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2020

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Symmetry-specific probes of strongly correlated materials:
Angle-dependent magnetoresistance and resonant ultrasound spectroscopy

by

Sylvia Lewin

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Physics

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Assistant Professor James Analytis, Chair

Professor Robert Birgeneau

Professor Graham Fleming

Fall 2020

Symmetry-specific probes of strongly correlated materials:
Angle-dependent magnetoresistance and resonant ultrasound spectroscopy

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Sylvia Lewin

Abstract

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Assistant Professor James Analytis, Chair

This thesis describes two distinct areas of research, and is accordingly presented in two parts.

The first subject is the use of semi-classical calculations of angle-dependent magnetoresistance to explain and predict the behavior of certain copper-based high-temperature superconductors. We show that the unusual angle-dependent magnetoresistance of the overdoped cuprate $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ may be explained by the presence of a (π, π) ordering. Additionally, we show that the angle-dependent magnetoresistance of $\text{HgBa}_2\text{CuO}_{4+\delta}$ can be used to constrain the possible nature of the Fermi surface reconstruction in the underdoped cuprates.

The second part of this work is dedicated to resonant ultrasound spectroscopy, an experimental technique to determine the mechanical resonances of an object. We have applied this technique to study the temperature-driven magnetic phase transitions of lithium iridate and iron-intercalated niobium disulfide. In the case of lithium iridate, we show that there is no elastic signature of the proposed Kitaev paramagnet phase transition at roughly 100 K. In samples of iron-intercalated niobium disulfide with various levels of intercalation, we see clear signatures of the expected antiferromagnetic phase transition, in addition to the spin glass behavior. We are able to refine the freezing temperature of the spin glass for the under-intercalated compound. More importantly, we are able to determine the symmetry of the higher-temperature antiferromagnetic phase transition in a near-stoichiometric sample, thus determining the symmetry of the antiferromagnetic ordering.

To my family, who have always encouraged my curiosity.
Without you, I never would have embarked on this journey.

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Acknowledgments

I would like to sincerely thank everyone who helped and guided me in the course of conducting this research.

Thank you to Mom, Dad, Greg, Eleanor, James, J.D., and the rest of my family for your constant love, humor, and support.

Thank you to my partner, Alex Erlandson, and to Lina Necib, Deniz Gürbüz, Alexia Miller, Simca Bouma, Caroline Sofiatti, Michael Cole, Carolyn Kierans, Tess Smidt, Aaron Szasz, Eric Dodds, and all of my other dear friends. Your encouragement, jokes, commiseration, and company kept me happy and made (almost) every day in graduate school a joy.

Thank you to my fellow frisbee-players, bell-ringers, and members of the Society of Women in the Physical Sciences for giving me a community and an outlet for my energy outside of research.

Thank you to Arkady Shekhter, Paola Giraldo Gallo, and Jon Betts for being incredibly generous with your time and expertise.

Thank you to Alejandro Ruiz, Ella Lachman, Liz Peterson, Rainiero Bulacia, Kirk Duran, and Vikram Nagarajan for your work on the resonant ultrasound project with me. Thank you especially to Gabriel Perko-Engel, Shannon Haley, and Eran Maniv, without whom this project would not have been possible.

In addition to those who worked directly with me, thank you to Nicholas Breznay, Toni Helm, Ian Hayes, Robert Kealhofer, Nityan Nair, Philip Moll, Gilbert Lopez, Sooyoung Jang, Nikola Maksimovic, and all of my other wonderful labmates throughout the years. I learned so much from each of you and had a great time doing science with you!

Finally, thank you to James Analytis for showing me how exciting condensed matter physics can be and for guiding me along this journey. I am truly grateful.

Part I

Angle-Dependent Magnetoresistance

Chapter 1

Introduction

Angle-dependent magnetoresistance (ADMR) refers to a change in electrical resistivity with respect to the angle of an applied magnetic field, where the magnitude of the field is kept constant and only its direction is varied.¹ ADMR is expected to occur even in materials with perfect rotational symmetry, since changing the angle between the magnetic field and the electrical current will change the magnitude of the Lorentz force acting on the conduction electrons. Beyond this basic effect, many material properties can contribute to ADMR, such as anisotropic scattering rates.

For a Fermi liquid, with a Fermi surface and well-defined quasiparticles, ADMR is a rich source of information about the Fermi surface geometry. Under the influence of the Lorentz force, quasiparticles will trace out orbits on the Fermi surface that are perpendicular to the applied magnetic field. As the angle of the applied field is varied, the quasiparticles sample different values of the Fermi velocity that vary in relation with the Fermi surface morphology, changing the observed resistance.

In this work, we examine the interlayer ADMR of two different hole-doped cuprate superconductors, $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ and $\text{HgBa}_2\text{CuO}_{4+\delta}$. The hole-doped cuprates were the first discovered high-temperature superconductors. They have a rich and complicated phase diagram, as shown schematically in Fig. 1.1. Without hole doping, the parent compounds of the cuprate superconductors are antiferromagnetic Mott insulators. As the concentration of holes in the material increases—for the compounds we are considering, this is accomplished by increasing the oxygen content—antiferromagnetism recedes and superconductivity emerges. The phase diagram also includes a pseudogap phase [1], so named because it involves the Fermi surface becoming partially gapped and therefore broken into disconnected Fermi arcs. The nature of the pseudogap phase is still not well understood. Additionally, various types of charge density wave (CDW) order have been observed in nearly all hole-doped cuprate superconductors [2, 3] and may even be related to the emergence of the pseudogap [4]. Addi-

¹The abbreviation AMRO, for angle-dependent magnetoresistance oscillations, may alternatively be used. We have chosen to use ADMR throughout this work because we are often studying systems with high scattering rates relative to the magnetic field strength, such that oscillations in the ADMR signal are not observable.

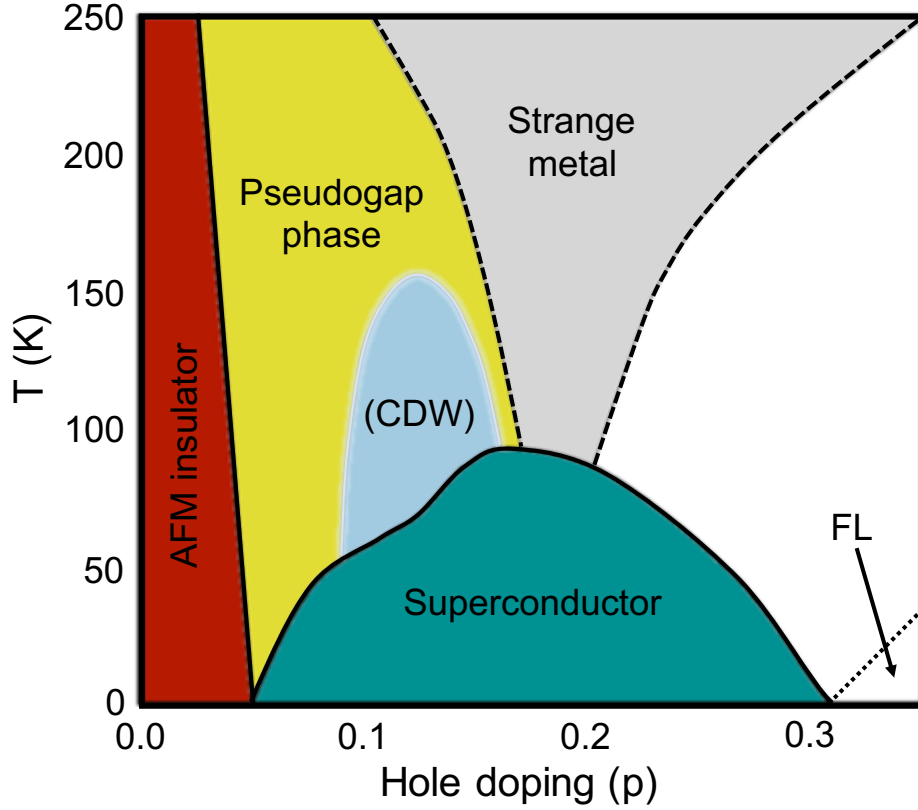


Figure 1.1: A general phase diagram for hole-doped superconductors, modeled after Ref. [7] and Ref. [8]. The solid lines indicate phase transitions into the insulating antiferromagnetic state and the superconducting state, respectively. The dashed lines indicate more subtle crossovers in behavior. In the strange metal region the electrical resistivity is linearly proportional to temperature, while the small region labeled FL is the Fermi liquid regime in which the resistivity is quadratic in temperature. The light blue dome labeled as (CDW) indicates the existence of CDW fluctuations; long-range CDW order appears under the superconducting dome when superconductivity is suppressed by an applied magnetic field.

tionally, nematicity seems to be a key feature of the hole-doped cuprates, appearing in both the pseudogap phase and some forms of CDW ordering [5, 6].

Of the broken symmetries connected to unconventional superconductivity, antiferromagnetism remains one of the most important, appearing in cuprate, iron-pnictide, organic, and heavy fermion materials [9, 10, 11]. It has been shown theoretically that antiferromagnetic fluctuations can mediate and enhance superconductivity [12, 13]. Then again, nematic fluctuations can also mediate unconventional superconductivity and enhance the superconducting transition temperature [14, 15]. Understanding the nature of the broken symmetry phases across the whole thermodynamic phase diagram of the cuprates is a key step toward understanding the origin of high-temperature superconductivity.

Cuprate superconductors are quasi-two-dimensional (Q2D) materials that all include CuO_2 layers. In Ch. 2 we introduce the mathematical definitions and equations that can be used to calculate interlayer ADMR for Q2D materials. Moreover, building on work in Ref. [16], we develop novel methods for calculating ADMR in Q2D materials when the Fermi surface is reconstructed due to long-range order. We already know that ADMR is a sensitive probe of the Fermi surface of a material [17, 18, 19, 20, 21]. However, the interpretation of ADMR measurements requires efficient and versatile calculations of the magnetotransport of a given Fermi surface so that models can be compared to experimental results. The mathematical methods we introduce open up new possibilities for the use of ADMR to determine the ordering wavevector of ordered states in the cuprates.

Importantly, ADMR can be observed even in materials that do not show quantum oscillations. Thus, the measurement is useful in systems in which sample disorder is high or in which the order has a small correlation length, as is often the case in the cuprates [4, 2]. Also in contrast to quantum oscillations, ADMR is measured at a fixed field strength, meaning that it may even be used to probe field-induced changes in the Fermi surface. In the case of Fermi surface reconstruction, ADMR is also sensitive to the energy scale of any (translational) symmetry-breaking order [22]. This energy scale is related to a “magnetic breakdown field,” as we describe in Ch. 2.

For Q2D systems such as the cuprates, ADMR is calculated in the same manner regardless of whether the system has a coherent three-dimensional Fermi surface or incoherent interlayer transport (coherence is defined here as the requirement that the interlayer transfer integral $t_\perp$ is much greater than the scattering rate $\hbar/\tau$) [23].² Therefore, ADMR can yield useful symmetry information in either case; the only difference is the interpretation of $t_\perp$. Throughout this work we will refer to the geometry of interlayer Fermi surface warping, but it should be understood that we could alternatively refer to the variation of interlayer hopping about the Fermi surface.

In the overdoped regime of the hole-doped cuprates, quantum oscillation measurements and angle-resolved photoemission spectroscopy show a large hole-like Fermi surface [24, 25]. Therefore, it is unsurprising that the ADMR of overdoped $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ at 45 T and 4.2 K can be well-modeled by a large hole-like Fermi surface with isotropic scattering [17]. However, at higher temperatures the ADMR is no longer captured by this simple model. In Ch. 3 we calculate ADMR for interlayer transport of cuprate superconductors in the presence of (π, π) order. We successfully fit experimental data from $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ using our model, showing that behavior previously attributed to anisotropic scattering in this material may in fact be due to (π, π) ordering. In Ch. 3 we also illustrate the physical motivation behind this model and its possible implications.

As shown in Fig. 1.1, the underdoped cuprates host a multitude of different ordered phases. Quantum oscillation measurements in various hole-doped cuprates at low temperatures and high magnetic fields have provided evidence of Fermi surface reconstruction arising

²Coherent and weakly incoherent interlayer transport will have different signatures in ADMR only when the applied field is nearly in-plane, which is a regime that we have not included in these calculations[23]

from symmetry-breaking order [26, 27, 28], but the nature of the broken symmetry remains a matter of considerable debate. Antiferromagnetic (π, π) reconstruction has been proposed [29], but mounting evidence suggests that a (possibly field-induced) charge density wave [30, 31, 32, 33, 34, 35] may be driving the reconstruction.

In Ch. 4 we model the ADMR of $\text{HgBa}_2\text{CuO}_{4+\delta}$ in the underdoped regime where the Fermi surface is reconstructed by an ordered state, possibly a CDW state [35]. We show that ADMR measurements can be employed to unambiguously distinguish the form of the Fermi surface's interlayer warping, placing severe constraints on the symmetry and nature of the reconstructing order. We describe experimentally accessible conditions in which these calculations can be put to the test.

Chapter 2

Mathematical framework

2.1 Quasiparticle motion in a magnetic field

Consider a quasiparticle on the Fermi surface of a material under a magnetic field, $\mathbf{B}$. Due to the Lorentz force, the quasiparticle will have a change in momentum given by

$$\frac{d\mathbf{k}}{dt} = \frac{e}{\hbar} \mathbf{v} \times \mathbf{B}. \quad (2.1)$$

Since $\mathbf{v}$ is perpendicular to the Fermi surface, the quasiparticle will orbit the Fermi surface in a plane perpendicular to the magnetic field. The period of the quasiparticle orbit will be

$$\mathcal{T} = \frac{\hbar}{eB} \oint \frac{dk}{v_{\perp}} \quad (2.2)$$

where the integral is around the quasiparticle orbit and $v_{\perp}$ is the component of $\mathbf{v}$ that is normal to $\mathbf{B}$ for a given $\mathbf{k}$. The cyclotron frequency ω_c is defined as

$$\omega_c = \frac{2\pi}{\mathcal{T}}. \quad (2.3)$$

From Eq. 2.3, it is clear that ω_c is constant for a given orbit about the Fermi surface when the magnetic field strength and direction are fixed. The cyclotron mass m_c is defined as $m_c \equiv eB/\omega_c$; in general, it is not the same as the quasiparticle's effective mass. We can also define a so-called “phase variable”:

$$\psi = \omega_c \frac{\hbar}{eB} \int \frac{dk}{v_{\perp}}, \quad (2.4)$$

which has the properties that $\frac{d\psi}{dt} = \omega_c$ and $\psi = 2\pi$ for a complete orbit [36].

2.2 The Shockley-Chambers tube integral

From the Boltzmann transport equation, it is possible to derive a general formula for electrical conductivity in the presence of an applied magnetic field. For temperatures such that $k_B T \ll E_F$, the conductivity tensor can be expressed as follows:

$$\sigma_{\alpha\beta} = \frac{e^2}{4\pi^3 \hbar^2} \int dk_H \frac{m_c}{\omega_c} \int_0^{2\pi} d\psi' \int_0^\infty d\psi v_\alpha(\psi', k_H) v_\beta(\psi' - \psi, k_H) e^{-\psi/\omega_c \tau}, \quad (2.5)$$

where all velocities are taken to be at the Fermi surface, τ is the quasiparticle relaxation time, and k_H is the component of momentum parallel to the magnetic field [36, 37]. This is known as the Shockley-Chambers tube integral, or sometimes simply the Shockley tube integral.

With a slight change of variables, this becomes

$$\sigma_{\alpha\beta} = \frac{e^2}{4\pi^3 \hbar^2} \int dk_H \frac{m_c}{\omega_c} \int_0^{2\pi} d\psi' \int_{-\infty}^{\psi'} d\psi'' v_\alpha(\psi', k_H) v_\beta(\psi'', k_H) e^{(\psi'' - \psi')/\omega_c \tau}. \quad (2.6)$$

It can be shown that, since v_α and v_β are periodic about the Fermi surface, this is equivalent to

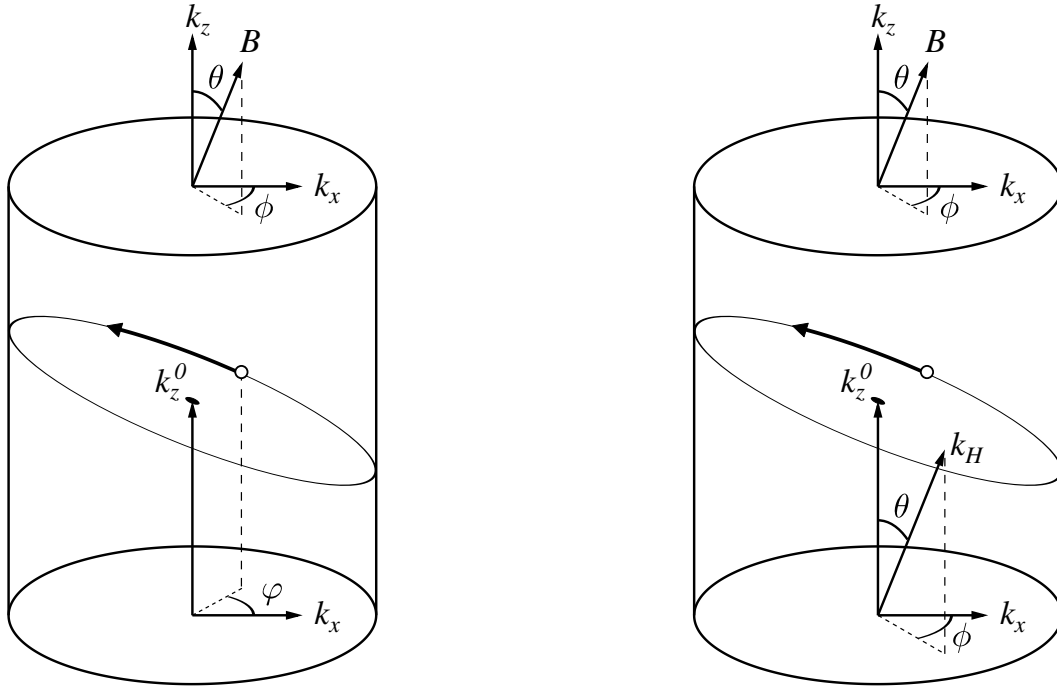
$$\sigma_{\alpha\beta} = \frac{e^2}{4\pi^3 \hbar^2} \int dk_H \frac{m_c}{\omega_c} \int_0^{2\pi} d\psi' \int_{\psi'}^\infty d\psi'' v_\beta(\psi', k_H) v_\alpha(\psi'', k_H) e^{(\psi' - \psi'')/\omega_c \tau}. \quad (2.7)$$

It is worth noting that ω_c and m_c are constants for a given orbit, but integrating across k_H means integrating across every possible orbit; therefore, ω_c and m_c are not necessarily constants in this integral.

2.3 The Shockley-Chambers tube integral in cylindrical coordinates

The materials we investigate are quasi-two-dimensional (Q2D), which means that their Fermi surfaces will be in the form of warped cylinders. We will define the cylindrical axis to be along k_z , i.e. z is the interlayer direction for our Q2D material. Consider a magnetic field of strength B whose direction is specified by a polar angle (θ) with respect to k_z and an azimuthal angle (ϕ) with respect to k_x . In the presence of such a field, quasiparticles in a Q2D material will trace out orbits on the cylindrical Fermi surface that are perpendicular to the field direction. The quasiparticle position can therefore be specified by two coordinates: φ , which gives its azimuthal position, and k_z^0 , which specifies the k_z position of the center of the orbital plane; see Fig. 2.1a.

Equation 2.7 gives the conductivity in terms of the phase variable, ψ , and the component of momentum perpendicular to the magnetic field, k_H . Note that the phase variable ψ in equation 2.7 is defined by $d\psi = \omega_c dt$; by construction, this quantity increases at a constant



(a) The position of a quasiparticle, represented in this figure by an open circle, can be specified by the central height of the orbit it is tracing (k_z^0) and its azimuthal position (φ). Note that φ is defined with respect to k_x , as is ϕ , the azimuthal angle of the applied magnetic field. The polar angle of the applied field, θ , is defined with respect to k_z .

