coherent coupling between $\mathbf{k}$ and $\mathbf{k} + Q_x$ while fluctuations in the amplitude $\langle \Delta(\mathbf{r})^2 \rangle = \Delta_{LRA}^2$ remain non-vanishing, so that a “pseudogap” is opened. We represent this situation mathematically via an 8x8 matrix electron propagator $\mathcal{G}_\sigma$ including both $\mathbf{k}$ and $\mathbf{k} + Q_x$ terms as
\[
G_{\sigma} = \begin{pmatrix}
g_{\gamma_1} & 0 & 0 & 0 & 0 & \sigma f & 0 & 0 \\
0 & g_{\gamma_1} & 0 & 0 & \sigma \tilde{f} & 0 & 0 & 0 \\
0 & 0 & g_{\gamma_2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \tilde{g}_{\gamma_2} & 0 & 0 & 0 & 0 \\
0 & \sigma \tilde{f} & 0 & 0 & g_X & 0 & 0 & 0 \\
\sigma \tilde{f} & 0 & 0 & 0 & 0 & \tilde{g}_X & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & g_Y & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \tilde{g}_Y \\
\end{pmatrix}
\]

(6.7)

\[
g_{\gamma_1}(k, w) = \left( w - \varepsilon_{\gamma_1 k} - \frac{\Delta^2_{SDW} + \Delta^2_{LRA}}{w - \tilde{\varepsilon}_{Xk} + i\xi^{-1}} \right)^{-1}
\]

(6.8)

\[
\tilde{g}_X(k, w) = \left( w - \varepsilon_{Xk} - \frac{\Delta^2_{SDW} + \Delta^2_{LRA}}{w - \tilde{\varepsilon}_{\gamma_1 k} + i\xi^{-1}} \right)^{-1}
\]

(6.9)

\[
G_Y(k, w) = (w - \varepsilon_{Yk})^{-1}
\]

(6.10)

\[
G_{\gamma_2}(k, w) = (w - \varepsilon_{\gamma_2 k})^{-1}
\]

(6.11)

\[
f(k, w) = \frac{\Delta_{SDW}}{(w - \varepsilon_{\gamma_1 k})(w - \tilde{\varepsilon}_{Xk}) - (\Delta^2_{SDW} + \Delta^2_{LRA})}
\]

(6.12)

\[\sigma\] denotes the electron spin and a tilde denotes the same function evaluated at \(k + Q_x\).

Following reference [62], we have also included a phenomenological broadening parameter \(\xi\) measured in units of the lattice spacing \(a\) and related to the correlation length of the phase fluctuations.
The extra terms in $g_{X,\gamma}$ express the effect of coherent and incoherent spin fluctuations in opening up a gap, while $f$ expresses the effect of coherent backscattering associated with long ranged order. We distinguish the fully normal phase ($\Delta_{SDW} = \Delta_{LRA} = 0$), the fluctuating nematic phase ($\Delta_{SDW} = \Delta_{LRA} \neq 0$) and the ordered phase ($\Delta_{SDW} \neq \Delta_{LRA} \neq 0$).

### 6.5.3 QPI Calculations in Real Space from Model

We now use standard formulas to compute the change in density of states, $\delta n(r, w)$, due to a non-magnetic impurity located at the origin. In the first Born approximation we have

$$\delta n(r, w) = Tr[MG(r, w+i\delta)V(G(-r, w+i\delta))]$$

with $G(r)$ the Fourier transform of the $G$ defined above, $M$ the square of the matrix element linking the STM tip to the band states, and $V$ the impurity scattering (all bold faced quantities are 8x8 matrices in the reduced zone defined above). We make the simplifying assumptions that the impurity scattering potential and STM matrix elements are momentum and band independent (connecting all momenta to all momenta and all bands to all bands, with equal amplitudes). Carrying out the sum one finds

$$\delta n(r, w) = -\frac{VM}{\pi} \lim_{\delta \to 0^+} \left( \sum_{\sigma} \left[ \sum_{ij} G_{ij\sigma}(r, w+i\delta) \right] \left[ \sum_{kl} G_{kl\sigma}(-r, w+i\delta) \right] - \delta \leftrightarrow -\delta \right)$$