(b) The vector $\mathbf{k}_H$ is the component of the quasiparticle momentum that is parallel to the applied magnetic field. For a given quasiparticle, $\mathbf{k}_H$ extends to the plane of that quasiparticle's orbit.

Figure 2.1: Illustration of terms defined in Sec. 2.3.

rate. In general, a quasiparticle's azimuthal position will not change at a constant rate about an orbit, so φ and ψ are distinct. For a Q2D material with a known Fermi surface, the quasiparticle velocity is straightforward to calculate as a function of φ and k_z^0 . Therefore, we will now rewrite the Shockley-Chambers tube integral in terms of these variables.

In equation 2.7, we can think of ψ' as the initial value of the phase variable and ψ'' as the value of the phase variable after some time t ; that is, $\psi'' = \psi' + \omega_c t$, where t varies from 0 to ∞ . Then we can convert the second integral into an integration over time:

$$\sigma_{\alpha\beta} = \frac{e^2}{4\pi^3\hbar^2} \int dk_H \frac{m_c}{\omega_c} \int_0^{2\pi} d\psi' \int_{\psi'}^{\infty} dt \omega_c v_\beta(0, k_H) v_\alpha(t, k_H) e^{-t/\tau}. \quad (2.8)$$

The relationship between the azimuthal position and the phase variable for any orbit is

given by

$$\frac{d\psi}{d\varphi} = \frac{d\psi/dt}{d\varphi/dt} = \frac{\omega_c}{\omega(\varphi)}, \quad (2.9)$$

where ω is the rate of change of the quasiparticle's azimuthal position and depends on φ .

Let us define φ_0 as the quasiparticle's azimuthal position at $t = 0$ and rewrite the first integral in terms of φ_0 . Note that the limits of integration do not have to change: both φ_0 and ψ range from 0 to 2π around an orbit.

$$\sigma_{\alpha\beta} = \frac{e^2}{4\pi^3\hbar^2} \int dk_H \frac{m_c}{\omega_c} \int_0^{2\pi} d\varphi_0 \frac{\omega_c}{\omega(\varphi_0)} \int_0^\infty dt \omega_c v_\beta(0, k_H) v_\alpha(t, k_H) e^{-t/\tau}. \quad (2.10)$$

We can define a variable φ that is the azimuthal position at time t , for a quasiparticle with starting azimuthal position φ_0 . Then $\frac{d\varphi}{dt} = \omega(\varphi)$ and $\varphi(t=0) = \varphi_0$, yielding

$$\begin{aligned} \sigma_{\alpha\beta} = & \frac{e^2}{4\pi^3\hbar^2} \int dk_H \frac{m_c}{\omega_c} \int_0^{2\pi} d\varphi_0 \frac{\omega_c}{\omega(\varphi_0)} \int_{\varphi_0}^\infty d\varphi \frac{\omega_c}{\omega(\varphi)} \\ & v_\beta(\varphi_0, k_H) v_\alpha(\varphi, k_H) \exp\left(-\int_{\varphi_0}^\varphi \frac{d\varphi'}{\omega(\varphi')\tau}\right). \end{aligned} \quad (2.11)$$

Note that we have written τ as a constant rather than as a function of φ' . For the materials studied in this work, we consider the quasiparticle relaxation time to be a constant at all points on the Fermi surface (the only exception being in Subsection 4.4.4). There are materials in which the scattering rate does depend on the azimuthal angle in reciprocal space, in which case τ would be parameterized as $\tau(\varphi')$ and we would not be able to take it outside the integral over φ' .

The vector $\mathbf{k}_H$ points parallel to the magnetic field; the magnitude of $\mathbf{k}_H$ specifies the plane of a quasiparticle's orbit, as shown in Fig. 2.1b. We define another vector, $\mathbf{k}_z^0$, as the k_z position of that plane at the center of the Fermi surface. We can see that $k_H = k_z^0 \cos(\theta)$ and therefore convert our integral over k_H to one over k_z^0 .

We can also substitute $m_c = eB/\omega_c$ and simplify to obtain

$$\begin{aligned} \sigma_{\alpha\beta} = & \frac{e^3 B \cos(\theta)}{4\pi^3\hbar^2} \int dk_z^0 \int_0^{2\pi} d\varphi_0 \frac{v_\beta(\varphi_0, k_z^0)}{\omega(\varphi_0)} \\ & \times \int_{\varphi_0}^\infty d\varphi \frac{v_\alpha(\varphi, k_z^0)}{\omega(\varphi)} \exp\left(-\int_{\varphi_0}^\varphi \frac{d\varphi'}{\omega(\varphi')\tau}\right). \end{aligned} \quad (2.12)$$

2.4 The form of ω for Q2D materials with small interplane warping

Note that we have assumed ω depends on φ but is independent of k_z^0 . This assumption is appropriate when the interplane warping is small ($t_\perp \ll E_F$).

Technically, we should write $\omega(\varphi, \theta)$, as ω also depends on the polar orientation of the applied magnetic field.

For a perfectly cylindrical Fermi surface, the angular frequency is equal to the cyclotron frequency and is given by $\omega = \omega_c = \omega_0 \cos(\theta)$, where ω_0 is a constant [37]. Specifically, $\omega_0 = eB/m^*$, where m^* is the quasiparticle effective mass (*not* the cyclotron mass).¹

For ω to be well-described by the expression above, it must be the case that the interlayer warping is small and that the in-plane Fermi surface is circular. While the interlayer warping is indeed small for the Q2D materials we will study, it is not necessarily the case that they are isotropic in-plane. Therefore, we must derive an expression for ω in the more general case of an in-plane Fermi momentum $k_F(\varphi)$ that varies as a function of the azimuthal angle.

We define $\omega = \frac{d\varphi}{dt}$, where φ is the azimuthal position of a quasiparticle in the k_x - k_y plane. In general, a quasiparticle orbiting around the Fermi surface will have periodic motion in both k_z and φ . However, in the case we are considering of small interlayer warping, a change in k_z will have a negligible effect on the quasiparticle's in-plane motion. Therefore, we can calculate ω as if the quasiparticle were only moving in the k_x - k_y plane; this motion will be driven by the component of the magnetic field in the interlayer direction, $B \cos(\theta)$.

If we define $k_{\parallel}$ to be the component of momentum along the in-plane orbit, then the quasiparticle equation of motion can be written as follows:

$$\frac{dk_{\parallel}}{dt} = \frac{eB \cos(\theta)}{\hbar} v_F(\varphi), \quad (2.13)$$

where $v_F(\varphi)$ is the in-plane Fermi velocity. By definition $v_F(\varphi) = \frac{\hbar k_F(\varphi)}{m^*}$, so

$$\frac{dk_{\parallel}}{dt} = \frac{eB \cos(\theta)}{m^*} k_F(\varphi). \quad (2.14)$$

We want $\frac{d\varphi}{dt}$, so we must now find the relationship between $k_{\parallel}$ and φ . This turns out to simply be the equation for an arc-length in polar coordinates. Noting that $dk_{\parallel}$ is the differential displacement along the orbit and the radius of the in-plane orbit is given by $k_F(\varphi)$, we have

$$\frac{dk_{\parallel}}{d\varphi} = \sqrt{k_F(\varphi)^2 + \left(\frac{dk_F(\varphi)}{d\varphi} \right)^2}. \quad (2.15)$$

Putting everything together, this yields

$$\omega = \frac{d\varphi}{dt} = \frac{d\varphi}{dk_{\parallel}} \frac{dk_{\parallel}}{dt} = \frac{eB \cos(\theta)}{m^*} \frac{k_F(\varphi)}{\sqrt{k_F(\varphi)^2 + \left(\frac{dk_F(\varphi)}{d\varphi} \right)^2}}. \quad (2.16)$$

¹Equivalently, we can state that the cyclotron mass for a cylindrical Fermi surface is $m_c = m^* / \cos(\theta)$. The fact that $m_c = m^*$ when $\theta = 0$, i.e. when the quasiparticle follows a simple circular orbit, can be derived from the equations in Sec. 2.1 and the fact that $v_F = \frac{\hbar k_F}{m^*}$.

We can simplify the above expression by noting that

$$\cos(\gamma(\varphi)) = \frac{k_F(\varphi)}{\sqrt{k_F(\varphi)^2 + \left(\frac{dk_F(\varphi)}{d\varphi}\right)^2}}, \quad (2.17)$$

where $\gamma(\varphi)$ is the angle between $v_F(\varphi)$ and $k_F(\varphi)$ [38]. Then we arrive at the form

$$\omega = \frac{eB \cos(\theta)}{m^*} \cos(\gamma(\varphi)). \quad (2.18)$$

Therefore, in a Q2D material with small interplane warping,

$$\omega \approx \omega_0 \cos(\theta) \cos(\gamma(\varphi)), \quad (2.19)$$

where $\gamma(\varphi)$ is the angle between the in-plane Fermi velocity and the in-plane Fermi momentum, which varies about the Fermi surface and is entirely determined by the Fermi surface geometry². Note that if the in-plane Fermi surface is circular, $\cos(\gamma(\varphi)) = 1$ so this simplifies to the expression for the cylindrical Fermi surface.

2.5 The Fermi velocity

Since ADMR is a probe of interlayer conductivity, we want to calculate σ_{zz} . We need an expression for v_z , which we can obtain from a symmetry-constrained model of the Fermi surface.

For a general Q2D material, we can expand the Fermi wavevector in spherical harmonics [40]:

$$k_F(\kappa_z, \varphi) = \sum_{\mu, \nu \geq 0} k_{\mu\nu}^{\{s\}^c} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (\nu \kappa_z) \times \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (\mu \varphi) \quad (2.20)$$

where κ_z ranges from $-\pi$ to π over h_{BZ} , the height of the Brillouin zone. We can write

$$\kappa_z = \frac{2\pi k_z}{h_{\text{BZ}}} \quad (2.21)$$

given that k_z varies from $-h_{\text{BZ}}/2$ to $h_{\text{BZ}}/2$.

In this work, we are only considering the ADMR of tetragonal Q2D materials. For a simple tetragonal system, $h_{\text{BZ}} = 2\pi/c$, where c is the interlayer lattice parameter; in a body-centered tetragonal structure we find $h_{\text{BZ}} = 4\pi/c$. At this point it is helpful to note that for a simple tetragonal system the interlayer spacing $d_\perp$ is equal to the interlayer dimension of the unit cell c , while $d_\perp = c/2$ for a body-centered tetragonal system. In other words, for both systems we have $h_{\text{BZ}} = 2\pi/d_\perp$. Additionally, the systems we are considering have a mirror

²An alternate, equivalent form of Eq. (2.19) is given in Ref. [39].

symmetry that transforms $k_z \rightarrow -k_z$, which means that $\sin(\nu\kappa_z)$ terms are not allowed. Given all this, we can rewrite Eq. 2.20 for the systems we are modeling as

$$k_F(k_z, \varphi) = \sum_{\mu, \nu \geq 0} k_{\mu\nu}^{\{c\}} \cos(\nu d_\perp k_z) \times \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (\mu\varphi). \quad (2.22)$$

We will only be considering expansions including the terms $\nu = 0$ and $\nu = 1$, since this has been shown to be sufficient to describe the Fermi surface of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [17] and we are using a minimal model for $\text{HgBa}_2\text{CuO}_{4+\delta}$. The parameters $k_{\mu 0}$ describe the in-plane Fermi contour, while the terms $k_{\mu 1}$ relate to the interlayer dispersion.

So for the systems we are studying, we can describe the Fermi surface as [17, 41, 23, 42]:

$$E_F(k_z, \varphi) = \frac{\hbar^2 k_F^2(\varphi)}{2m^*} - 2t_\perp(\varphi) \cos(d_\perp k_z). \quad (2.23)$$

where the in-plane Fermi surface is defined by

$$k_F(\varphi) = \sum_{\mu \geq 0} k_{\mu 0}^{\{c\}} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (\mu\varphi) \quad (2.24)$$

and the interlayer hopping integral is given by

$$t_\perp(\varphi) = \sum_{\mu \geq 0} k_{\mu 1}^{\{c\}} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} (\mu\varphi). \quad (2.25)$$

Note that further crystal symmetries may constrain which values of $k_{\mu 0}^{\{c\}}$ and $k_{\mu 1}^{\{c\}}$ are allowed to be non-zero. Such constraints for $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ are derived in detail in Ref. [41] and will be discussed in Ch. 3.

Using Eq. 2.23 along with the definition $v_z = \frac{1}{\hbar} \frac{dE(\mathbf{k})}{dk_z}$, we find the interlayer velocity to be

$$v_z(\mathbf{k}, \varphi) = \frac{2d_\perp t_\perp(\varphi)}{\hbar} \sin(d_\perp k_z). \quad (2.26)$$

Therefore,

$$\begin{aligned} \sigma_{zz} = & \frac{d_\perp^2 e^3 B \cos(\theta)}{\pi^3 \hbar^4} \int_{-\pi/d_\perp}^{\pi/d_\perp} dk_z^0 \int_0^{2\pi} d\varphi_0 \frac{t_\perp(\varphi_0) \sin(d_\perp k_z(\varphi_0))}{\omega(\varphi_0)} \\ & \times \int_{\varphi_0}^{\infty} d\varphi \frac{t_\perp(\varphi) \sin(d_\perp k_z(\varphi))}{\omega(\varphi)} \exp\left(-\int_{\varphi_0}^{\varphi} \frac{d\varphi'}{\omega(\varphi')\tau}\right). \end{aligned} \quad (2.27)$$

Note that in the equation above, we have explicitly written k_z as a function of φ_0 and φ , respectively. In the following section we will explain this dependence.

2.6 Expressing k_z as a function of φ

The value k_z should be more accurately written as $k_z(k_z^0, \varphi)$: a quasiparticle's position in k space depends on the orbit it is following, as well as its azimuthal position on that orbit. It turns out that the expression for k_z also depends on whether the Fermi surface intersects the Brillouin zone.

If a Fermi surface is entirely contained within a Brillouin zone, each quasiparticle will stay on a single orbit through its lifetime, and we can see from simple geometric considerations that

$$k_z = k_z^0 - k_F(\varphi) \tan(\theta) \cos(\varphi - \phi). \quad (2.28)$$

Let us now consider the case of a Fermi surface that crosses the Brillouin zone boundary. When a quasiparticle Bragg diffracts at the Brillouin zone boundary it will have a momentum change given equal to a reciprocal lattice vector. In this case, the quasiparticle will jump to a different “slice” of the Fermi surface[16], changing its value of k_z^0 but preserving k_z (see Fig. 2.2). The amount by which k_z^0 changes after Bragg diffraction will depend on the details of the Fermi surface and Brillouin zone geometries, as explained in the next section.

As a further complication, each time a quasiparticle reaches the Brillouin zone boundary it has a non-zero probability p to avoid Bragg diffraction and effectively tunnel through the gap in k space to stay on its original orbit [43]. In semiclassical terms, the quasiparticle path in real space may be curved sufficiently by the magnetic field to avoid Bragg diffraction. This phenomenon is known as magnetic breakdown (MB). The quasiparticle can either Bragg-diffract or undergo magnetic breakdown at each intersection of the Fermi surface and the Brillouin zone; therefore, these intersections are known as “MB junctions.”³

The MB probability is given by $p = e^{-B_0/B}$, where the breakdown field B_0 is a material-specific parameter related to the size of the energy gap at the Brillouin zone boundary, which is itself proportional to the size of the gap in k space between Fermi surface sections [22]. Note that in a Q2D material, the quasiparticle faces a larger k space tunneling barrier when its orbit is tilted away from the interlayer direction; in fact, we find that the breakdown field will be proportional to $\frac{1}{\cos(\theta)}$ [44]. We choose to express the MB probability as $p = e^{-B_0/B \cos(\theta)}$ so that B_0 itself has no angular dependence.

Taking Bragg diffraction and MB into account, we can see that for a given quasiparticle

$$k_z = k_z^0 - k_F(\varphi) \tan(\theta) \cos(\varphi - \phi) + \sum_j n_j(\varphi) \Delta k_z^{(j)}, \quad (2.29)$$

where j indexes all of the MB junctions, n_j indicates the number of times the quasiparticle has Bragg-diffracted at the j th MB junction, and $\Delta k_z^{(j)}$ is the amount by which k_z^0 changes each time the quasiparticle Bragg-diffracts from the j th MB junction [16]; $\Delta k_z^{(j)}$ can be found through simple geometric means, as described in the following section. We set $n_j(\varphi_0) = 0$.

³MB can also occur away from the Brillouin zone boundary, provided that two Fermi surface pockets have a small enough separation between them in k space.

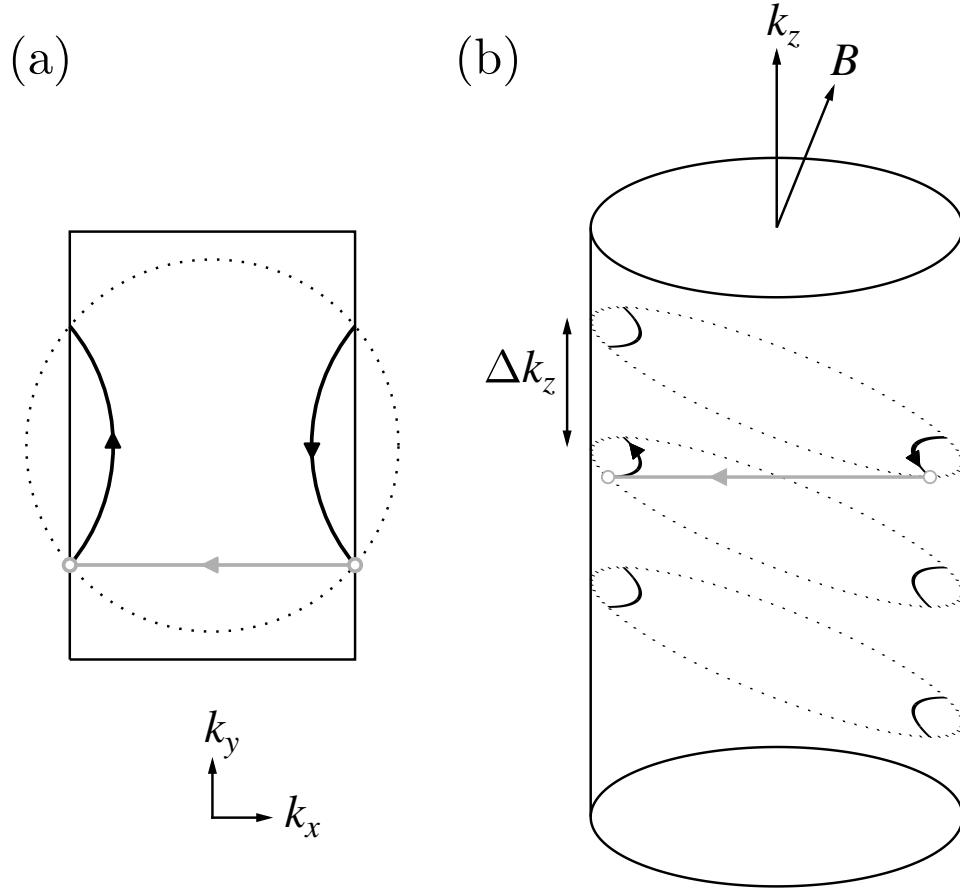


Figure 2.2: An illustration of the effect of Bragg diffraction on quasiparticle motion, including a) a top-down and b) an angled view. In this example, the original Fermi surface is cylindrical while the reconstructed Brillouin zone is rectangular. The dotted lines indicate quasiparticle orbits around the unreconstructed Fermi surface, while the solid arcs show a new quasiparticle orbit about the reconstructed Fermi surface. The solid gray line indicates the Bragg diffraction vector. As illustrated by the figure above, the value of k_z will be the same before and after Bragg diffraction; however, the value of k_z^0 will change by Δk_z as the quasiparticle moves to a different orbit about the Fermi surface. The value of Δk_z for a given MB junction depends on the geometry of the Fermi surface and the Brillouin zone.