(6.13)

where the Roman indices denote elements of the $G$ matrix defined above. Carrying out the sum over elements and spin degrees of freedom we find (the 2 is from the spin sum)
\[
\delta(k, w) = -\frac{2VM}{\pi} \lim_{\delta \to 0} (\delta n_1(r, w + i\delta) + \delta n_2(r, w + i\delta) - \delta \leftrightarrow -\delta) \quad (6.14)
\]

\[
\delta n_1(k, w) = \sum_{ij} (g_i(r, w + i\delta) + \tilde{g}_i(r, w + i\delta)e^{iQ x \cdot r})(g_j(-r, w + i\delta) + \tilde{g}_j(-r, w + i\delta)e^{-iQ x \cdot r}) \quad (6.15)
\]

\[
\delta n_2(r, w) = 2(1 + \cos(Q_x \cdot r))(f(r, w + i\delta) + \tilde{f}(r, w + i\delta))(f(-r, w + i\delta) + \tilde{f}(-r, w + i\delta)) \quad (6.16)
\]

\[
\delta n(r, w) \text{ defined in this way may be directly compared to the experimentally determined "cropped" QPI associated with a single impurity. In figure 6.11 we used } \\
\xi^{-1} = 0, \Delta_{LRA} = 0.05, \text{ (panel f) and } \Delta_{LRA} = 0.1 \text{ (panel e).}
\]

The temperature dependence of anisotropy parameter results shown in figure 6.17 were obtained using a mean-field like ansatz for the magnetic correlation length and the mean-field order parameter:

\[
\xi^{-1} = \xi_0^{-1}\sqrt{\frac{T - T_N}{T_S - T_N}} \quad \Delta_{SDW} = \Delta_0\sqrt{1 - \frac{T}{T_N}} \quad (6.17)
\]

with \( T_N = 40K, T_S = 52K, \xi_0 = 20, \Delta_0 = 0.14 \text{ and } \Delta_{LRA} = 0.052 \). To model the momentum space data we simply Fourier transform the real-space calculations and take the absolute value.
6.6 Temperature and Doping

We now study the entire doping and temperature phase diagram of the system NaFe\textsubscript{1-x}Co\textsubscript{x}As. Figure 6.19 shows a real space STS scan of NaFe\textsubscript{1-x}Co\textsubscript{x}<0.01As at 6K, well within the long-ranged magnetically ordered phase (\(T < T_{SDW}\)), showing several domain boundaries like those seen in the parent compound. Domain boundaries are observed only for dopings \(x < 0.02\) in agreement with previous\cite{63} specific heat and resistivity measurements that establish bulk long-range structural order. At higher doping, it becomes difficult to directly visualize the electronic anisotropy in real space due to the large number of dopants. However, we can study the prevalence of anisotropy in the images by studying their Fourier transforms\cite{34,40} and observing their \(C_2\) or \(C_4\) symmetry. For regions of the phase diagram that display domains, measurements are conducted within a single domain. Figure 6.20a-g shows the evo-
Figure 6.20: Nematic anisotropy as a function of doping in Fourier space. Shown are a sequence of Fourier transforms of spectroscopy images obtained on NaFe$_{1-x}$Co$_x$As for various values of $x$. All images are obtained at $V=+10$ mV. It is seen that the shape of the nematic structure in Fourier space evolves with doping, but the anisotropy itself persists across the superconducting dome and only disappears for $x=0.12$ which is beyond the superconducting dome. (colors correspond to phase diagram in figure 5.2)

olution of the FT of STS images near the Fermi energy (cropped to one-half of the first Brillouin Zone) for different doping concentrations and temperatures. While we clearly observe $C_2$ symmetry in most of the phase diagram, we have never observed domains or domain boundaries at dopings and temperatures outside the regime of long ranged SDW order (i.e. figure 6.20c-e). This indicates the disappearance of long-range order but the persistence of nematic fluctuations as doping is increased beyond the critical doping for the SDW order, similar to the phenomena we observed in the parent compound as temperature is increased above $T_S$. A close examination of the FTs in figure 6.20a-f shows that while the details of the patterns continuously evolve with doping, the wavevectors at which anisotropy is observed are fairly similar in magnitude across the phase diagram. ARPES measurements[64][65] of the doping-dependent band structure in NaFe$_{1-x}$Co$_x$As show fairly small changes in the dispersions of the bands and the chemical potential from the parent compound to the overdoped side of the phase diagram. Our work on the parent compound described
above shows that in order to get QPI features at wavevectors similar to experiment, it is essential to include band folding due to spin density wave order or fluctuations. This indicates that the anisotropy observed in our STS data comes primarily from spin order and fluctuations even for doped samples.