Note that in Eqs. 2.28 and 2.29 we have neglected the effects of interlayer warping on quasiparticle motion. For the Q2D materials we study we assume the interlayer warping is much weaker than the in-plane warping, so this is a reasonable omission except near $\theta = 90^\circ$.

2.7 Calculating Δk_z for a given pair of MB junctions

Consider a quasiparticle undergoing Bragg diffraction between two MB junctions, from azimuthal position φ_i to position φ_f . As illustrated in Fig. 2.2, the quasiparticle will undergo a change in both φ and k_z^0 but it will keep the same value of k_z . Combining this restriction with Eq. 2.28 leads to the condition

$$k_z^{0(i)} - k_F(\varphi_i) \tan(\theta) \cos(\varphi_i - \phi) = k_z^{0(f)} - k_F(\varphi_f) \tan(\theta) \cos(\varphi_f - \phi), \quad (2.30)$$

and therefore

$$\begin{aligned} \Delta k_z^{(i \rightarrow f)} &= k_z^{0(f)} - k_z^{0(i)} \\ &= \tan(\theta) [k_F(\varphi_f) \cos(\varphi_f - \phi) - k_F(\varphi_i) \cos(\varphi_i - \phi)]. \end{aligned} \quad (2.31)$$

Note that when a quasiparticle Bragg diffracts from the MB junction at φ_i , it can only go to the junction at φ_f . The Bragg diffraction connections between MB junctions are determined by which MB junctions are connected by a reciprocal lattice vector. Therefore, we can denote $\Delta k_z^{(i \rightarrow f)}$ simply as $\Delta k_z^{(i)}$, as we do in Eq. 2.29.

See Sec. 3.2 for an example of how to calculate all of the $\Delta k_z^{(j)}$ for a specific reconstructed Fermi surface.

2.8 Solving the Shockley-Chambers tube integral

We can substitute Eq. 2.29 into Eq. 2.27 and integrate over k_z^0 . We then have

$$\begin{aligned} \sigma_{zz} &= \frac{d_\perp e^3 B \cos(\theta)}{\pi^2 \hbar^4} \int_0^{2\pi} d\varphi_0 \frac{t_\perp(\varphi_0)}{\omega(\varphi_0)} \int_{\varphi_0}^\infty d\varphi \frac{t_\perp(\varphi)}{\omega(\varphi)} \\ &\quad \times \cos \left(-G(\varphi) + d_\perp \sum_j n_j(\varphi) \Delta k_z^{(j)} + G(\varphi_0) \right) \exp \left(- \int_{\varphi_0}^\varphi \frac{d\varphi'}{\omega(\varphi') \tau} \right), \end{aligned} \quad (2.32)$$

where we have defined

$$G(\varphi) \equiv d_\perp k_F(\varphi) \tan(\theta) \cos(\varphi - \phi). \quad (2.33)$$

From the expressions above, it should be clear that the conductivity is a function of both θ and ϕ ; that is to say, it is a function of the magnetic field direction. This is the basis for ADMR. For brevity, we write σ_{zz} rather than $\sigma_{zz}(\theta, \phi)$ throughout this work.

We can express $t_\perp$ as $t_\perp(\varphi) = t_\perp^0 f(\varphi)$. If we also insert Eq. 2.19, then for ease of notation we can write our conductivity in units of $d_\perp e^3 B (t_\perp^0)^2 / \pi^2 \hbar^4 \omega_0^2$ so that it is dimensionless:

$$\begin{aligned} \sigma_{zz} = & \frac{1}{\cos(\theta)} \text{Re} \left[\int_0^{2\pi} d\varphi_0 \frac{f(\varphi_0)}{\cos(\gamma(\varphi_0))} \int_{\varphi_0}^{\infty} d\varphi \frac{f(\varphi)}{\cos(\gamma(\varphi))} \right. \\ & \times \exp \left(i[G(\varphi) - G(\varphi_0)] - id_{\perp} \sum_j n_j(\varphi) \Delta k_z^{(j)} - \frac{1}{\omega_0 \tau \cos(\theta)} \int_{\varphi_0}^{\varphi} \frac{d\varphi'}{\cos(\gamma(\varphi'))} \right) \Big]. \end{aligned} \quad (2.34)$$

Note that we have used $\cos(x) = \text{Re}[e^{ix}]$ to obtain the form above.

2.8.1 Fermi surface in a single Brillouin zone

In the simpler case of a Fermi surface that does not intersect the Brillouin zone boundary, we have

$$\begin{aligned} \sigma_{zz} = & \frac{1}{\cos(\theta)} \text{Re} \left[\int_0^{2\pi} d\varphi_0 \frac{f(\varphi_0)}{\cos(\gamma(\varphi_0))} \int_{\varphi_0}^{\infty} d\varphi \frac{f(\varphi)}{\cos(\gamma(\varphi))} \right. \\ & \times \exp \left(i[G(\varphi) - G(\varphi_0)] - \frac{1}{\omega_0 \tau \cos(\theta)} \int_{\varphi_0}^{\varphi} \frac{d\varphi'}{\cos(\gamma(\varphi'))} \right) \Big]. \end{aligned} \quad (2.35)$$

Taking advantage of the periodic nature of $f(\varphi)$, $\gamma(\varphi)$, and $G(\varphi)$, we can rewrite Eq. 2.35 as [37, 39]

$$\begin{aligned} \sigma_{zz} = & \frac{1}{1 - P(0, 2\pi)} \frac{1}{\cos(\theta)} \text{Re} \left[\int_0^{2\pi} d\varphi_0 \frac{f(\varphi_0)}{\cos(\gamma(\varphi_0))} \right. \\ & \times \int_{\varphi_0}^{\varphi_0 + 2\pi} d\varphi \frac{f(\varphi)}{\cos(\gamma(\varphi))} \exp \left(i[G(\varphi) - G(\varphi_0)] \right) P(\varphi_0, \varphi) \Big], \end{aligned} \quad (2.36)$$

where

$$P(\varphi_1, \varphi_2) \equiv \exp \left(-\frac{1}{\omega_0 \tau \cos(\theta)} \int_{\varphi_1}^{\varphi_2} \frac{d\varphi'}{\cos(\gamma(\varphi'))} \right). \quad (2.37)$$

The equation above can be integrated numerically; when possible, the integral in P should first be solved analytically to make numerical integration more efficient.

2.8.2 Fermi surface across the Brillouin zone boundary: The vectorized form of the Shockley-Chambers tube integral

When the Fermi surface intersects the Brillouin zone boundary, the full version of Eq. 2.34 is needed. Recall that n_j in Eq. 2.34 is a count of the number of times a quasiparticle has Bragg-diffracted from the j th MB junction. Note that the value of the integrand changes whenever the quasiparticle undergoes Bragg diffraction, due to the term $\sum_j n_j(\varphi) \Delta k_z^{(j)}$.

If the probability of magnetic breakdown were $p = 1$, then quasiparticles would never Bragg-diffract and we would have $n_j(\varphi) = 0$ for all j and all φ . On the other hand, if

the probability of magnetic breakdown were $p = 0$, then quasiparticles would Bragg-diffract every time they reached an MB junction and $n_j(\varphi)$ would simply count the number of times the quasiparticle had reached the MB junction in question. Mathematically, we could write $n_j(\varphi) = \left\lfloor \frac{\varphi - \mathbf{M}_j}{2\pi} \right\rfloor + H(\mathbf{M}_j - \varphi_0)$, where $\mathbf{M}_j$ denotes the azimuthal position of the j th MB junction, H is the Heaviside step function, and $\lfloor x \rfloor$ indicates the floor of x .

In the more interesting case of $0 < p < 1$, it is impossible to write a closed-form expression for $n_j(\varphi)$, as the path of the quasiparticle will be non-deterministic. In order to evaluate the integrals in Eq. 2.34, we must be able to account for all possible trajectories of each quasiparticle. Building on Falicov and Sievert's treatment of magnetic breakdown for in-plane conductivity [45], Nowojewski *et al.* showed that this issue can be solved by writing a self-consistent, vectorized form of the Shockley-Chambers tube integral [16, 46]. This method has previously been used to study systems wherein ω does not vary with φ [47]. We have extended this method to account for the variation of ω about the Fermi surface. See App. A.1 for a detailed comparison between the original vectorized equation in Ref. [16] and the equations we use in this work.

Consider a Fermi surface with N MB junctions; we can think of our Fermi surface as being broken into N separate segments by the MB junctions. We will define a vector of length $N + 1$ called $\mathbf{M}$, which is a vector of the azimuthal positions of all the MB junctions plus a final element that is the first element plus 2π . When defining the elements of $\mathbf{M}$, it is important to ensure that the MB junctions line up as desired with the Fermi surface warping being considered. For consistency, it is easiest to set $\varphi = 0$ along the k_x direction and keep this in mind when defining both $\mathbf{M}$ and the Fermi surface warping.

As a simplification, we assume that the gaps that open in the Fermi surface upon reconstruction are of a negligible length in k space: we take the MB junction that ends one section of the Fermi surface to be in the same position as the MB junction that begins the next section.

Following the methods of Ref. [16], we separately consider the motion of quasiparticles starting in the different segments of the Fermi surface, then sum their contributions to the conductivity. To do so, we rewrite Eq. 2.34 in a vectorized form:

$$\sigma_{zz} = \frac{1}{\cos(\theta)} \text{Re} [\boldsymbol{\lambda}_{\varphi_0} \cdot (\boldsymbol{\lambda}_{\text{init}} + \boldsymbol{\Gamma}(\mathbf{I} - \boldsymbol{\Gamma})^{-1} \boldsymbol{\lambda}_{\varphi})]. \quad (2.38)$$

The dot product with $\boldsymbol{\lambda}_{\varphi_0}$ sums up all of the quasiparticle's possible initial positions. The vector $\boldsymbol{\lambda}_{\text{init}}$ accounts for contributions to conductivity from the time the quasiparticle is created until it reaches an MB junction, while $\boldsymbol{\lambda}_{\varphi}$ gives the contribution when the quasiparticle is between MB junctions. The matrix $\boldsymbol{\Gamma}$ describes the connections between orbit segments through both Bragg diffraction and magnetic breakdown, as well as accounting for the exponential damping of the integrand upon traversing a segment of the Fermi surface.⁴

⁴Note that the connections between Fermi surface segments, and therefore the definition of $\boldsymbol{\Gamma}$ for a given system, depend on whether a quasiparticle is traveling clockwise or counterclockwise around the Fermi surface. In this work we always consider the quasiparticles to be moving counterclockwise, as viewed from

If there are N distinct MB junctions, then $\boldsymbol{\lambda}$ are all length- N vectors, $\boldsymbol{\Gamma}$ is an $N \times N$ matrix, and $\boldsymbol{I}$ is the $N \times N$ identity matrix. The elements of the $\boldsymbol{\lambda}$ vectors are defined as follows:

$$\begin{aligned}\lambda_{\varphi_0}[j] &\equiv \int_{\boldsymbol{M}_j}^{\boldsymbol{M}_{j+1}} d\varphi_0 \frac{f(\varphi_0)e^{-iG(\varphi_0)}}{\cos(\gamma(\varphi_0))} \exp\left(\frac{-1}{\omega_0\tau \cos(\theta)} \int_{\varphi_0}^{\boldsymbol{M}_j} \frac{d\varphi'}{\cos(\gamma(\varphi'))}\right), \\ \lambda_{\varphi}[j] &\equiv \int_{\boldsymbol{M}_j}^{\boldsymbol{M}_{j+1}} d\varphi \frac{f(\varphi)e^{iG(\varphi)}}{\cos(\gamma(\varphi))} \exp\left(\frac{-1}{\omega_0\tau \cos(\theta)} \int_{\boldsymbol{M}_j}^{\varphi} \frac{d\varphi'}{\cos(\gamma(\varphi'))}\right), \\ \lambda_{\text{init}}[j] &\equiv \int_{\varphi_0}^{\boldsymbol{M}_{j+1}} d\varphi \frac{f(\varphi)e^{iG(\varphi)}}{\cos(\gamma(\varphi))} \exp\left(\frac{-1}{\omega_0\tau \cos(\theta)} \int_{\boldsymbol{M}_j}^{\varphi} \frac{d\varphi'}{\cos(\gamma(\varphi'))}\right).\end{aligned}\tag{2.39}$$

Each row (column) of the matrix $\boldsymbol{\Gamma}$ corresponds to a segment of the Fermi surface between two MB junctions. The first row (column) corresponds to the section of Fermi surface between the first and second MB junctions, as defined in the vector $\boldsymbol{M}$; the second row (column) corresponds to the section between the second and third MB junctions; and so on. An index i of $\boldsymbol{\Gamma}$ corresponds to the segment between $\boldsymbol{M}_i$ and $\boldsymbol{M}_{i+1}$. Using this correspondence, we can determine all of the elements of $\boldsymbol{\Gamma}$ as follows:

$$\boldsymbol{\Gamma}_{ij} = \begin{cases} 0 & \text{if section } i \text{ has no connection to section } j; \\ D_i p & \text{if section } i \text{ is connected to section } j \\ & \text{through magnetic breakdown;} \\ D_i(1-p) \exp\left(-id_{\perp}\Delta k_z^{(i+1 \rightarrow j)}\right) & \text{if section } i \text{ is connected to section } j \\ & \text{through Bragg diffraction.} \end{cases}\tag{2.40}$$

In the above, p is the probability of magnetic breakdown at a single junction and D_i is the exponential damping of the integrand as the quasiparticle traverses the i th section of the Fermi surface, which is given by

$$D_i = \exp\left(\frac{-1}{\omega_0\tau \cos(\theta)} \int_{\boldsymbol{M}_i}^{\boldsymbol{M}_{i+1}} \frac{d\varphi'}{\cos(\gamma(\varphi'))}\right).\tag{2.41}$$

The quantity $\Delta k_z^{(i+1 \rightarrow j)}$ is the amount by which k_z^0 changes when undergoing Bragg diffraction from the $(i+1)$ th MB junction to the j th MB junction. Note that after traversing the i th section of the Fermi surface, the quasiparticle would Bragg diffract from the $(i+1)$ th magnetic breakdown junction. The terms $\Delta k_z^{(i+1 \rightarrow j)}$ can be calculated as described in Section 2.7.

positive k_z .

It is also worth noting that in Eq. 2.38, the dot product $\boldsymbol{\lambda}_{\varphi_0} \cdot \boldsymbol{\lambda}_{\text{init}}$ yields a double integral with respect to φ_0 and φ and can be rewritten as

$$\begin{aligned} \boldsymbol{\lambda}_{\varphi_0} \cdot \boldsymbol{\lambda}_{\text{init}} = \sum_j \left[\int_{\mathbf{M}_j}^{\mathbf{M}_{j+1}} d\varphi_0 \int_{\varphi_0}^{\mathbf{M}_{j+1}} d\varphi \frac{f(\varphi_0)f(\varphi)e^{i[G(\varphi)-G(\varphi_0)]}}{\cos(\gamma(\varphi_0))\cos(\gamma(\varphi))} \right. \\ \left. \times \exp\left(\frac{-1}{\omega_0\tau\cos(\theta)} \int_{\varphi_0}^{\varphi} \frac{d\varphi'}{\cos(\gamma(\varphi'))}\right) \right]. \end{aligned} \quad (2.42)$$

On the other hand, the rest of the expression in Eq. 2.38 involves self-contained terms ($\boldsymbol{\lambda}_{\varphi_0}$, $\boldsymbol{\lambda}_{\varphi}$, $\boldsymbol{\Gamma}$ and $\boldsymbol{I}$) that can each be evaluated independently once the form of the Fermi surface, the location of the MB junctions, and the scattering rate are known. So the second part of Eq. 2.38 involves nothing more than vector and matrix multiplication.

At this point, it is worth emphasizing some of the assumptions we have made in deriving Eq. 2.38. Primarily, we have assumed that our material exhibits semiclassical behavior with well-defined quasiparticles and a well-defined Fermi surface. We have also assumed a Q2D material with small interlayer warping ($t_{\perp} \ll E_F$) such that we can neglect the effects of interlayer warping when calculating both $\omega(\varphi)$ and $k_z(\varphi)$. Additionally, we have assumed that the Fermi surface can be expressed in the form of Eq. 2.23, rather than the more general form of Eq. 2.20.

In Ch. 3 and Ch. 4, we will explore how Eq. 2.38 can be applied to two different cuprate superconductors. See Sec. 3.2 and Subsection 4.2.3 for examples of how to define $\boldsymbol{M}$ and $\boldsymbol{\Gamma}$ for specific systems.

Chapter 3

Fitting the ADMR of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ based on (π, π) ordering

3.1 Introduction¹

ADMR data from $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ provided the earliest transport evidence for the existence of a three-dimensional Fermi surface in an overdoped cuprate [17]. The temperature evolution of the ADMR is consistent with a superposition of isotropic and anisotropic scattering rates about the Fermi surface [39], and it was determined that these do not have the same temperature dependence: the isotropic scattering rate is quadratic with temperature (as expected of an ordinary Fermi liquid), while the anisotropic scattering rate is linear (connecting it to the non-Fermi liquid physics of the cuprate phase diagram). Additionally, the anisotropic scattering is strongest in the antinodal region of the Fermi surface. Therefore, it has been suggested that the anomalous scattering temperature dependence may be related to (π, π) fluctuations [39, 49, 50], which may originate from antiferromagnetism. A similar anomalous scattering has been observed in overdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ through angle-resolved photoemission spectroscopy measurements and has been posited to arise from antiferromagnetic fluctuations in that material[51]. We show here that the introduction of (π, π) order on the Fermi surface of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ will indeed affect the ADMR of this system in a similar way to the introduction of anisotropic scattering.

In Sec. 3.2, we make use of the mathematical methods that were developed in Ch. 2. We develop an equation for the interlayer ADMR of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ in the presence of (π, π) order, taking Bragg diffraction and magnetic breakdown into account. In Sec. 3.3 we apply this equation, using parameters of the known Fermi surface of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [17]. We show that the temperature dependence of the ADMR of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ can be captured by this model. In Sec. 3.5 we discuss the physical consequences of this model and its potential range of applicability for distinguishing between different kinds of broken symmetry order in the

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cuprates.

3.2 ADMR in the presence of (π, π) order

We wish to understand how the ADMR of the overdoped cuprates is affected by antiferromagnetism. We therefore consider the case of $\text{TL}_2\text{Ba}_2\text{CuO}_{6+\delta}$ under static (π, π) antiferromagnetic order, though noting that the model below does not depend on the origin of the (π, π) order. As shown in Fig. 3.1(a), the original Brillouin zone has a square cross section with primitive reciprocal lattice vectors along k_x and k_y ; we define all azimuthal angles in this chapter with respect to k_x . In the presence of (π, π) order, the Brillouin zone is halved in cross section, resulting in a reconstruction of the Fermi surface as shown in Figs. 3.1(b) and 3.1(c). This new reconstructed Brillouin zone will have primitive reciprocal lattice vectors along k'_x and k'_y , which are rotated by 45° with respect to k_x and k_y . Quasiparticles traversing the Fermi surface will Bragg diffract at the reconstructed Brillouin zone boundaries, so they will travel along three distinct Fermi surface pockets as shown in Fig. 3.1(d).

The MB junctions in this system are the points at which the original Fermi surface intersects the reconstructed Brillouin zone boundary. As can be seen in Fig. 3.1, this system has a total of eight MB junctions. As introduced in Ch. 2, $\mathbf{M}$ is a vector of the azimuthal positions of all the MB junctions plus a final element that is the first element plus 2π . For this system, we have

$$\mathbf{M} \equiv \frac{\pi}{4} - \xi + \left[0, 2\xi, \frac{\pi}{2}, \frac{\pi}{2} + 2\xi, \pi, \pi + 2\xi, \frac{3\pi}{2}, \frac{3\pi}{2} + 2\xi, 2\pi \right] \quad (3.1)$$

where the angle ξ is defined as shown in Fig. 3.1(d). The position of these MB junctions on the (unreconstructed) Fermi surface is shown in Fig. 3.2. Note that in labeling the MB junctions in Fig. 3.2 we have used 1-indexing, i.e. the first MB junction is labeled by “1” rather than by “0.” We will continue this convention of 1-indexing throughout this work, for definitions of $\mathbf{M}$, $\boldsymbol{\lambda}$, $\boldsymbol{\Gamma}$, etc.

In calculating ω , we approximate a nearly circular in-plane Fermi surface for $\text{TL}_2\text{Ba}_2\text{CuO}_{6+\delta}$, which is justified by ADMR and ARPES measurements [25, 17]. The assumption of small interlayer warping is also strongly supported by ADMR data [17]. With these assumptions, $\cos(\gamma(\varphi)) = 1$. Therefore, Eq. 2.19 simplifies to $\omega \approx \omega_0 \cos(\theta)$ and the $\boldsymbol{\lambda}$ vectors defined in Eq. 2.39 are also simplified. For our system, each of these vectors has eight elements with the j th element as follows:

$$\begin{aligned} \lambda_{\varphi_0}[j] &\equiv e^{-M_j/\omega\tau} \int_{M_j}^{M_{j+1}} d\varphi_0 f(\varphi_0) e^{\varphi_0/\omega\tau} e^{-iG(\varphi_0)} \\ \lambda_{\varphi}[j] &\equiv e^{M_j/\omega\tau} \int_{M_j}^{M_{j+1}} d\varphi f(\varphi) e^{-\varphi/\omega\tau} e^{iG(\varphi)} \\ \lambda_{\text{init}}[j] &\equiv e^{M_j/\omega\tau} \int_{\varphi_0}^{M_{j+1}} d\varphi f(\varphi) e^{-\varphi/\omega\tau} e^{iG(\varphi)}. \end{aligned} \quad (3.2)$$

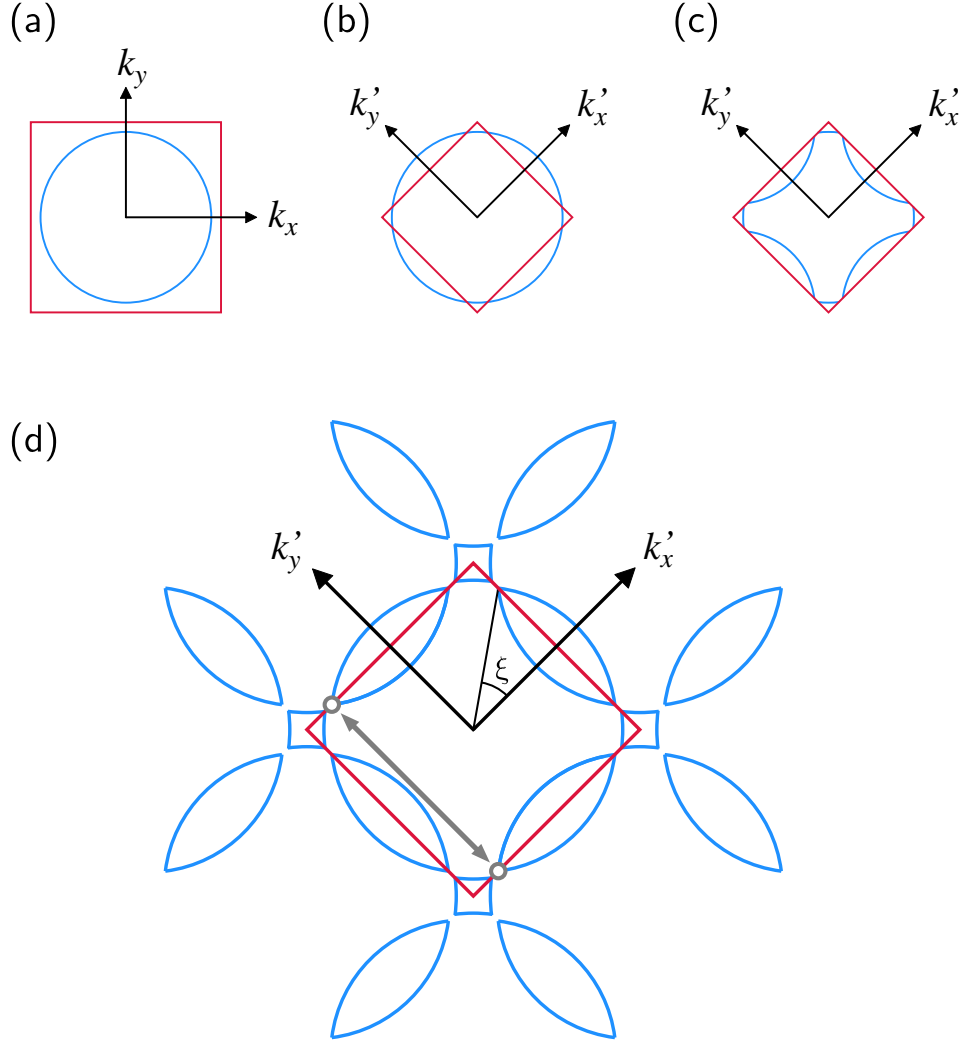


Figure 3.1: A schematic representation of the Fermi surface reconstruction of $\text{TL}_2\text{Ba}_2\text{CuO}_{6+\delta}$ under (π, π) antiferromagnetic order, as viewed along k_z . (a) The Fermi surface (in blue) and first Brillouin zone (in pink); (b) the reconstruction of the Brillouin zone and (c) reconstruction of the Fermi surface of the material following the onset of (π, π) antiferromagnetic order; (d) the repeated-zone view of the reconstructed Fermi surface, illustrating the small cross sections of Fermi surface that have replaced the unreconstructed cylindrical Fermi surface. The gray line illustrates Bragg diffraction between two magnetic breakdown junctions at the Brillouin zone boundary. The angle ξ is defined with respect to the reconstructed Fermi surface, as shown; it will be used in our conductivity calculations.

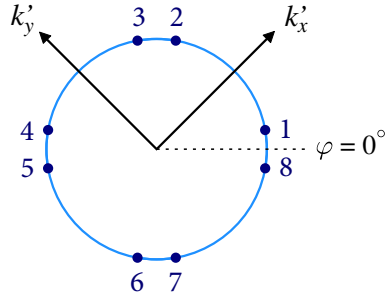


Figure 3.2: Position of the eight magnetic breakdown junctions on the Fermi surface of $\text{TL}_2\text{BA}_2\text{CuO}_{6+\delta}$ under (π, π) order. The reciprocal space axes shown correspond to the reconstructed Brillouin zone.

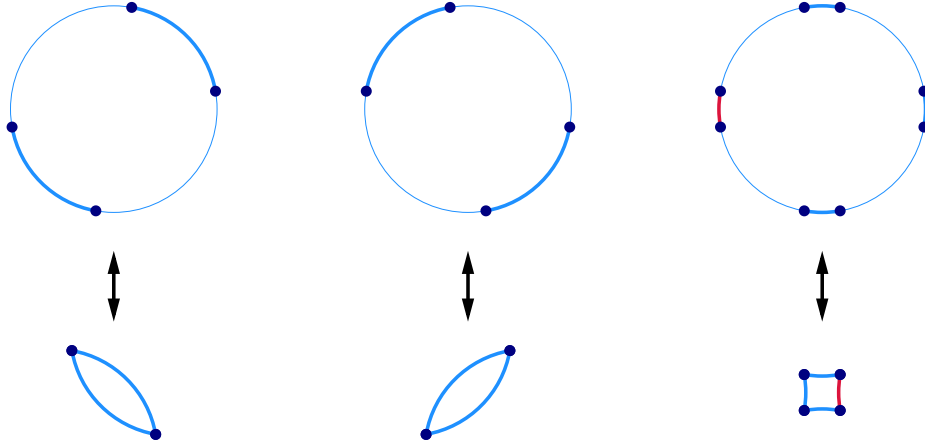


Figure 3.3: Three small Fermi surface pockets are formed when the Fermi surface of $\text{TL}_2\text{BA}_2\text{CuO}_{6+\delta}$ is reconstructed under (π, π) order.

The matrix $\mathbf{\Gamma}$, as defined in Eq. 2.40, accounts for the connections between orbit segments, as well as the exponential damping of the integrand upon traversing a segment of Fermi surface.

The exponential damping term is defined in Eq. 2.41 as

$$D_i = \exp \left(\frac{-1}{\omega_0 \tau \cos(\theta)} \int_{M_i}^{M_{i+1}} \frac{d\varphi'}{\cos(\gamma(\varphi'))} \right). \quad (3.3)$$

Since we are approximating $\cos(\gamma(\varphi)) = 1$, this simplifies to

$$D_i = \exp \left(\frac{-(M_{i+1} - M_i)}{\omega_0 \tau \cos(\theta)} \right). \quad (3.4)$$

From Eq. 3.1, we can see that $(\mathbf{M}_{i+1} - \mathbf{M}_i)$ will either have the value 2ξ or $(\pi/2 - 2\xi)$ for any given value of i . We can therefore define just two terms to account for all of the values of the exponential damping:

$$\begin{aligned} a &\equiv \exp\left(\frac{-2\xi}{\omega_0\tau \cos(\theta)}\right), \\ b &\equiv \exp\left(\frac{-(\pi/2 - 2\xi)}{\omega_0\tau \cos(\theta)}\right). \end{aligned} \quad (3.5)$$

Now, let us consider the connections between Fermi surface segments, as required by Eq. 2.40.

If a quasiparticle on the reconstructed Fermi surface of $\text{TL}_2\text{BA}_2\text{CUO}_{6+\delta}$ experiences magnetic breakdown, it will simply follow the full cylindrical (unreconstructed) Fermi surface. Therefore, we can see that section i is always connected to section $(i+1)$ by magnetic breakdown, since our convention is to consider quasiparticles moving counterclockwise about the Fermi surface.

As can be seen by comparing Fig. 3.1(d) and 3.2, the following MB junctions are connected by reciprocal lattice vectors of the reconstructed Brillouin zone: $1 \leftrightarrow 6$, $2 \leftrightarrow 5$, $3 \leftrightarrow 8$, $4 \leftrightarrow 7$. An easy way to understand these pairings is to examine the small Fermi surface orbits that the quasiparticle will follow if it Bragg diffracts at every junction, which are illustrated in Fig. 3.3. Recalling that an index i of $\mathbf{\Gamma}$ corresponds to the segment between $\mathbf{M}_i$ and $\mathbf{M}_{i+1}$, and that we consider our quasiparticle to be moving counterclockwise, we can determine that a quasiparticle traveling along section i of the Fermi surface will Bragg diffract from MB junction $(i+1)$. From that MB junction, it will go to the MB junction it is paired with by a reciprocal lattice vector, as listed above.

Once these connections are understood, the value of $\Delta k_z^{(j)}$ can be calculated using purely geometric means, as derived in Sec. 2.7. Since φ_j for every MB junction is given by $\mathbf{M}_j$, the values of φ_i and φ_f can easily be plugged into Eq. 2.31. For example, if a quasiparticle is going from MB junction 1 to MB junction 6 we have $\varphi_i = \frac{\pi}{4} - \xi$ and $\varphi_f = \frac{5\pi}{4} + \xi$. We can use these to solve for $\Delta k_z^{(1 \rightarrow 6)}$, which we denote as $\Delta k_z^{(1)}$ for the sake of brevity.

Then for our system, $\mathbf{\Gamma}$ is the following eight-by-eight matrix:

$$\mathbf{\Gamma} \equiv \begin{pmatrix} 0 & ap & 0 & 0 & aq\delta(2) & 0 & 0 & 0 \\ 0 & 0 & bp & 0 & 0 & 0 & 0 & bq\delta(3) \\ 0 & 0 & 0 & ap & 0 & 0 & aq\delta(4) & 0 \\ 0 & bq\delta(5) & 0 & 0 & bp & 0 & 0 & 0 \\ aq\delta(6) & 0 & 0 & 0 & 0 & ap & 0 & 0 \\ 0 & 0 & 0 & bq\delta(7) & 0 & 0 & bp & 0 \\ 0 & 0 & aq\delta(8) & 0 & 0 & 0 & 0 & ap \\ bp & 0 & 0 & 0 & 0 & bq\delta(1) & 0 & 0 \end{pmatrix},$$

where $q = 1 - p$ and we have defined $\delta(j) \equiv \exp[-id_{\perp} \Delta k_z^{(j)}]$.

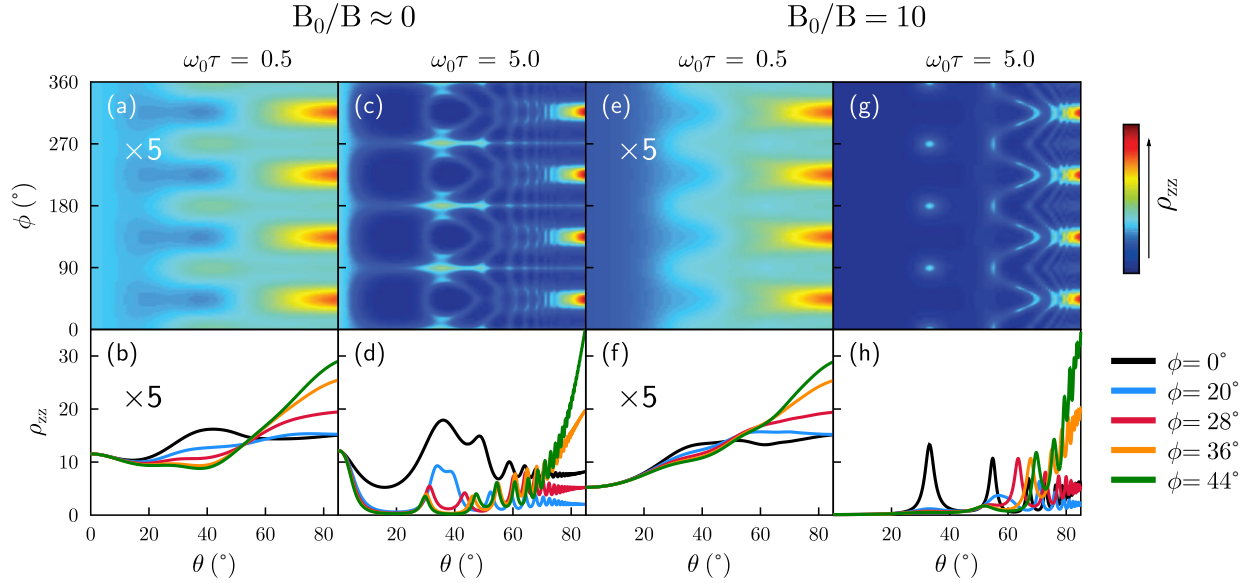


Figure 3.4: Calculated dimensionless resistivity of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ as a function of the orientation of applied magnetic field for different values of B_0/B and $\omega_0\tau$. We plot resistivity in units of $\pi^4\hbar^4\omega_0/m_0^*d_\perp(aet_\perp k_{21})^2$ so that it is dimensionless. The resistivity in plots (a, b) and (e, f) is scaled up by a factor of 5 for visual clarity. (a, c, e, g) Interlayer resistivity as a function of both θ and ϕ . (b, d, f, h) Interlayer resistivity as a function of θ for select values of ϕ ; these azimuthal angles were chosen to facilitate comparison to Ref. [17].

3.3 Calculated ADMR data for $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$

As detailed in Ch. 2, we can describe the Fermi surface of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ as:

$$E_F(k_z, \varphi) = \frac{\hbar^2 k_F^2(\varphi)}{2m^*} - 2t_\perp(\varphi) \cos(d_\perp k_z). \quad (3.6)$$

where the in-plane Fermi surface is defined by

$$k_F(\varphi) = \sum_{\mu \geq 0} k_{\mu 0}^{\{c\}} \left\{ \begin{matrix} \cos \\ \sin \end{matrix} \right\} (\mu\varphi) \quad (3.7)$$

and the interlayer hopping integral is given by

$$t_\perp(\varphi) = \sum_{\mu \geq 0} k_{\mu 1}^{\{c\}} \left\{ \begin{matrix} \cos \\ \sin \end{matrix} \right\} (\mu\varphi). \quad (3.8)$$

As explained in detail in Ref. [41], the point group symmetry of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ creates the following restrictions on the coefficients $k_{\mu\nu}$:

- All μ must be even;
- All cosine terms must have $\mu(\text{mod}4)=0$ and all sine terms have $\mu(\text{mod}4)=2$;
- All cosine terms must have even ν and all sine terms must have odd ν .

As described by Hussey *et al.* [17], the Fermi surface of $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ can be parameterized by the first two terms of Eq. 3.7 and the first three terms of Eq. 3.8. That is to say, we can define $k_F^\parallel(\varphi) \equiv k_{00} + k_{40} \cos(4\varphi)$ and $f(\varphi) \equiv k_{21} \sin(2\varphi) + k_{61} \sin(6\varphi) + k_{101} \sin(10\varphi)$.

Using this parameterization of the Fermi surface and the vectorized form of the Shockley-Chambers tube integral, we can calculate the out-of-plane resistivity as a function of angle. We compare these calculations to existing data for a sample with $T_c = 15$ K reported in Ref. [52]. The low-temperature (4.2 K) ADMR of $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ is well fit by a simple model with no antiferromagnetic order ($B_0 = 0$). Using this low-temperature data, the coefficients $k_{\mu\nu}$ that describe the Fermi surface can be fully determined in good agreement with previous work [17, 39, 41, 52]. See Section 3.4 for more information on our determination of these parameters and the parameter values.

Given the values of k_{00} and k_{40} , we can now use geometric methods to solve for ξ in this system. The angle ξ is defined as shown in Fig. 3.1(d). If the Fermi surface were completely cylindrical, it would obey

$$\cos(\xi) = \frac{\pi}{a_{\text{AF}} k_F},$$

where a_{AF} is the in-plane lattice parameter of the antiferromagnetically ordered system and k_F is the Fermi momentum. We may neglect the interlayer warping of the Fermi surface, which is relatively weak, but not the in-plane warping. Therefore, we have the relation

$$\cos(\xi) = \frac{\pi}{a_{\text{AF}} [k_{00} + k_{40} \cos(4\xi)]},$$

which can be solved self-consistently for ξ . We know that $a_{\text{AF}} = \sqrt{2}a$. We use $a = 0.3866$ nm, as given by Analytis *et al.* [41]. Using the values of k_{mn} that we have determined, we find $\xi \approx 40^\circ$. We use this value of ξ in all of our calculations that involve Bragg diffraction and magnetic breakdown.

With ξ determined, we can now find out how the ADMR of $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ will change with the introduction of (π, π) order. The ADMR of the unreconstructed Fermi surface can be produced by setting $B_0 = 0$, as shown in Figs. 3.4(a)-3.4(d) for two convenient values of $\omega_0\tau$. Note that $\omega_0\tau = 0.5$ reproduces the experimental ADMR observed by Hussey *et al.* at 4.2 K [17]. The ADMR for a system with (π, π) antiferromagnetic order is shown in Figs. 3.4(e)-3.4(h). This shows many qualitative differences from the unreconstructed state. The peak at $\theta = 0$ is strongly suppressed in the reconstructed Fermi surface. In addition, there are more Yamaji angles (peaks in the ADMR) for low polar angles θ in the unreconstructed state than the reconstructed state.

The evolution of the ADMR as we go from $B_0/B \approx 0$ to $B_0/B = 10$ for $\omega_0\tau = 0.5$ bears a striking resemblance to the evolution of the ADMR in $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ with increasing

temperature, most notably the disappearance of the hump at $\theta = 0$ [39, 53]. This seems surprising, given that $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ is not known to exhibit any static antiferromagnetic order, though it has been shown to have strong antiferromagnetic fluctuations [54].

We have already used fits to the 4.2 K ADMR data from Ref. [52] to determine k_{mn} for our system. Now, we wish to see if calculations of ADMR that include magnetic breakdown effects can be fit to the higher-temperature data from this same sample.