![Phase diagram of observed nematic domains and nematic anisotropy from STM measurements, superposed with bulk measurements of the phase diagram.](image)

Figure 6.21: Phase diagram of observed nematic domains and nematic anisotropy from STM measurements, superposed with bulk measurements of the phase diagram. We note that domains are only observed in STM where bulk orthorhombic order is known to exist. Nematic anisotropy is observed across the phase diagram and only disappears for samples that are not superconducting. (letters on data points correspond to figure 6.20)

Our doping dependent measurements show that electronic anisotropy exists both inside (figure 6.20a-e) and outside (figure 6.20f) the superconducting dome. We do see changes in the strength and wavevectors of the anisotropy across $T_{SC}$ (for example, comparing figure 6.20e and 6.20f), and detailed future measurements that track the same area of the sample across $T_{SC}$ can help address the interplay between the superconducting gap and nematic fluctuations. For the highly overdoped, non-superconducting sample we see $C_4$ symmetry in the FT, indicating the absence of any long-range nematic order or nematic fluctuations (figure 6.20g). A detailed ex-
ploration of the phase diagram of NaFe$_{1-x}$Co$_x$As, plotted in figure 6.21 along with our measured regions, can help in understanding the interplay between nematicity and superconductivity in these compounds[66][23]. The co-existence of these two phenomena and how each of them responds to strain provides an interesting dynamic for further study, especially given the evidence for a nematic quantum critical point in the superconducting dome in some families of the pnictides[67].

6.7 Optimally Doped NaFeAs

In the interest of better understanding the QPI across $T_{SC}$ and the nature of co-existence or competition between nematicity and superconductivity, we turn to studying the optimally doped compound NaFe$_{1-x}$Co$_{x=0.02}$As inside and outside the superconducting dome for the exact same area on the sample.

![Figure 6.22: Real space image of a spectroscopy map of optimally doped NaFeAs at 6k with $V_{bias} = 30$mV and $I = 200$pA.](image)

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6.7.1 Inside the Superconducting Dome at 6K

Looking at figure 6.22, we see a the real space STS image of a 230nm² measured at 6.4K. In our measurements on the optimally doped sample, we again never found a domain boundary in this region of the phase diagram (see figure 6.21 data point labeled d). We can see in the real space spectroscopic images a faint strip-order below the Fermi level, figure 6.22a-h, and above the Fermi level, figure 6.22i-p, we the faint strip-order disappear.

![Real Space STS Images](image)

Figure 6.23: Fourier transform of the real space image of a spectroscopy map of optimally doped NaFeAs at 6k.

As we have seem, it can be quite difficult to see strip-order in real space. Taking the Fourier Transform (FT) we can get a more redably see the periodicities in the real space spectroscopic measurements. In figure 6.23, we have taken the FT or the real space STS scans from figure 6.22. In figures 6.23a-h we can easily see the similar 3 stripes running along the $k_y$ direction, with one centered and two slightly
off center on the $k_x$ axis. It also exhibits $C_2$ rotational symmetry along with strong off axis peaks similar to what we have seen from the SDW/nematic phases (see figure 6.2b-c, 6.6b, 6.12a). Interestingly, we see the disappearance of our nematicity above the Fermi level where the FT looks a bit more $C_4$ symmetric. Given that we’re in the superconducting phase, there is a gap near the Fermi level and we should have electron-hole symmetry. Yet in our QPI measurements in figure 6.23 we don’t see this symmetry. Furthermore, it’s important to point out that we still see our nematic electronic order in the superconducting dome.

Figure 6.24: Energy cross-sections along (a) $k_x$ direction and (b) $k_y$ direction at 6k. White dots show dispersion.

We can get a better perspective of the dispersion we see in figure 6.23 by taking a cross-section of our STS measurements. We do this for the two direction in momentum space. This cross-section is plotted in figure 6.24 for energy vs $k_x$ (figure 6.24a) and energy vs $k_y$ (figure 6.24b). White dots are plotted to help guide the eye to the most intense dispersing features. We notice very weak dispersion along the $k_x$ direction.
(figure 6.24a) and strong dispersion along the $k_y$ direction (figure 6.24b), at least for these two dispersing features.

![Graph showing dispersion](image)

Figure 6.25: Fourier transform of the real space image of a spectroscopy map with arrow showing dispersion in 2D momentum space from -10meV to 10meV at 6k.

Plotting these identified dispersing features in the 2D momentum space, we can start to associate certain areas of intense QPI scattering, figure 6.25. As we notice in figure 6.24a, the arrow red in figures 6.25a-u on the $k_x$ axis barely disperses. On the other hand, the orange arrow along the $k_y$ direction clearly disperses to higher wavelength from -10mev to +10meV. Again, lack of electron-hole symmetry across the Fermi level is quite unexpected and hints to interesting underlying physics.

### 6.7.2 Above the Superconducting Dome at 30K

Looking at figure 6.26, we see a the real space STS image of a 230nm^2 measure at 30.2K. In our measurements on the optimally doped sample, we again never found a domain boundary in this region of the phase diagram (see figure 6.21 above the superconducting dome and above data point labeled d). Again, at this temperature
Figure 6.26: Real space image of a spectroscopy map of optimally doped NaFeAs 30K with $V_{bias} = 30$ mV and $I = 200$ pA.

(30K), we can see in the real space spectroscopic images a faint strip-order below and around the the Fermi level, figure 6.26a-g, and then we see the strip-order disappear, figure 6.22j-p.

As before is becomes more obvious if we take the FT where we can easily see the periodicities in the real space spectroscopic measurements. In figure 6.27, we have taken the FT or the real space STS scans from figure 6.26. In figures 6.27a-g we can easily see the similar 3 stripes running along the $k_y$ direction, with one centered and two slightly off center on the $k_x$ axis. It also exhibits $C_2$ rotational symmetry along with strong off axis peaks similar to what we have seen from the SDW/nematic phases (see figure 6.2b-c, 6.6b, 6.12a). Again we see the disappearance of our nematicity above the Fermi level (slightly more above then at 6K) where the FT looks a bit more $C_4$ symmetric. No we are no longer in the superconducting phase and we don’t expect any electron-hole symmetry. The QPI measurements of
Figure 6.27: Fourier transform of the real space image of a spectroscopy map of optimally doped NaFeAs 30K.

this sample in the superconducting phase and above it seem quite similar with some minor difference.

Do the same thing as before to see the dispersion in figure 6.27 we take the a cross-section of our STS measurements. We do this for the two direction in momentum space. This cross-section is plotted in figure 6.28 for energy vs $k_x$ (figure 6.28a) and energy vs $k_y$ (figure 6.28b). White dots are plotted to help guide the eye to the most intense dispersing features. Here we see more differences from the QPI in the superconducting phase and above it.

Plotting these identified dispersing features in the 2D momentum space, we can associate certain areas of intense QPI scattering, figure 6.29. Differing from the 6K data, we notice in figure 6.28a, the red arrow in figures 6.29a-u on the $k_x$ axis barely disperses. On the other hand, the orange arrow along the $k_y$ direction clearly really doesn’t disperse at all.
6.7.3 Comparing to QPI calculated from ARPES

Now we move to comparing our measure STM QPI with what we would expect from QPI calculated from earlier ARPES measurements on NaFeAs. To first approximation, equivalent dopeing NaFeAs doesn’t change the band structure but does change the Fermi level. In princible the expected QPI features won’t change but where they happen on the energy axes does.

Starting from the electronic band structure for the parent compound of NaFeAs, we plot what the band structure looks along the $k_x$ and the $k_y$ direction, figure 6.30a-b respectively. Both plots in figure 6.30a-b look quite similar with some minor differenced arrisine from the different distances for the the crystallographic directions $a$ and $b$. The band structure between the $k_x$ and $k_y$ direction differ more drastically once we enter the orthorhombic/SDW phase. Recalling that in SDW phase we get
a doubling of the periodicity along the crystallographic \( a \) direction due to the antiferromagnetic alignment of the spins along said direction while the crystallographic \( b \) direction’s periodicity remains the same due to the ferromagnetic alignment of the spins along the \( b \) direction. The white dotted lines in figure 6.30c show where the band folding occurs. Looking at figure 6.30c-d we have the folded band structure. We notice the bands along the folded direction (\( a \) direction) are have this new periodicity. We see the outer electron and hole pockets now centered around gamma (\( \Gamma \)), figure 6.30c. Along the \( b \) crystallographic direction we we also see new structure centered around the gamma point (\( \Gamma \)), figure 6.30d. These new bands are coming solely from the folding along the \( a \) crystallographic direction and therefore this doe not produce a new periodicity along the \( b \) crystallographic direction. Comparing figure 6.30c to figure 6.30d we more clearly see that 3 identical structures in figure 6.30c at a periodicity of half the Brillouin zone while in figure 6.30d we have 3 similar structures but not identical, preserving out one Brillouin zone periodicity.
Figure 6.30: NaFeAs bands in the orthorhombic state along the (a) $k_x$ direction (dotted lines indicate folding line) and (b) $k_y$ direction. In the SDW phase we get a doubling of the crystal periodicity along one direction and get band folding along that direction. (c) Shows the folded band structure along $k_x$ direction where the folding occurred and along the (d) $k_y$ direction.