To study the temperature-dependent ADMR above 4.2 K, we allowed only two free parameters: $\omega_0\tau$ and B_0 . Note that in contrast to Ref. [52], $\omega_0\tau$ is fixed to be *isotropic* with azimuthal angle φ . We ran simulations across a large range of parameter space and used a least-squares fitting approach to determine the values of $\omega_0\tau$ and B_0 at each temperature. Our best fit to the data is shown in Fig. 3.5, showing excellent quantitative agreement with the ADMR of $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$. The temperature dependence of $\omega_0\tau$ and of B_0 as determined from the fits to data are shown in Fig. 3.6.

As can be seen in Fig. 3.4, more features are apparent in the ADMR when $\omega_0\tau$ is higher, making it easier to distinguish the effects of changing B_0 . If $\omega_0\tau$ is decreased (by lowering magnetic fields, raising temperatures, or lowering sample quality), each quasiparticle will traverse less of the Fermi surface before it scatters. As illustrated in Fig. 6 of Ref. [42], this causes the amplitude of ADMR to be reduced, which makes an accurate determination of B_0 more difficult. Thus, the error of our fitting parameters is greater at higher temperatures. Indeed, Ref. [52] includes ADMR data taken at 90 K and 110 K, but we were not able to accurately determine B_0 at those elevated temperatures.

While Ref. [52] reproduced the observed ADMR using an anisotropic scattering rate, we find good quantitative agreement with the data using a magnetic breakdown model with an isotropic scattering rate. Bragg scattering at a MB junction mimics the effect of an anisotropic scattering rate on an unreconstructed Fermi surface. However, importantly, the magnetic breakdown model connects specific parts of the Fermi surface in a single (Bragg) scattering event, while the anisotropic scattering rate is a broad modulation of the quasiparticle lifetime about the Fermi surface. The similarity of the two models in reproducing the ADMR suggests that the apparent anisotropic scattering rate is a symptom of antiferromagnetism, perhaps involving short-range fluctuations. This could explain the different temperature dependence of the isotropic and anisotropic components of the scattering rate observed in Ref. [39].

3.4 Parameter fitting and error bars

We expect the parameters $k_{\mu\nu}$ to be constant with temperature, as they describe the Fermi surface geometry. Therefore, we can fit these parameters from our 4.2 K data, since we do not expect reconstruction and magnetic breakdown to occur at this temperature. From band structure calculations [55] and from previous ADMR studies [17], we expect this material to have no c -axis dispersion along the zone diagonals, as well as along the lines $k_x = \pi$ and

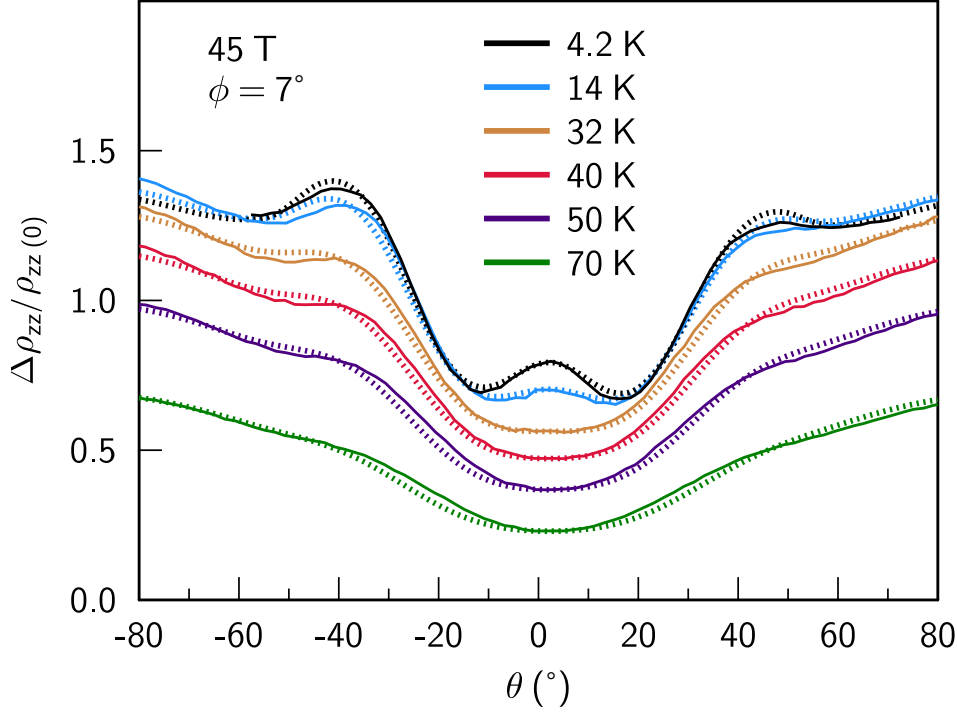


Figure 3.5: Temperature dependence of the interlayer ADMR of overdoped $\text{TL}_2\text{BA}_2\text{CUO}_{6+\delta}$ ($T_c = 15$ K) at a fixed field of 45 T and a fixed azimuthal direction of $\phi = 7^\circ$. The solid lines are c -axis magnetoresistivity data, taken from French *et al.* [52]. These data have been normalized to the zero-field resistivity of the sample at each temperature. The dashed lines are simulations of ADMR for $\text{TL}_2\text{BA}_2\text{CUO}_{6+\delta}$ under antiferromagnetic order, calculated as described in the text. The simulations have been scaled to match the data at $\theta = 0^\circ$ for each temperature. When producing these simulations, all the parameters related to Fermi surface geometry were fixed and the only parameters allowed to vary with temperature were $\omega_0\tau$ and B_0 .

$k_y = \pi$. In order for this to be realized, it must be the case that $1 - k_{61}/k_{21} + k_{101}/k_{21} = 0$.²

We simulated conductivity for a wide swath of parameter space and used a least-squares fitting to data to arrive at the following: $k_{00} = 7.34 \text{ nm}^{-1}$, $k_{40} = -0.25 \text{ nm}^{-1}$, $k_{61}/k_{21} = 0.69$ (and therefore $k_{101}/k_{21} = -0.31$).³

Simultaneously with fitting the Fermi surface geometry, we used the 4.2 K data to fit for the misalignment of the crystal with respect to the magnetic field (see Analytis *et al.* for details on the significance and calculation of this misalignment [41]). We obtained the best

²Note that only the ratios k_{61}/k_{21} and k_{101}/k_{21} are relevant to our calculations, not the values of these parameters; this is because we are calculating the interlayer conductivity only up to a constant of proportionality, and these parameters do not affect the in-plane conductivity.

³To be precise, we fit for the unitless parameters $k_{00}c$ and $k_{40}c$, then obtained values for k_{00} and k_{40} using $c = 2.32 \text{ nm}$ from Analytis *et al.* [41].

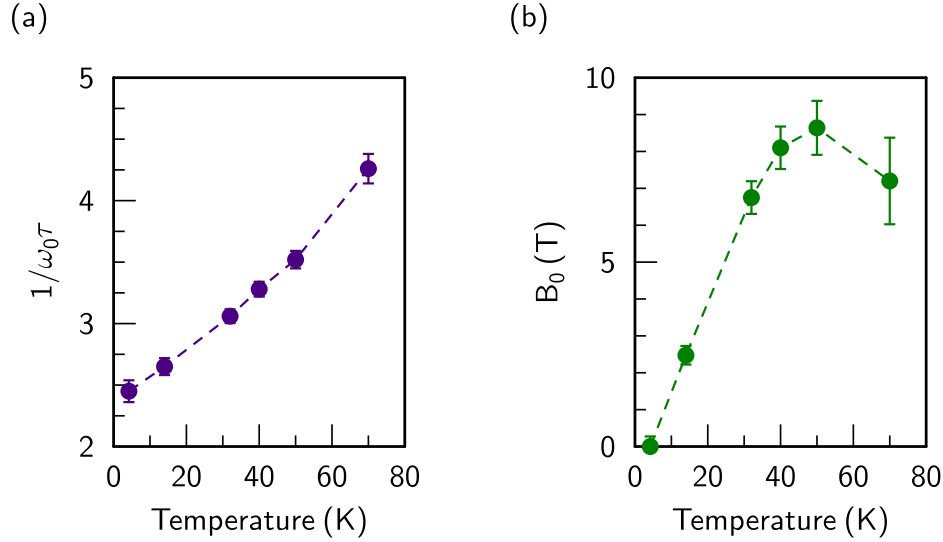


Figure 3.6: Temperature dependence of (a) $1/\omega_0\tau$ and (b) B_0 extracted from fits to data. Error bars are standard errors extracted from the covariance matrix of the least-squares fitting at each temperature (see Section 3.4).

fits to data from $\Phi_{asym} = -0.6^\circ$, $\Theta_{asym}^x = -2.5^\circ$, and $\Theta_{asym}^y = -2.8^\circ$.

Once we have fit these parameters at 4.2 K, the only parameters free to fit for the data as a function of temperature are B_0 and $1/\omega_0\tau$. For each temperature, we simulated conductivity across a broad range of B_0 and $1/\omega_0\tau$ and used a least-squares fitting to arrive at the following values for the best fits to data:

T (K)	B_0 (T)	$1/\omega_0\tau$
4.2	0	2.50
14	2.5	2.65
32	6.8	3.06
40	8.1	3.28
50	8.6	3.52
70	7.2	4.26

Table 3.1: The parameters that give the best fits to data at each temperature. Note that we assumed $B_0 = 0$ at 4.2 K in order to perform our fits for Fermi surface geometry and alignment.

The error bars shown on B_0 and $1/\omega_0\tau$ in Fig. 3.6 are the standard error of those parameters. At each temperature, the values of B_0 and $1/\omega_0\tau$ that give the best fit to data are

those for which the sum of squared error (SSE) between data and simulation is minimized. We can fit the SSE to a functional form in terms of B_0 and $1/\omega_0\tau$ about that minimum. We use this functional form to approximate the Hessian matrix for these two parameters, the inverse of which is the covariance matrix, $\mathbf{C}$. The standard error for each parameter is then simply given by $\sqrt{C_{ii}/(N-2)}$, where N is the number of data points we used for the fitting at that temperature (and two is the number of parameters we fit). Which diagonal element of $\mathbf{C}$ corresponds to each parameter depends on how we construct the Hessian matrix.

3.5 Discussion

The behavior of $\omega_0\tau$ in Fig. 3.6(a) indicates an approximately quadratic increase in the scattering rate with temperature, as expected for a Fermi liquid. The evolution of B_0 may reflect deeper physics. As shown in Fig. 3.6(b), B_0 increases quickly with temperature, peaking at around 45 K. The parameter B_0 is a measure of the probability of Bragg scattering. For a static reconstructed Fermi surface, this is related to the separation between reconstructed sections, which is in turn proportional to the band gap [22]. Therefore, under static reconstruction we would expect B_0 to be largest at 0 K and decrease weakly with increasing temperature [56, 22]. In the presence of antiferromagnetic fluctuations, similar scattering events might still occur at points where the reconstructed Brillouin zone intersects the Fermi surface. In this case, B_0 will play two roles: in addition to parameterizing the separation between sections of Fermi surface, it also reflects the probability of Bragg scattering within the time/length scale of the fluctuations.⁴ Note that in the overdoped cuprates, there is a known crossover in the transport from Fermi-liquid-like to non-Fermi-liquid-like behavior with increasing temperature that is thought to be associated with critical fluctuations [57]. In this picture, the increase of B_0 with temperature seen in Fig. 3.6(b) can be interpreted as an increase in antiferromagnetic fluctuations. As the temperature rises and antiferromagnetic fluctuations grow, quasiparticles have a nonzero chance of undergoing Bragg diffraction when they reach MB junctions, so B_0 attains a nonzero value. At still higher temperatures, the antiferromagnetic correlation time is so short that the effect of Bragg scattering decreases, resulting in a decrease in B_0 . The evolution of B_0 looks strikingly similar to the evolution of the imaginary part of the dynamic susceptibility $\text{Im}\chi$, which is a measure of the magnetic scattering, seen in a number of neutron experiments in cuprate superconductors (consider, for example, Fig. 10 of Ref. [58]). We therefore suggest that the temperature dependence of B_0 in Fig. 3.6(b) reflects the effect of antiferromagnetic fluctuations on the magnetotransport.

For the above to be plausible, the antiferromagnetic fluctuations of the system should be on a long enough time scale to affect the quasiparticles' motion about the Fermi surface: the time scale of an antiferromagnetic fluctuation should be longer than the time it takes for a

⁴The general form of the breakdown probability would be $p = 1 + g(T)(e^{-B_0/B \cos(\theta)} - 1)$, where $g(T)$ parameterizes the temperature-dependent strength of fluctuations. However, adding extra parameters in this way does not add any clarity to our interpretation of the ADMR data.

quasiparticle to traverse a section of Fermi surface from one MB junction to the next. The antiferromagnetic fluctuations in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ near optimal doping have a frequency that is roughly linearly proportional to temperature [59]. Taking this as a guide, we estimate that the time scale of an antiferromagnetic fluctuation will be of the order $\tau_{AF} \sim \frac{\hbar}{k_B T}$. Meanwhile, the time for a quasiparticle to cross the smallest section of Fermi surface between two MB junctions is given by $\tau_{QP} \sim \frac{1}{\omega} \frac{\pi/2 - 2\xi}{2\pi}$. Therefore, our condition $\tau_{AF} > \tau_{QP}$ is equivalent to

$$\hbar\omega > \frac{\pi/2 - 2\xi}{2\pi} k_B T. \quad (3.9)$$

For this system, the requirement is approximately

$$\frac{\omega}{T} > 3.6 \times 10^9 \text{ s}^{-1} \text{ K}^{-1}. \quad (3.10)$$

Using $m^* \approx 5m_e$ [60], we find $\omega \approx 1.6 \times 10^{12} \text{ s}^{-1}$ at 45 T and with $\theta = 0^\circ$. Therefore, antiferromagnetic fluctuations could be expected to affect quasiparticle motion up to $T \approx 400 \text{ K}$ (assuming that the fluctuations would persist to this temperature), much higher than the temperature regime studied in this chapter.

The magnetic breakdown picture of the effect of antiferromagnetic fluctuations on ADMR could be substantially improved by including a more realistic model of the MB junctions in a fluctuating system that includes, for example, a distribution of ordering wave vectors about (π, π) [29]. Nevertheless, this simple model captures many of the important features observed in the temperature-dependent ADMR without the need for a multicomponent scattering with a different nodal and antinodal temperature dependence [52, 41, 39]. This model may also prove useful for understanding further transport properties of $\text{TL}_2\text{Ba}_2\text{CuO}_{6+\delta}$ (see Appendix A.2). Moreover, our results suggest there is a potential link between B_0 and the dynamic susceptibility $\text{Im}\chi$. If this connection can find a sound theoretical basis, it may open the way for the use of ADMR as an experimental probe of magnetic scattering.

3.6 Conclusion

We have shown that a (π, π) Fermi surface reconstruction with a temperature-dependent magnetic breakdown field can fit the ADMR of $\text{TL}_2\text{Ba}_2\text{CuO}_{6+\delta}$, an overdoped compound with no static order. Interestingly, similar behavior has recently been observed in the optimal and overdoped regime of the electron-doped cuprate $\text{Nd}_{2x}\text{Ce}_x\text{CuO}_4$ [61]. In these compounds, angle-resolved photoemission has shown evidence of Fermi surface reconstruction despite the absence of long-range antiferromagnetic order. This indicates that the Fermi surface reconstruction we propose for $\text{TL}_2\text{Ba}_2\text{CuO}_{6+\delta}$ may be a more general phenomenon in the overdoped cuprates.

The agreement between our fits and the ADMR data suggests that the features attributed to scattering anisotropy in these systems [39, 52, 41] may in fact be due to fluctuations of a (π, π) ordering such as antiferromagnetism, and indeed that the MB field B_0 can potentially be used as an experimental measure of such fluctuations. This would make ADMR a good

complement to scattering probes of fluctuations, such as neutron scattering and resonant inelastic x-ray scattering. Future ADMR experiments at higher magnetic fields and in materials where $\text{Im}\chi$ has been determined independently by neutron scattering would provide an instructive comparison to test the validity of this connection.

Chapter 4

ADMR as a probe of Fermi surface warping in $\text{HgBa}_2\text{CuO}_{4+\delta}$

4.1 Introduction¹

Characterizing the Fermi surface of the underdoped cuprates is a major challenge in understanding their strange metal properties. Quantum oscillations in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (YBCO) first revealed that these materials have a coherent and measurable Fermi surface at magnetic fields above H_{c2} [26]. Since this initial study, quantum oscillations have now also been observed in underdoped $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg1201); these measurements all indicated the presence of small Fermi surface pocket(s), presumably arising from Fermi surface reconstruction due to electronic order [26, 62, 63, 64, 35]. Charge density wave (CDW) correlations have been directly observed in both YBCO and Hg1201 through x-ray scattering [65, 66, 67], making this an attractive candidate for the origin of the reconstruction. However, the details of the symmetry and shape of these small pockets, which is a major determining factor of normal state properties, remains unknown. In this study, we propose that angle-dependent magnetoresistance (ADMR) can reveal clear signatures of the morphology of the Fermi surface, and we propose straightforward experiments that can be performed in available magnetic fields.

The layered structure of the cuprate superconductors leads to a Q2D Fermi surface in the form of a warped cylinder. For a full understanding of these materials' properties and the order that drives their reconstruction, it is necessary to characterize not only the cross-sectional shape of the Fermi surface but also its interlayer warping. Sebastian *et al.* performed detailed studies of Shubnikov–de Haas oscillations in $\text{YBa}_2\text{Cu}_3\text{O}_{6.67}$ and found that their data were consistent with a staggered twofold warping along k_z [Fig. 4.1b] rather than a simple cosine warping [Fig. 4.1a] [68]. Their analysis suggested this could be caused by CDW order with $q \sim (h, k, \frac{1}{2})$, but recent scattering studies suggest that the ordering wavevector for the

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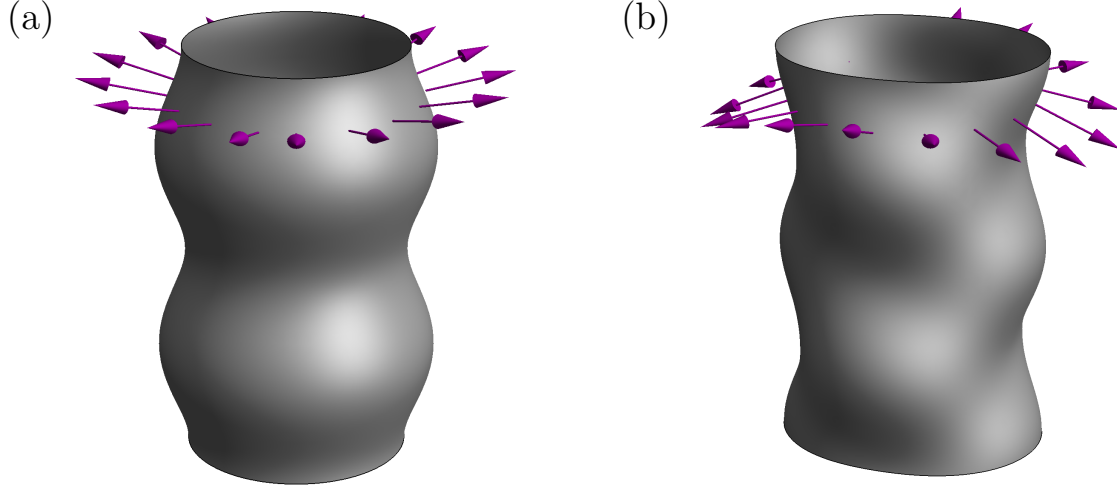


Figure 4.1: A Q2D Fermi surface with a) simple cosine interlayer warping and b) staggered twofold interlayer warping. In both cases, the in-plane Fermi surface is circular before interlayer warping is imposed, and two periods of the interlayer warping are shown for clarity. The arrows extending from each figure indicate the direction of the Fermi velocity for those points on the Fermi surface.

three-dimensional CDW is $q \sim (h, k, 1)$ [34]. Furthermore, the quantum oscillation data can alternatively be explained without a twofold warping, and even without a three-dimensional Fermi surface [69, 70]. This is thought to be possible because the mirror symmetry between the bilayer planes of YBCO is broken by CDW order [71]. The ambiguity in interpreting the quantum oscillation results highlights the need for a new symmetry-sensitive probe of the three-dimensional Fermi surface.