We can now calculate the QPI from our orthorhombic/SDW phase to compare to our 6K and 30K data do try to identify any difference from our STM QPI data sets. To find the QPI from our bands we essentially do an auto-correlation for the 2D momentum space at each energy slice. The resulting plot of the auto-correlation calculation highlights the all the possible scattering vectors of that band structure (see figure 4.3 and figure 4.4). In figure 6.31 we have the resultant QPI structures from the bands in the orthorhombic/SDW phase along the $a$ and $b$ crystallographic direction. First looking at the 6K dataset we plot our strong QPI features from figure 6.22 over our calculated QPI (white dots in figure 6.31). We notice a couple of things from these plots. Our measures STM QPI does not match our expected
QPI along the $a$ direction. In the $b$ direction it looks like the strong dispersion we see might be coming from scattering from the center hole pocket to the outer electron pockets. Looking at figure 6.32 it becomes a bit more clear where we are getting these scattering vectors. Figure 6.32a shows the three bands involved in these scattering vectors coming from the hole pocket at the gamma point and two electron pockets at the edge of the Brillouin zone. Figure 6.32b show the expected QPI from the three bands in figure 6.32a. The green arrow in figure 6.32 shows one of the possible scattering vectors that match the QPI we see along the $b$ crystallographic direction in figure 6.31b. While these band might explain our strong QPI features along the $k_y$ direction, more interestingly, the QPI in the $k_x$ direction is doesn’t match what we would expect from the this band structure.

![Figure 6.31: Calculated QPI in the orthorhombic/SDW phase along the (a) $a$ crystallographic direction and the (b) $b$ crystallographic direction. White dots correspond to measured QPI from STM at 6K (see figure 6.31).](image)

We now turn to comparing our 30K data to the calculated QPI from our orthorhombic/SDW phase. In figure 6.33 we have the resultant QPI structures from the bands in the orthorhombic/SDW phase along the $a$ and $b$ crystallographic direction. Looking at the 30K dataset we plot our strong QPI features from figure 6.26 over our calculated QPI (white dots in figure 6.33). We notice a couple of things from these plots. Our measures STM QPI does not match our expected QPI along the $a$ direction and the $b$ direction. While the QPI along the $b$ crystallographic direction
Figure 6.32: (a) Three bands from the orthorhombic/SDW phase showing a hole pocked (blue) and two electron pockets (red) along the \( b \) crystallographic direction. (b) The expected QPI from the three bands in plot (a). Green arrow shows one scattering vector which matches measure QPI along the \( b \) direction (see figure 6.31b.  

doesn’t match, it also barely disperses which might indicated that these features aren’t coming from QPI scattering mechanics. Also similar to what we saw in our 6K dataset (figure 6.31) the QPI in the \( a \) direction doesn’t match what we would expect from this band structure. These interesting differences require a bit more investigation.

Figure 6.33: Calculated QPI in the orthorhombic/SDW phase along the (a) \( a \) crystallographic direction and the (b) \( b \) crystallographic direction. White dots correspond to measured QPI from STM at 30K (see figure 6.33).
Chapter 7

QPI and MoTe2 Topological Surface State

There has been a lot of recent interest in MoTe2 for the prediction of having a surface state with Weyl Fermions.

7.0.1 Weyl Fermions

Weyl fermions are a massless 1/2-spin particle that is predicted by Hermann Weyl in his solution to the Dirac Equation[68]. The Dirac equation was derived by taking the energy-momentum relationship

\[ E^2 = (pc)^2 + (mc^2)^2 \]  

and substituting the appropriate energy operator (Hamiltonian operator) and momentum operator from quantum mechanics, leading to

\[ E^2 - (pc)^2 = (mc^2)^2 \]
\[
\left(-\frac{1}{c^2} \frac{d^2}{dt^2} + \nabla^2\right) \phi = (mc^2)^2 \phi
\]  
(7.3)

Given the Klein-Gordon equation but due to the second order time derivative \( \phi \) can’t be interpreted as the square root of the probability density of the particle. Dirac found that by taking the square root of the wave operator in equation 7.3 solve this problem, and further more by using the Pauli matrices for a spin-1/2 particle he was able to come to Dirac equation for a spin-1/2 particle

\[
(c\left(\sum_{n=1}^{3} \alpha_n P_n\right) + \beta mc^2)\Psi = i\hbar \frac{d}{dt} \Psi
\]  
(7.4)

where \( \alpha_n \) are 4x4 matrices using Pauli matricies and \( \beta \) is the 4x4 identity matrix. Weyl’s equation comes from setting \( m = 0 \). This leads to the left handed and right handed Weyl spinors of the form

\[
\Psi = \begin{bmatrix} \chi_1 \\ \chi_2 \end{bmatrix} e^{-i(k \cdot r - wt)}
\]  
(7.5)

### 7.0.2 Weyl Semimetal

It is predicted that materials that break time reversal symmetry and inversion symmetry will have quasiparticles that behave like Weyl fermions [69][70][71][72][73][74][75][76][77][78]. This has also been observed [79][80][81]. The Weyl fermion quasiparticle excitations manifest themselves in these materials at what is termed the "Weyl point" where we get the intersection of a electron and hole pocket. Furthermore due to the the crystal-momentum on a quasiparticle in these materials, the quasiparticles don’t need to travel at the true speed of light, which is what is predicted for a true massless particle. There is a type-I Weyl semimetal which consist of
electron and hole pocket intersecting only at one point in the energy axis. In a 
type-II Weyl semimetal this intersection can happen across along a rang of ener-
gies. It turns out that it is necessary for the breaking of Lorentz invariance for 
the type-II Weyl semimetal [73] an therefor differs from the Weyl spinors coming 
from equation7.4. In Weyl semimetals, the Weyl points are connected in pairs of 
opposite chirality by a Fermi arc surface state [72][82], meaning open contours of 
constant energy. This would create very interesting QPI due scattering to and from 
the points of these arcs. People have been able to measure type-I Weyl semimet-
als [83][84][85][86][79][80][81][87][88][89][90][91][92][93][94] and there have been fewer 
observation of type-II Weyl semimetals such as MoTe$_2$ [95][78][96][97][98][99] and 
WTe$_2$[100][101][102][103][104]. People have studied these Fermi arcs by using trans-
port, exploring unique transport characteristics that are predicted for the Weyl band 
structure and the Fermi arcs [105][106][107][108][109][110][111][112]. Transport exper-
iments have been done on Weyl semimmetals [113][114][115][69][116][117][118][119][120][121] 
but definitively proving these transport features to Fermi arcs is very difficult. We use 
a surface probe to directly measure the surface state and employ tunable temperature 
conditions.

7.0.3 MoTe2

We studied type-II Weyl semimetal MoTe$_2$ which is a transition metal dichalcogenide 
with different phases at high temperatures[122][123]. The crystal has two states, ei-
ther hexagonal (2H) or monoclinit (1T”) phase at room temperature. The monoclinic 
phase undergoes a structural transition to orthohombic at 250K, called the Td phase. 
In this phase the molybdenum (Mo) atoms are centered of a buckled tellurium (Te) 
octahedron, see figure 7.1.
Figure 7.1: (a,b) $MoTe_2$ crystal structure where black box shows one unit cell.

The Td phase breaks inversion symmetry and as noted in section 7.0.2, this is required for the type-II Weyl semimetal band structure. In the monoclinic 1T' phase, we maintain inversion symmetry and therefore we get a topologically trivial. We exploit this by measuring the sample in the orthorhombic and monoclinic phase where we can compare their respective electronic properties using STM QPI measurements along with ARPES measurements.

7.0.4 Surface State QPI

The crystals where grown by the flux method and quenched from high temperature to keep the 1T’ phase at room temperature. Measurements are performed on in-situ cleaved crystals. STM topographic measurements taken over large areas, figure 7.2a show clean, flat surfaces with defects on the two different atomic sites along with the FT (inset) of the topographic image with circles identifying the atomic periodicity of the lattice. Figure 7.2b shows a zoomed in topographic image of the surface of $MoTe_2$ with atomic lengths color coded to the periodicities shown in the inset of figure 7.2a. Figure 7.3 shows two-dimensional cuts of the band structure measured
by ARPES along the cuts X-Γ-Y over a wide range of energy. Our measurements are consistent with theoretical calculations and previous measurements [95][78][96] on other crystals showing the Td phase. Taking real space spectroscopic measurements, and taking the Fourier transform (FT) to measure the QPI present in the sample, defects are in fact crucial, acting as elastically scatterers of quasiparticles for our measurements.

![Image of MoTe₂](image.png)

**Figure 7.2:** (a) Constant-current STM topographic image of MoTe₂ at 6K. Rows are parallel to the b-axis of the crystal and come from the c-axis buckling in the Td crystal structure. (Inset) Fourier transform of topography showing atomic periodicities (b) Closer topopagragic image of MoTe₂.