In this work, we will show that interlayer (ρ_{zz}) ADMR measurements of Hg1201 can be a powerful tool for characterizing the interlayer warping as well as the symmetry of the reconstructed Fermi surface. Hg1201 has the highest transition temperature of the monolayer cuprates, a simple tetragonal structure, and relatively little disorder or buckling in the CuO_2 planes compared to other cuprate high-temperature superconductors [72]. Interlayer ADMR measurements of YBCO have been used to determine that its in-plane Fermi surface shape is most likely a square or diamond, which is consistent with a CDW reconstruction.[73] However, the bilayer splitting in YBCO made it difficult to pinpoint the interlayer warping of the Fermi surfaces in that study. Since Hg1201 only has a single copper-oxygen plane per unit cell, it avoids this complication. In addition, the copper-oxygen chains in the YBCO structure, which are known to affect transport properties at higher temperatures, are absent in Hg1201. All of these characteristics make Hg1201 an ideal model material for investigation with ADMR.

Using semi-classical calculations, we will show that a measurement of interlayer ADMR in Hg1201 at a single azimuthal angle can be used to clearly distinguish between the two types of interlayer warping shown in Fig. 4.1. From measurements at multiple azimuthal

angles, even more symmetry information can be revealed. With strong enough magnetic fields, ADMR may also provide information about the periodicity of the interlayer warping and the shape of the in-plane Fermi surface. In Section 4.2 we describe the constraints placed on our model of Hg1201 from quantum oscillation experiments. We also introduce the various Fermi surface geometries that we consider and outline the mathematical details of our calculations. We calculate the expected interlayer ADMR in Section 4.3, illustrating qualitative distinctions that arise from different Fermi surface geometries and particularly from different interlayer warpings. Finally, in Section 4.5 we discuss the application of our ADMR results to actual measurements, and we define an experimentally accessible range of temperatures and magnetic fields in which our results can be applied.

4.2 Experimental constraints and model parameters

4.2.1 The Fermi surface geometry

Since Hg1201 is a layered, Q2D system, its Fermi surface must be in the form of a warped cylinder. Quantum oscillation measurements in underdoped samples of Hg1201 have found a single frequency for each sample, in the range of 840-900 T for different dopings [64, 35], which corresponds to roughly 3% of the Brillouin zone area. These measurements were taken with the magnetic field in the interlayer direction; that is, they measured the in-plane Fermi surface cross section. The results indicate that the Fermi surface consists of a single pocket (or multiple pockets of the same size). The existence of a single quantum oscillation frequency also indicates that the interlayer warping cannot be large; in fact, an upper limit of $t_{\perp} < 0.35$ meV was determined, which is three orders of magnitude smaller than the intralayer nearest-neighbor hopping [35].

As described in Ch. 2, we can parameterize the Fermi surface as

$$E_F(k_z, \varphi) = \frac{\hbar^2 k_F^2(\varphi)}{2m^*} - 2t_{\perp} f(\varphi) \cos(d_{\perp} k_z). \quad (4.1)$$

The term $f(\varphi)$ gives the azimuthal dependence of the interlayer warping, while $k_F(\varphi)$ describes the in-plane Fermi surface. The simple cosine warping shown in Fig. 4.1a corresponds to $f(\varphi) = 1$; in terms of Eq. 2.25, this means that $k_{\mu 1}^{\{c\}} = 0$ for all terms in the expansion of $t_{\perp}(\varphi)$ except the term $k_{01}^{\{c\}}$. Meanwhile, the staggered twofold warping in Fig. 4.1b is given by $f(\varphi) = \sin(2\varphi)$, which corresponds to $k_{21}^{\{s\}}$ being the only non-zero coefficient in the expansion of $t_{\perp}(\varphi)$.

The main result of this chapter is that the ADMR of Hg1201 can clearly distinguish cosine versus staggered twofold interlayer warping. We want to show that this is a qualitative distinction that can be made regardless of the details of the in-plane Fermi surface shape. To that end, we produce simulations for a variety of in-plane Fermi surface shapes. We consider a circular Fermi surface, the simplest option; various elliptical Fermi surfaces; and diamond-shaped pockets, ranging from square to concave circular arcs. The choice to

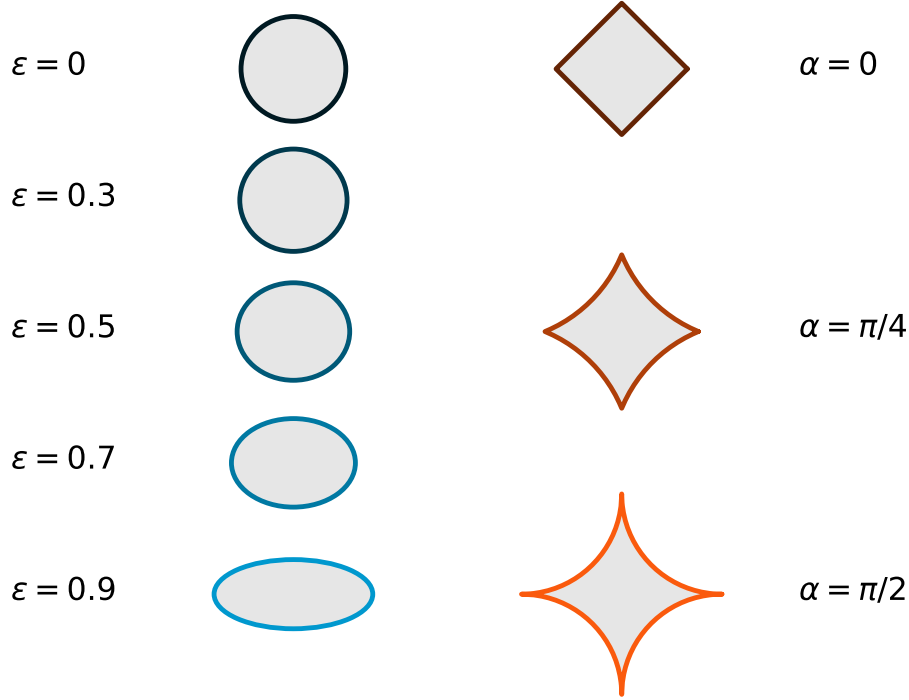


Figure 4.2: The various in-plane Fermi surface shapes considered in this chapter. The left column shows ellipses with increasing eccentricity (ϵ) from top to bottom. The right column shows diamond-shaped pockets with increasing concavity from top to bottom; α is the angle that must be subtended on a circle to create each arc that makes up the pocket. Note that the area enclosed by all of these shapes is the same; we constrain the cross-sectional area to be consistent with quantum oscillation measurements, as described in the text.

consider diamond-shaped pockets is motivated by the hypothesis that the small Fermi surface pocket in Hg1201 is due to a CDW reconstruction, as described in Ref. [35]. Fig. 4.2 illustrates the eight different in-plane Fermi surfaces we consider: five ellipses of various eccentricity and three different diamond-shaped pockets. As we vary the in-plane Fermi surface shape, we constrain its cross-sectional area such that it always corresponds to quantum oscillations of frequency 893 T, as reported for an underdoped sample with T_c of 74 K [35].

We need a function $k_F(\varphi)$ that describes each of the in-plane Fermi surfaces shown in Fig. 4.2; this will give us $\gamma(\varphi)$ (through use of Eq. 2.17) and $G(\varphi)$ (from Eq. 2.33). We do not expand $k_F(\varphi)$ in cylindrical harmonics, as in Eq. 2.24, simply because it is not convenient for the Fermi surfaces we are considering here.

The ellipses are defined as follows:

$$k_F(\varphi) = \frac{1}{\sqrt{(\cos(\varphi)/a)^2 + (\sin(\varphi)/b)^2}}, \quad (4.2)$$

where a and b are the major and minor axes of the ellipse, respectively. The area of an

ellipse is given by $A = \pi ab$, and the eccentricity is defined as $\epsilon = \sqrt{1 - (b/a)^2}$. In our calculations, we use the cross-sectional Fermi surface area that has been determined by quantum oscillation measurements; therefore, for every ϵ we consider, it is straightforward to calculate the appropriate a and b . Note that Eq. 4.2 describes an ellipse that is centered at the origin, which is necessary for the interlayer warping to be properly imposed on the in-plane Fermi surface.

The diamond-shaped pockets have a more complicated definition, given as follows:

$$k_F(\varphi) = \frac{R}{2 \sin(\beta)} \left((\cos(\beta) + \sin(\beta))(|\cos(\varphi)| + |\sin(\varphi)|) - \sqrt{2 + (2 \cos(\beta) \sin(\beta) + 1)(2|\sin(\varphi) \cos(\varphi)| - 1)} \right). \quad (4.3)$$

In the above equation, $\beta \equiv \alpha/2$, where α is the angle that must be subtended on a circle to make each arc that forms the diamond-shaped pocket; in this study, we consider $\alpha = 0$, $\pi/4$, and $\pi/2$. The constant R is the distance from the center of the pocket to the tip of each arc. In order to constrain the Fermi surface area to be a certain A_{FS} , we must set R as follows:

$$R = \sqrt{\frac{2A_{\text{FS}} \sin^2(\beta)}{F(\beta)}}, \quad (4.4)$$

where

$$F(\beta) \equiv \int_0^{\pi/2} \left((\cos(\beta) + \sin(\beta))(\cos(\varphi) + \sin(\varphi)) - \sqrt{2 + (2 \cos(\beta) \sin(\beta) + 1)(2 \sin(\varphi) \cos(\varphi) - 1)} \right)^2 d\varphi \quad (4.5)$$

We use a different equation for the diamond-shaped pockets when considering magnetic breakdown effects (that is, when using the vectorized form of the Shockley tube integral). As shown in Fig. 4.3, in this scenario the origin (the center of the Brillouin zone) is in the middle of the 4 pockets, so that the arcs appear convex instead of concave. In this case, R is still defined by Eq. 4.4 (since it is still the area of the concave pockets that is constrained), but we use

$$k_F(\varphi) = \frac{R}{2 \sin(\beta)} \left((-\cos(\beta) + \sin(\beta))(|\cos(\varphi)| + |\sin(\varphi)|) + \sqrt{2 + (1 - 2 \cos(\beta) \sin(\beta))(2|\sin(\varphi) \cos(\varphi)| - 1)} \right). \quad (4.6)$$

Equations 4.3 and 4.6 actually diverge for $\alpha = 0$, that is, for a square pocket. For that case, we use the simpler equation

$$k_F(\varphi) = \frac{\sqrt{A_{\text{FS}}/2}}{|\cos(\varphi)| + |\sin(\varphi)|}. \quad (4.7)$$

This equation is valid either for a Fermi surface contained within the Brillouin zone or for pockets in the four corners of the Brillouin zone, since tiling four tilted squares in the corners produces a square of the same size in the center.

The diamond-shaped pockets we consider all have their tips pointing along k_x and k_y , which is the orientation we would expect if they arise from a CDW reconstruction [35]. The orientation of the staggered twofold warping with respect to the diamonds is based on the results of Ref. [68].

The ellipses we consider all have their major axes along k_x and minor axes along k_y . However, elliptical Fermi surface pockets could very well be tilted off-axis; this is illustrated, for instance, in Ref. [26]. In Subsection 4.4.2, we demonstrate that if such “tilting” exists it will have only minor effects on the ADMR and will not affect any of the conclusions drawn in this chapter.

4.2.2 Angular frequency and scattering time

In addition to the Fermi surface geometry, ADMR is also affected by ω , the angular frequency of a quasiparticle about the Fermi surface, and τ , the quasiparticle scattering time.

The form of ω given in Eq. 2.19 relies on the assumption that we can neglect interlayer warping when calculating the angular frequency. In other words, we assume that a change in k_z will have a limited effect on the quasiparticle’s in-plane motion. We can calculate the size of this effect in our system, given the values of $k_F(\varphi)$ for all of the Fermi surfaces we consider and the limit of $t_{\perp} < 0.35$ meV from quantum oscillation measurements[35]. For a circular Fermi surface, we find that the maximum possible change of a quasiparticle’s in-plane Fermi momentum due to interlayer motion will be less than 1%, independent of the quasiparticle’s azimuthal position. For every other Fermi surface we consider, the maximum possible change will vary based on $k_F(\varphi)$ but will be at most 2.1% (along the minor axes of the ellipse with $\epsilon = 0.9$) and typically closer to 1%. Due to the small size of this effect, the motion in k_z and in φ can be considered separable, and we can base our calculation of ω on the motion of the quasiparticle about the in-plane Fermi surface. Therefore, Eq. 2.19 is a valid approximation for this system.

For most of this work we assume that the scattering rate, τ , is constant at all points on the Fermi surface. The effects of an anisotropic scattering rate are explored in Subsection 4.4.4, where it can be seen that they do not affect the conclusions of this work.

For the purposes of our calculations, we do not care about ω_0 or τ individually, but only $\omega_0\tau$. For Hg1201, we expect $\omega_0\tau \approx 0.35$ at 45 T and at a temperature of a few degrees Kelvin [35]. We perform calculations with $\omega_0\tau = 0.1, 1$, and 10 to show how ADMR results can be expected to vary with changing magnetic fields and temperatures.

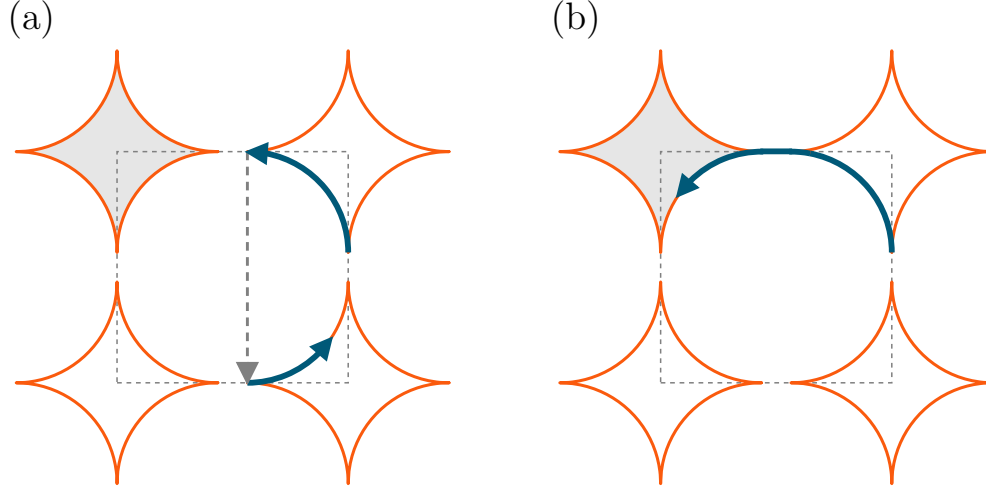


Figure 4.3: Concave diamond-shaped pockets at the corners of a Brillouin zone, as predicted for a biaxial CDW reconstruction. The dotted line marks the Brillouin zone boundary. Panel a) shows the path of a quasiparticle that undergoes Bragg diffraction, while panel b) shows the path of a quasiparticle that undergoes magnetic breakdown. The shaded pocket in each panel is meant to emphasize the fact that even when considering magnetic breakdown effects, the area we fix to match quantum oscillation measurements is that of the diamond-shaped pockets.

4.2.3 Bragg diffraction and MB

For all calculations involving the elliptical Fermi surface pockets, we assume that the Fermi surface is contained within a single Brillouin zone and we use Eq. 2.36 to calculate the ADMR.

However, it is important to be able to account for Bragg diffraction and magnetic breakdown if the small Fermi surface pockets in Hg1201 are the result of a biaxial CDW reconstruction [35, 67]. In this scenario, there will be four diamond-shaped Fermi surface pockets in the corners of the reconstructed Brillouin zone [74], as illustrated in Fig. 4.3. Quasiparticles are expected to Bragg-diffract when they reach a Brillouin zone boundary, as shown in Fig. 4.3(a). If Bragg diffraction always occurs, then the quasiparticles simply trace out the concave electron-like Fermi surface pockets. But if a quasiparticle undergoes magnetic breakdown at the Brillouin zone boundary, it will instead traverse the larger hole-like Fermi surface, as shown in Fig. 4.3(b).

Taking such effects into account requires the use of the vectorized form of the Shockley-Chamber tube integral, as given in Eq. 2.38. In the case of diamond-shaped Fermi surface pockets in the four corners of the Brillouin zone, as shown in Fig. 4.3, the vector $\mathbf{M}$ of MB junctions will be

$$\mathbf{M} = \left[0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}, 2\pi \right]. \quad (4.8)$$

As a reminder, we are making the simplifying assumption that the gaps between pockets are of negligible length in k space, so that the MB junction that ends one section of the Fermi surface is in the same position as the MB junction that begins the next section.

For a quasiparticle that is traveling counterclockwise on the Fermi surface, we find

$$\mathbf{\Gamma} \equiv D \begin{pmatrix} 0 & p & 0 & qe^{-id_{\perp}\Delta k_z^{(2 \rightarrow 4)}} \\ qe^{-id_{\perp}\Delta k_z^{(3 \rightarrow 1)}} & 0 & p & 0 \\ 0 & qe^{-id_{\perp}\Delta k_z^{(4 \rightarrow 2)}} & 0 & p \\ p & 0 & qe^{-id_{\perp}\Delta k_z^{(5 \rightarrow 3)}} & 0 \end{pmatrix}, \quad (4.9)$$

where $p = e^{-B_0/B \cos(\theta)}$ is the magnetic breakdown probability, we have defined $q = 1 - p$, and we have defined $D \equiv \exp\left(-\int_0^{\pi/2} \frac{d\varphi'}{\omega(\varphi')\tau}\right)$. We are able to use a single prefactor of D rather than including D_i in the matrix elements (as in Eq. 2.40) because in this case $\int_{\mathbf{M}_i}^{\mathbf{M}_{i+1}} \frac{d\varphi'}{\omega(\varphi')\tau}$ is the same for all i . This is due to the 4-fold symmetry of the in-plane Fermi surface and magnetic breakdown junctions.

In the matrix above, $\Delta k_z^{(i+1 \rightarrow j)}$ is the amount by which k_z^0 changes when a quasiparticle undergoes Bragg diffraction from the junction at $\mathbf{M}[i+1]$ to the junction at $\mathbf{M}[j]$. This can be found geometrically for each pair of MB junctions, as explained in Sec. sec:deltakz. Note that in writing each Δk_z in Eq. 4.9 we have used 1-indexing for $\mathbf{M}$, e.g. $\mathbf{M}[1] = 0$, $\mathbf{M}[2] = \frac{\pi}{2}$, and so on.

4.3 Main results

We now apply the equations developed in Ch. 2 to underdoped Hg1201. We consider a simple cosine warping, corresponding to $f(\varphi) = 1$, as well as a staggered twofold warping, corresponding to $f(\varphi) = \sin(2\varphi)$. We consider all of the in-plane Fermi surface shapes described in Section 4.2, with their cross-sectional areas fixed to match quantum oscillation measurements [64, 35]. Each in-plane Fermi surface shape gives us $\cos(\gamma(\varphi))$ directly (see Eq. 2.17). In addition to the in-plane shape, $G(\varphi)$ is determined by the direction of the magnetic field (θ and ϕ) as well as the value of c , the interlayer lattice constant. We use $d_{\perp} = c = 9.517 \text{ \AA}$, the value of the interlayer lattice parameter in as-grown Hg1201 with $T_c \approx 80 \text{ K}$ [75].²

We take $\rho_{zz} = \frac{1}{\sigma_{zz}}$, which is justified for a material such as Hg1201 that has $v_z \ll v_x, v_y$ [77]. Since we are only calculating σ_{zz} up to a constant of proportionality, we plot all of our results as $\rho_{zz}(\theta)/\rho_{zz}(\theta = 0)$.

²The constraint used for the cross-sectional Fermi surface area is from a sample that also had an as-grown T_c of roughly 80 K but that was subsequently heat-treated in a nitrogen-rich atmosphere to achieve a T_c of 74 K [35]. This treatment may slightly decrease the interlayer lattice parameter since it removes interstitial oxygen, but such an effect should be negligible: only a fraction of a percent change, based on similar behavior in YBCO [76].

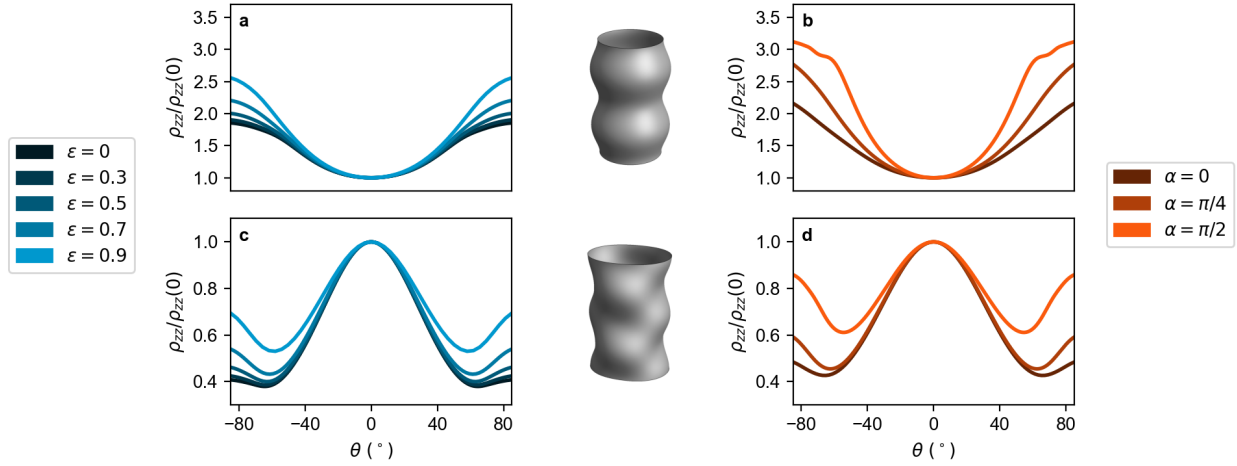


Figure 4.4: Calculated ADMR of Hg1201 with $\omega_0\tau = 1$ and $\phi = 0$ for various combinations of in-plane shape and interlayer warping. The top panels show ADMR for a simple cosine interlayer warping with a) elliptical and b) diamond-shaped in-plane Fermi surfaces. The bottom panels show ADMR for a staggered twofold interlayer warping with c) elliptical and d) diamond-shaped in-plane Fermi surfaces. While the different in-plane Fermi surfaces cause some variation, there is a clear qualitative distinction between the two interlayer warpings regardless of the in-plane shape.

The main result of this chapter is summarized in Fig. 4.4, which shows the expected ADMR for all of the in-plane Fermi surfaces considered (Fig. 4.2) with $\phi = 0$ and $\omega_0\tau = 1$ and with the Fermi surface contained in a single Brillouin zone. There are quantitative distinctions between the ADMR for different diamond-like and ellipsoidal in-plane Fermi surfaces, but the most notable result is that there is a clear qualitative difference between the two interlayer warpings, even given highly different in-plane Fermi surface geometries: the simple cosine warping causes a dip in resistance at $\theta = 0$ (i.e., with the magnetic field in the interlayer direction), while the staggered twofold warping yields a hump. This qualitative distinction is not affected by varying ϕ , as shown in Subsection 4.4.1, nor does it depend on the value of $\omega_0\tau$. As shown in Fig. 4.5, varying $\omega_0\tau$ from 0.1 to 10 yields the same qualitative difference, and though the distinction becomes less pronounced as $\omega_0\tau$ decreases and $\alpha \rightarrow \pi/2$, it is always present. This result demonstrates that ADMR can be used to unambiguously reveal the interlayer warping for a wide range of scattering times and magnetic fields, in a way that is independent of the in-plane shape. At higher $\omega_0\tau$ (i.e., at higher magnetic fields and lower temperatures), angle-dependent magnetoresistance oscillations are apparent, which can be used to discern the in-plane Fermi surface.

A full study of the ADMR of Hg1201 as a function of ϕ can be used to gain additional information about the Fermi surface geometry. As demonstrated in Subsection 4.4.1, the symmetry of a Fermi surface will be reflected in the symmetry of the ADMR. The ϕ -dependence of ADMR is a vital source of information; we do not focus on it in this work

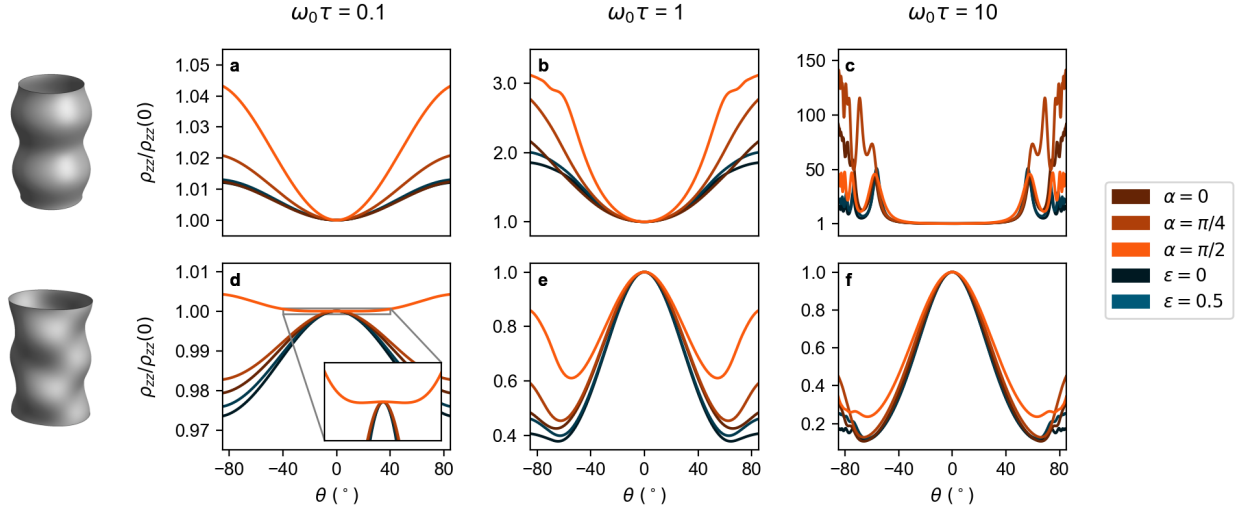


Figure 4.5: Calculated ADMR of Hg1201 for select in-plane Fermi surface shapes, with $\phi = 0$ and with (a,d) $\omega_0\tau = 0.1$, (b,e) $\omega_0\tau = 1$, and (c,f) $\omega_0\tau = 10$. Plots in the top row show ADMR calculated with a simple cosine interlayer warping, while those in the bottom row show ADMR calculated with a staggered twofold interlayer warping.

simply because its usefulness and interpretation are already well understood [17, 40, 73].

For all of the above, we employ Eq. 2.36 to calculate the ADMR of the circular and elliptical in-plane Fermi surfaces, as well as the diamond-shaped pocket with $\alpha = 0$. The calculation for concave diamond-like pockets ($\alpha > 0$) takes an excessively long time to execute, most likely due to the fact that the integrand in Eq. 2.37 is quite complicated and cannot be solved analytically. So for these in-plane Fermi surface shapes, we instead use the vectorized form of the Shockley tube integral (Eq. 2.38), and, for the purposes of considering a Fermi surface in a single Brillouin zone, we set $B_0/B = 10\,000$. In this limit, the probability of breakdown approaches 0 and therefore the quasiparticles always trace out the concave diamond-shaped pockets, as shown in Fig. 4.3(a); this is physically equivalent to the Fermi surface being contained in a single Brillouin zone.

Using Eq. 2.38 with differing values of B_0/B allows us to explore the effect of magnetic breakdown on these systems. As noted previously, magnetic breakdown effects may be relevant when considering the possibility of diamond-shaped pockets being formed by CDW reconstruction. Therefore, we have calculated the ADMR of the diamond-shaped Fermi surfaces using Eq. 2.38 with three different values of B_0/B , still setting $\omega_0\tau = 1$ and $\phi = 0$. The results are shown in Fig. 4.6; note that with $B_0/B = 0.0001$ there will be near total magnetic breakdown, while $B_0/B = 10\,000$ leads to effectively zero magnetic breakdown, the same result shown in Fig. 4.4. Quantum oscillation measurements of Hg1201 have set a lower bound of $B_0 \gtrsim 200$ T [35]. Given this, and the fact that $B_0/B = 1$ and $B_0/B = 10\,000$ produce remarkably similar results, we conclude that magnetic breakdown effects can safely be neglected for this scenario.

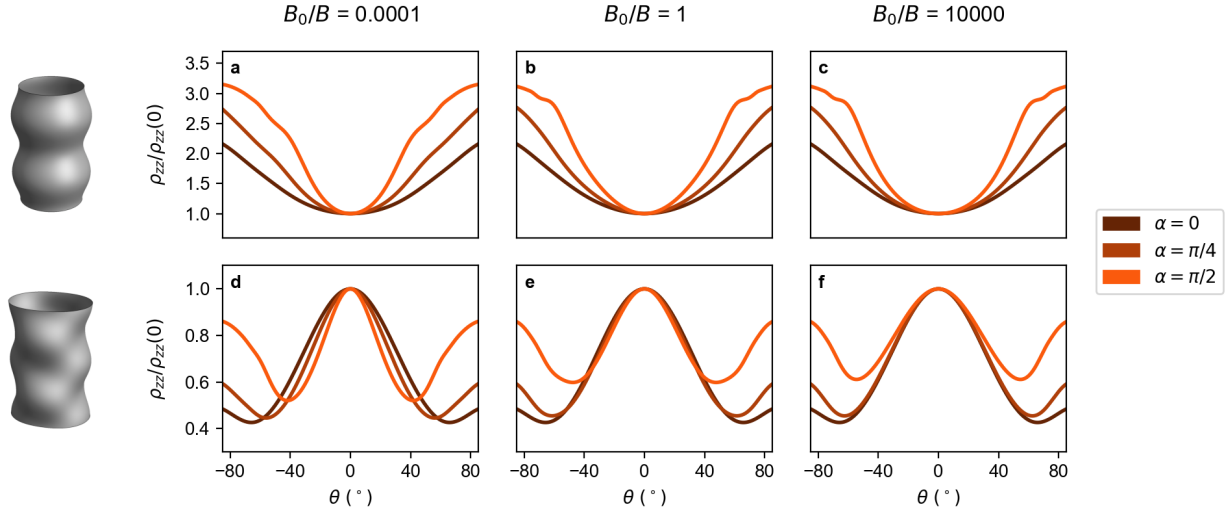


Figure 4.6: Calculated ADMR of Hg1201 for diamond-shaped in-plane Fermi surfaces with $\phi = 0$ and $\omega_0\tau = 1$ and with various degrees of magnetic breakdown: (a,d) $B_0/B = 0.0001$, (b,e) $B_0/B = 1$, and (c,f) $B_0/B = 10000$. Plots in the top row show ADMR calculated with a simple cosine interlayer warping, while those in the bottom row show ADMR calculated with a staggered twofold interlayer warping.

4.4 Additional results

4.4.1 Varying ϕ

ADMR as a function of ϕ , the azimuthal angle of the applied field, can provide valuable insights regarding a material's Fermi surface geometry. We show some examples of ADMR with varying ϕ in Fig. 4.7 to emphasize two points: first, that the symmetry of the Fermi surface determines the symmetry of the ADMR; second, that the qualitative distinction between the two types of interlayer warping considered here is present regardless of the value of ϕ .

To produce Fig. 4.7 we consider four different in-plane Fermi surfaces and two different interlayer warpings. For each combination of these, we calculate ADMR with values of ϕ ranging from 0° to 360° in 15° increments. The results are only shown up to 90° because beyond that, all of the results would lie over curves that are already plotted. Indeed, for most of the Fermi surfaces considered there is already considerable degeneracy below 90° : for example, for the diamond-shaped pockets there is a mirror symmetry about 45° , and for the circular Fermi surface with simple cosine warping there is complete rotational symmetry. The symmetry of each Fermi surface is reflected in the ϕ -dependence of its ADMR, as it must be.

Note that regardless of ϕ , a Fermi surface with simple cosine warping yields a local minimum of the resistivity at $\theta = 0$, while a Fermi surface with staggered twofold warping

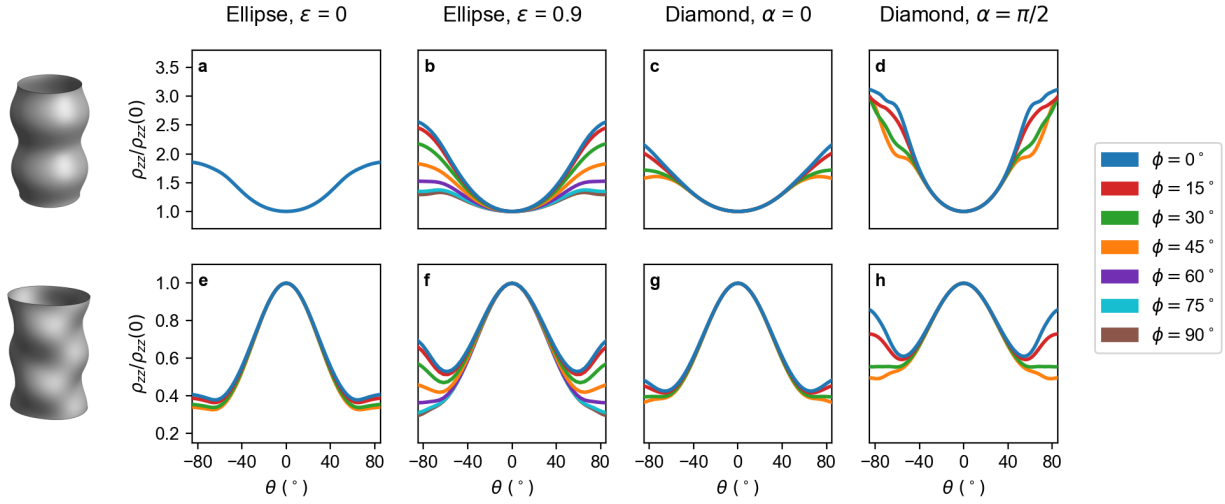


Figure 4.7: Calculated ADMR of Hg1201 with a simple cosine interlayer warping (top row) or a staggered twofold interlayer warping (bottom row) for 8 different values of ϕ as indicated in the legend. Results are shown for four different in-plane Fermi surfaces: (a,e) circular, (b,f) elliptical, (c,g) square diamond, and (d,h) concave diamond.

yields the opposite.

4.4.2 Tilt of elliptical in-plane Fermi surfaces with respect to interlayer warping

For all of the calculations above, we considered ellipses with their major axes along k_x and minor axes along k_y . As mentioned in Subsection 4.2.1, for elliptical Fermi surfaces it is physically reasonable to consider that the elliptical axes may be tilted away from the reciprocal space axes.

For the simple cosine warping, tilting the ellipses in the $k_x - k_y$ plane is simply a matter of rotating the whole Fermi surface, since the interlayer warping has no azimuthal dependence. But for the staggered twofold warping, the alignment between the in-plane shape and interlayer warping could affect the magnetoresistance in a non-trivial way. To verify that this will not affect our general conclusions, we calculate ADMR for an ellipse with its major axes tilted away from k_x by some amount φ_{tilt} . We use an ellipse with $\epsilon = 0.9$ and fix the azimuthal angle of the magnetic field to $\phi = 0$. The results are shown in Fig. 4.8. With the simple cosine warping, changing the orientation of the in-plane ellipse simply rotates the entire Fermi surface. Therefore, it is equivalent to rotating the applied magnetic field to a different value of ϕ ; this can be seen by comparing Fig. 4.8(a) to Fig. 4.7(b). For the staggered twofold warping, changing the orientation of the in-plane ellipse does modify the overall magnetoresistance beyond a simple rotation; however, a comparison between Fig. 4.8(b) and Fig. 4.7(f) reveals that the change is minimal and does not alter the conclusions

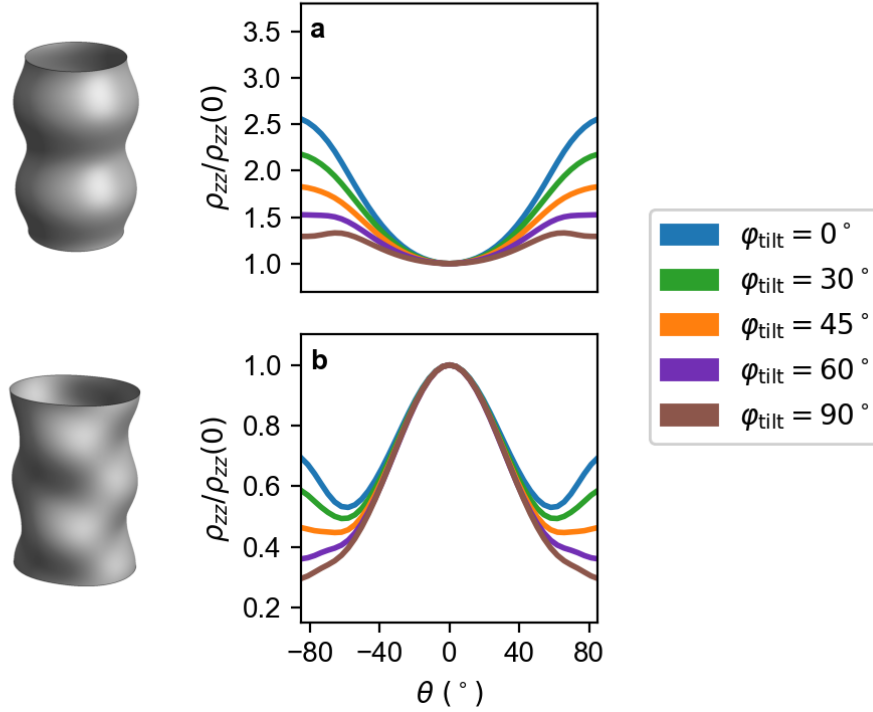


Figure 4.8: Calculated ADMR of Hg1201 for an elliptical Fermi surface with various orientations. The in-plane Fermi surface is an ellipse with $\epsilon = 0.9$. The variable φ_{tilt} indicates the angle between k_x and the major axis of the ellipse. The magnetic field is fixed at $\phi = 0$ for all calculations. a) Results for a simple cosine interlayer warping. b) Results for a staggered twofold interlayer warping.

of this chapter.

4.4.3 Periodicity of the interlayer warping

Sebastian *et al.* showed that their quantum oscillation data for YBCO could be explained by a CDW ordering with $l = 1/2$ that yields an interlayer warping of periodicity $\frac{2\pi}{c}$. However, x-ray scattering measurements of the same compound found a three-dimensional CDW order with $l \sim 1$ [34]. If we assume the same type of reconstruction that Sebastian *et al.* suggested, the CDW wavevector from Ref. [34] should lead to an interlayer warping of period $\frac{4\pi}{c}$. Doubling the periodicity is mathematically equivalent to reducing $d_{\perp}$, the interlayer spacing, by half.