In figure 7.4a,b we have real space spectroscopic images at -35 and 50 mV, respectively. Will scattering around defects tend to be weak in this case, collectively across all defects we can get a stronger signal of our QPI scattering. The change in the local density of states is similar to measurements on topological insulator materials[125]. In the inset of figure 7.4 are the FT of the real space images. The important features to notice are in inset 7.4a are horizontal “wings” aligned with the a-axis of the crystal (red box, inset to figure 7.4a) and vertical stripe-like feature in the inset of figure 7.4b.
Figure 7.3: Two-dimensional cuts of the band structure along the high-symmetry directions X-Γ-Y over a wide range of energy as measured by ARPES (2nd derivative applied) at 90 K. Red dashed lines are theoretical predictions of the bulk band structure. Figure is from reference [124].

(green box) which is aligned with the b-axis of the crystal.

7.0.5 Theoretical Bands

To say more about our QPI measurements we compare them to theoretical calculations from the MoTe$_2$ band structure of the surface electronic structure. Using density-functional theory (DFT) we calculate[74] using lattice parameters from x-ray diffraction at 100K. This calculation produces four Weyl points at $k = (0.1011, 0.0503, 0)$ and points related by the reflections $M_{x,y}$. Each pair of these Weyl points located at the same value of $k_x$ is necessarily connected by Fermi arc surface states as stated earlier. We also have trivial surface states in momentum space. Calculating the surface band structure at each energy by projecting the full DFT calculation onto the surface, or by tight-binding model constructed from DFT. The calculated surface band structure at three energies is shown in figure 7.5. We see bulk and surface bands but since the surface states are two-dimensional, we can be easily picked out from the
other surface bands by thresholding the surface spectral density. The surface states contrast sharply with their surrounding bulk bands. This allows us to track dispersion of these surface states in energy. The surface bands are fairly localized in energy and first appear around -80meV, then lose intensity and hybridize strongly with the bulk bands above -10 meV. The evolution of hole and electron pockets matches with our measurements from ARPES, as shown in figure 7.6 which are consistent with previous measurements of \( \text{MoTe}_2 \)\cite{95}\cite{126}\cite{96}.

If we were to use calculations using a slightly different lattice constant such as in reference \cite{75} produce different a surface state band structure. In our calculations\cite{74} there is one Weyl point in each quadrant of the Brillouin zone where the Fermi arc is a
topological surface state connecting the Weyl points across the k_y axis. In the other calculation there are two Weyl points in each quadrant of the Brillouin zone with much smaller Fermi arcs and connect the Weyl points located within each quadrant. There is also a topologically trivial singly degenerate surface state. The surface state being single degenerate is unexpected given it’s Rashba partner seems to be missing in the surface bands[97]. Both of these calculations certainly have different properties for the topological surface state bands, the dispersion of these bands are quite similar.

7.0.6 Theoretical QPI

We can use the theoretical band structure to calculate the expected theoretical QPI. We can then use this to compare to our measured QPI from our STM measurements. There are selection rules that affect the relative intensities for different scattering vectors (q) coming from the crystal and time-reversal symmetry conservation laws[125], structure of the scattering potential[127][128], and matrix elements. For these measurements we assume that the scattering impurities are non-magnetic like in other transition-metal dichalcogenides[127].

Due to certain selections rules as mentioned above, the experimental QPI only show a subset of the theoretically allowed scattering vectors. Our calculated surface band structure, figure 7.7a, is made up of the projections of bulk bands, figure 7.7b,
and the surface states, figure 7.7c. Being able to separate the different parts of the band structure allows us to calculate the predicted QPI scattering pattern between the bulk bands and the fermi arcs (figure 7.7d), only between the projected bulk bands (figure 7.7e), and only between the surface state fermi arcs (figure 7.7f). We can now compare these theoretical QPI scattering patterns on the our QPI measurements. The features that stand out from our QPI measurements are the "wing" as seen in the inset of figure 7.4a) which seems to come from the fermi arc scattering QPI pattern in figure 7.7f. It should be also noted while these QPI scattering wavelength exist the QPI between the Fermi arc and the projected bulk bands, the intensity is much less than just from the scattering between the surface state Fermi arcs. More telling is the fact that these catering wavelength are not present in the bulk band scattering to other bulk bands (figure 7.7e), which leads us to conclude that these scattering features are from Fermi arc scattering.

Figure 7.7: (a) The calculated surface band structure at 65meV. (b) The part of the surface bands that come from the projected bulk bands onto the surface at 65meV. (c) The part of the surface bands that come from the surface state Fermi arcs at 65meV. (d-f) The calculated QPI from (a-c) respectively, at 65meV.
Now we compare the dispersion of the features seen in our measured experimental QPI to the calculated QPI from our theoretical surface state bands. In figure 7.8a-f we have the dispersion of the QPI scattering between Fermi arc surface states from -85meV to -35meV. There are two main features of the dispersion that we focus on. We have the "wing" along the $k_x$ direction coming from scattering across the Brillouin zone between both Fermi arcs. As we go up in energy we get the "spreading" of the "wings" along the $k_y$ direction originating from the spreading of the Fermi arc surface state bands along the same direction. The other prominent features is the elongation of the QPI scattering pattern at small wavelength along the $k_y$ direction near $\Gamma$. This features originates from scattering with-in each arc along the $k_y$ direction. A similarly to the "wings", the outward dispersion in $k_y$ comes from the "spreading of the Fermi arc along the $k_y$ direction.

Figure 7.8: (a-f) The expected QPI scattering pattern from our calculated Fermi arc surface state bands from -85meV to -35meV

In order to compare to our experimental QPI measurements we have to take into account a Fermi level shift in our sample. This Fermi level shift in our sample may
comec from either doping\cite{95}\cite{129}, sample aging\cite{130}, chemical inhomogeneity\cite{131}, or non-stoichimetry\cite{118} that occurs in topological insulators\cite{129}\cite{130}\cite{131} and semimetals\cite{95}\cite{118}. Therefore while our theory predicts that our Fermi arcs emerge around 85meV, in measurements of this material the Fermi arcs will likely emerge at a different energy.

![Figure 7.9](image)

Figure 7.9: (a-i) We have our measured QPI data set from -40meV to 40meV on the left side of each plot and the calculated theoretical QPI on the right side of each plot. Overlaid over each of the plots the the outline of our expected QPI coming from our model.

In figure 7.9a-i we have our experimentally measured QPI from -40meV to 40meV. In this figure we have plotted our measure QPI on the left side of the Brillouin zone and the expected theoretical QPI on the right side of the Brillouin zone. To further help in this comparison we have outlined the theoretical QPI and overlaid it across the entire Brillouin zone. In this set of images in figure 7.9 we study the dispersion on the small wavelength features dispersing along $k_y$ near $\Gamma$. We see a very nice qualitative and quantitative match between our QPI calculated from theory and our measure QPI. We indeed see the spreading along the $k_y$ direction the $\Gamma$ point and
very similar wavelength as in our theory QPI calculations.

Figure 7.10: (a-i) We have our measured QPI data set from -40meV to 40meV on the left side of each plot and the calculated theoretical QPI on the right side of each plot. Overlaid over each of the plots the the outline of our expected QPI coming from our model. Our measured QPI data has been thresholded in order to observe the dispersion of the outer wings on the $k_x$ axis.

In figure 7.10a-i we again have our experimentally measured QPI from -40meV to 40meV. This time we have thresholded the measured QPI to saturate the more intense center QPI scattering dispersion in order to observe the outer dispersion on the $k_x$ axis. Like we did in figure 7.9, we have plotted our measure QPI on the left side of the Brillouin zone and the expected theoretical QPI on the right side of the Brillouin zone. To further help in this comparison we have outlined the theoretical QPI and overlaid it across the entire Brillouin zone. Again, we see a very nice qualitative and quantitative match between our QPI calculated from theory and our measure QPI. We actually see the emergence of these “wings” coming from scattering across the Brillouin zone at -40meV. And as predicted from theory, we have the “spreading” of
the "wings" along the $k_y$ direction following the dispersion of the Fermi arcs in the same direction.

### 7.0.8 Topological Protected Surface State

It turns out that the trivial surface state band structures at higher temperatures is similar, but not exactly, like the the topologically non-trivial Fermi arcs surface state. The orthorhombic to monoclinic structural transition has a small ($\sim 3$ degrees) distortion of the c-axis stacking while otherwise leaving the structure intact. However we can exploit the fact that in the transition, the inversion symmetry is recovered in the monoclinic phase, implying that the high-temperature phase does not have Weyl points with topologically protected Fermi arc surface states. Performing these measurements at room temperature actually reveals the absence of any measurable QPI scattering in this sample. We interpret this as the loss of the topological surface state in the monoclinic phase. At lower temperatures, in the Td orthorhombic phase, we recover the topologically protected surface state and therefore very robust against disorder, at least at small scattering momentums. At higher temperatures, in the monoclinic phase, no topologically protected state exist and hence why we fail to measure the QPI scattering due to the states fragility to disorder (as has been observed in other metallic surface states[132]). This scenario, where topological protection is responsible for our observed low-temperature QPI is more compatible with the four Weyl point calculation rather than the eight Weyl point calculation (where the large surface state is trivial at both low and high temperature).

We can combine our previous strain techniques from section 6.2 we could move the phase boundary down to lower temperatures where we can easily change temperatures allowing us to turn the topological protection on and off.


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