We repeat our calculations for a circular in-plane Fermi surface, but now using $d_{\perp} = 4.7585 \text{ \AA}$ rather than the actual interlayer lattice parameter of $c = 9.517 \text{ \AA}$. The results are shown in Fig. 4.9. Clearly, changing the interlayer lattice parameter produces a quantitative change in the ADMR of Hg1201. However, given the many unknown parameters with regards to this Fermi surface, such a change may be difficult to distinguish at $\omega_0\tau = 1$; for example,

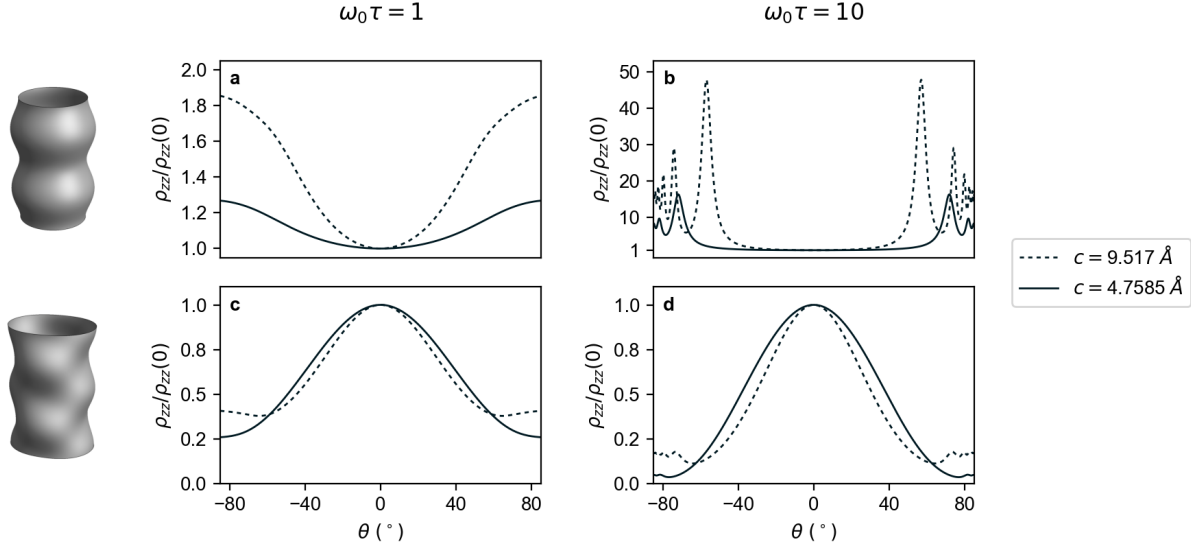


Figure 4.9: Calculated ADMR of Hg1201 with two different interlayer lattice parameters. Results are shown for a circular in-plane Fermi surface with a simple cosine interlayer warping (top row) or a staggered twofold interlayer warping (bottom row). (a,c) $\omega_0\tau = 1$, (b,d) $\omega_0\tau = 10$.

with a simple cosine interlayer warping, halving c produces roughly the same change as increasing the eccentricity of the in-plane Fermi surface (cf. Fig. 4.4). On the other hand, with $\omega_0\tau = 10$ the ADMR results have more structure, as angle-dependent magnetoresistance oscillations are evident. Thus it may be possible to use ADMR to determine the periodicity of the interlayer warping, but only if measurements can be taken at very low temperatures and high magnetic fields such that $\omega_0\tau \gg 1$.

4.4.4 Anisotropic scattering

The assumption of a constant scattering rate, τ , is not necessarily justified for this system. For instance, if the Fermi surface is diamond-shaped due to CDW reconstruction, then the density of states should be enhanced at the tips of the diamonds where a gap is opened, leading to an increase in τ at those points. To determine whether such a variation in τ would affect the results of this chapter, we calculate the ADMR of a square diamond pocket ($\alpha = 0$) with a scattering rate τ that varies as $\tau(\varphi) = \tau_0/(1 - 0.5 \cos(4\varphi))$. This particular form is chosen so that the integral in Eq. 2.37 can be solved analytically; it results in a scattering rate that is greatest at the tips of the diamond and that varies by a factor of 3 about the Fermi surface. We also calculate the ADMR of an elliptical Fermi surface with a non-constant scattering rate. In this case, it is less clear how the scattering rate should be expected to vary; however, it is reasonable to assume that it will respect the twofold rotational symmetry of the Fermi surface. To that end, we calculate the ADMR of an

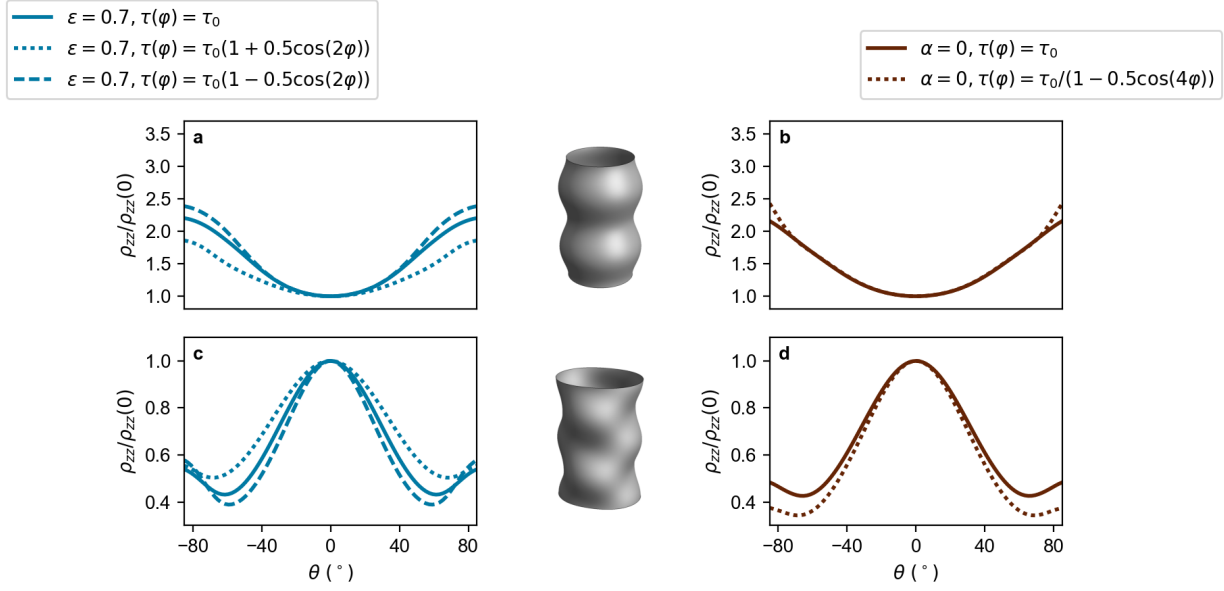


Figure 4.10: Calculated ADMR of Hg1201 with various scattering rates, where $g(\varphi)$ parameterizes the variation of the scattering rate, τ , about the Fermi surface. Results are shown for Fermi surfaces with a simple cosine interlayer warping (top row) or a staggered twofold interlayer warping (bottom row). Results are shown for two different in-plane Fermi surfaces: (a,c) elliptical with $\epsilon = 0.7$ and (b,d) square diamond with $\alpha = 0$.

elliptical Fermi surface ($\epsilon = 0.7$) with two different variations of the scattering rate: one for which τ is greatest along the major axis of the ellipse, and one for which it is greatest along the minor axis. From the results shown in Fig. 4.10, it is clear that a non-constant scattering rate will have some impact on the magnetoresistance of Hg1201 but will not affect the qualitative distinction that is the main result of this chapter. The results shown in Fig. 4.10 are for $\omega_0\tau_0 = 1$ and $\phi = 0$.

4.5 Discussion

For a tetragonal crystal such as Hg1201—indeed for any material that has a twofold rotational symmetry about the z -axis—the ADMR must be symmetric about $\theta = 0$. This means that either a local minimum or local maximum in resistivity must occur when the field is in the interlayer direction. However, whether it will be a minimum or a maximum for a given Fermi surface geometry, as well as whether this distinction will be significant enough to easily measure, cannot be determined by symmetry constraints alone. For Fermi surfaces that have a constant $k_F(\varphi)$ like those in Fig. 4.1, we can solve Eq. 2.36 analytically and prove that a simple cosine warping will lead to a local minimum of resistivity at $\theta = 0$, while staggered twofold warping leads to a local maximum. Through numerical calculations, we have shown that this effect is robust to the various in-plane Fermi surface geometries we consider and to

magnetic breakdown effects. We have also shown that the concavity of the ADMR will be broad enough in θ and the associated change in resistivity will be large enough to measure in experimentally achievable temperatures and magnetic fields.

It is worth noting that while this effect on the resistivity decreases as $\omega_0\tau \rightarrow 0$, it should always be evident in a sufficiently accurate experiment. Assuming $\omega_0\tau = 0.1$ is enough to resolve the effect, we can estimate the temperature and field ranges at which the ADMR should be measured. Fig. 4.11 shows a schematic diagram of where ADMR measurements are feasible for a sample of Hg1201 with $T_c = 71K$. At 45 T and a few degrees Kelvin, Hg1201 has $\omega_c\tau \approx 0.35$ with the magnetic field perpendicular to the layers ($\theta = 0$), where ω_c is the cyclotron frequency [35].³ This gives a bound of $\omega_0\tau \geq 0.35$ for those conditions, since ω_c is the average of angular velocity ω about an orbit and therefore $\omega_c \leq \omega_0$ (see Eq. 2.19). We estimate that $\omega_0\tau = 0.35$ at 45 T and 3 K (since Ref. [35] does not specify the temperature but includes measurements between 1.8 K and 4 K). The dashed line demarcating $\omega_0\tau = 0.1$ and the gradient representing $\omega_0\tau$ in Fig. 4.11 are based on this estimate and on the approximation that τ decreases linearly with temperature. The superconducting dome is drawn by estimating the upper critical field to be $H_{c2} = 40$ T at low temperatures [35] and using a shape inspired by the upper critical field evolution of cuprate superconductors in Ref. [78]. For a Q2D material, $H_{c2}(\theta)$ is highly anisotropic [79, 80, 81], but it will only increase by at most a few percent in the range $-15^\circ < \theta < 15^\circ$. This angular range should be adequate to resolve staggered or simple cosine warping in the ADMR.

One interesting possibility is that the Fermi surface of Hg1201 may change as a function of temperature or magnetic field due to reconstruction. This could be a change not only in geometry but also in size. From calculations of ADMR for the circular in-plane Fermi surface and the square in-plane Fermi surface, we find that the distinction between a local minimum or a local maximum in ADMR for the two interlayer warpings will not be affected by a change in the Fermi surface's cross-sectional area, even if it is a factor of 10 larger or smaller than the Fermi surface area we have used throughout this chapter. However, the qualitative behavior of the ADMR away from $\theta = 0$ will be affected by a change in Fermi surface size; in the case of the simple cosine interlayer warping, we also see that the fractional change of the resistivity as a function of field angle will be considerably greater for a larger Fermi surface. Therefore, a change in the Fermi surface size will be easily discerned if very distinct ADMR results are seen with small changes of magnetic field strength or temperature.

A caveat in this discussion is that we have assumed the Fermi surface of Hg1201 to be a single Q2D pocket. Quantum oscillation measurements only detect one Fermi surface pocket in Hg1201, but this does not preclude the existence of additional open Fermi surface sheets. If such sheets are present, they would also contribute to interlayer magnetoresistance, making the interpretation of ADMR measurements more complicated. While quasi-one-dimensional Fermi surface sheets are difficult to detect directly, open orbits should lead to Lebed minima in the ADMR [82]; if these minima are not observed at high $\omega_0\tau$, this would be evidence that such sheets do not exist or contribute to the magnetoresistance. The density of states

³This is the average result across samples with $T_c = 71K$ and $T_c = 74K$.

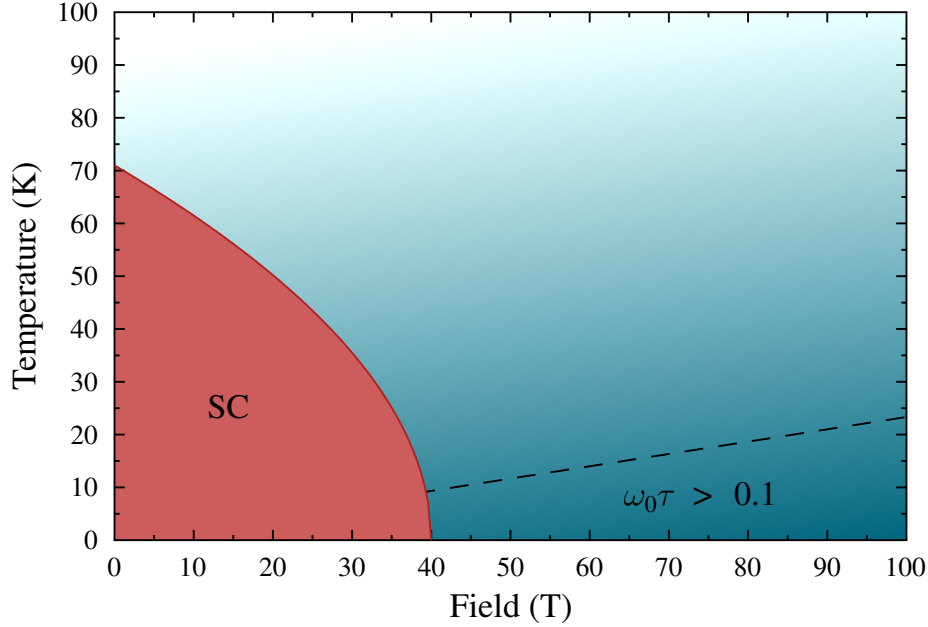


Figure 4.11: A schematic diagram of where the ADMR measurements described in this chapter would be feasible, based on the data and assumptions described in the text. The dome on the left labeled “SC” is the superconducting region, based on an estimate of H_{c2} with the magnetic field in the interlayer direction. Outside the superconducting region, the color gradient represents the value of $\omega_0\tau$, with darker color denoting a larger value. The dashed line indicates an estimated cutoff for the criterion $\omega_0\tau \geq 0.1$; the region below the dashed line is where the distinction between interlayer warpings could most clearly be distinguished by ADMR measurements.

associated with such sheets can also be estimated through careful analysis of the wave form of quantum oscillations [83]. Such an analysis could be used to determine how important a role, if any, quasi-one-dimensional sheets play in this material.

4.6 Conclusion

We have calculated the expected interlayer ADMR for underdoped Hg1201 using several possible Fermi surface geometries. We have shown that the simple cosine and staggered twofold interlayer warpings will have two clearly distinct experimental signatures regardless of whether the in-plane Fermi surface is circular, elliptical, or diamond-shaped. We have also shown that magnetic breakdown between Fermi surface pockets should not affect these results. Since ADMR, unlike quantum oscillations, is measured at a fixed field strength, it could be used to study the Fermi surface geometry of Hg1201 at various temperatures and magnetic fields, as illustrated in Fig. 4.11. Such information on the field- and temperature-

dependence of the Fermi surface would be complementary to other experiments that can probe how the ordered states in Hg1201 evolve. If changes in the Fermi surface geometry can be connected to the evolution of CDW order, or some other ordered state, it would help conclusively answer the question of what drives Fermi surface reconstruction in the underdoped cuprates.

Part II

Resonant Ultrasound Spectroscopy

Chapter 5

Introduction and theory

5.1 Introduction

Every type of bond that holds a solid object together is ultimately electronic in nature, whether it is related to electrons being shared or transferred between ions, or related to atoms or molecules interacting via their dipole moments. Therefore, it is only natural that the elasticity of a material—a measure of how difficult it is to deform these bonds in different manners—is intimately related to the state of the electrons in the system. As elasticity is a tensor, determining elasticity can provide insight into the symmetry of a given electronic phase as well as the symmetry of any order parameter that drives a phase transition. Elasticity is sensitive even to second-order phase transitions.

Resonant ultrasound spectroscopy (RUS) is a method to measure the natural resonances of an object of interest. As we will describe below, the frequencies of these natural resonances depend directly on the object's elasticity. This work focuses on the use of RUS to study temperature-driven phase transitions in exotic magnetic materials. Simply from the evolution of a sample's resonant frequencies as a function of temperature, we can extract information about the nature of any phase transition in the sample. If we are able to determine the elasticity of a sample from its resonant frequencies, even more details about the order parameter of the phase transition can be obtained.

The remainder of this chapter is devoted to an introduction of the theory behind RUS, including the expected behavior of elasticity near a phase transition. In Ch. 6, we describe the design and construction of the experimental apparatus that we used to perform our RUS measurements. We also detail the data analysis methods that we have used to extract relevant information from measurements of natural resonances. Ch. 7 is devoted to the candidate Kitaev material β -Li₂IrO₃ and our use of RUS to study its reported magnetic phase transition near 100 K. In Ch. 8, we share RUS results for several different iron-intercalated transition metal dichalcogenides of the form Fe_xNbS₂. These materials exhibit antiferromagnetism that is switchable by an applied current, as well as spin glass behavior. We show how resonant frequencies respond to the various temperature-driven magnetic phase

transitions for three different intercalation values: $x = 0.31$, 0.33 , and 0.35 . For $x = 0.33$, we also analyze the elasticity as a function of temperature in order to determine the symmetry of one of its antiferromagnetic phases.

5.2 Mechanical resonance

The idea of resonance is a familiar one in classical mechanics: when an object is driven at its resonant frequency, it will vibrate with a larger amplitude than if it is driven off-resonance. Inherent in this description is the idea that all parts of the object are vibrating at a single frequency and in phase; in other words, the object is undergoing a normal mode of vibration. Each normal mode of a system has an associated frequency, and these frequencies are precisely the resonant frequencies of the system.¹

The objective of any RUS experiment is to measure the resonant frequencies of a system, usually as a function of some external parameter such as temperature or magnetic field. Our RUS setup allows us to measure resonant frequencies as a function of temperature. The details of our experimental apparatus are outlined in Ch. 6, but its principle of operation is simple to understand: we excite the sample of interest at a certain frequency and measure its response. As we vary the frequency of the excitation, we see a characteristic response when we reach a resonant frequency of the sample.

We can consider our sample as a damped harmonic oscillator that is driven by a periodic force. If the resonant frequency of the system is f_0 , it is being driven at frequency f , and it has damping constant β then we can write the equation of motion as

$$\ddot{x} + \beta\dot{x} + (2\pi f_0)^2 x = \alpha \cos(2\pi ft), \quad (5.1)$$

where α is a constant that is proportional to the amplitude of the driving force. We use x_{phase} to denote component of the oscillator motion that is in phase with the driving force, while x_{quad} denotes the quadrature component (that is, the component with a phase difference of $\pi/2$ radians from the driving force). Using Eq. 5.1, we can solve for each of these as a function of f [84]:

$$\begin{aligned} x_{\text{phase}} &= \frac{a(f_0^2 - f^2)}{(f_0^2 - f^2)^2 + \gamma^2 f^2}, \\ x_{\text{quad}} &= \frac{a\gamma f}{(f_0^2 - f^2)^2 + \gamma^2 f^2}. \end{aligned} \quad (5.2)$$

For convenience, we have defined $\gamma = \beta/2\pi$ and $a = \alpha/4\pi^2$.

¹The terms “mechanical resonances”, “natural resonances”, and “acoustic resonances” are all used in the literature to refer to a sample’s normal modes of vibration; the terms “characteristic frequencies”, “resonant frequencies”, “normal frequencies” and “natural frequencies” may be used for the frequencies associated with such modes.

Assume that we are in the low-damping limit, $\gamma \ll f_0$. In this limit, as long as the driving frequency is close to the resonant frequency then Eq. 5.2 can be simplified [84, 85]:

$$\begin{aligned} x_{\text{phase}} &\approx \frac{a}{2f_0} \frac{f_0 - f}{(f_0 - f)^2 + (\gamma/2)^2}, \\ x_{\text{quad}} &\approx \frac{a}{2f_0} \frac{\gamma/2}{(f_0 - f)^2 + (\gamma/2)^2}. \end{aligned} \quad (5.3)$$

In this low-damping limit, x_{quad} is a Lorentzian as a function of f , while x_{phase} is a dispersive Lorentzian.

We can write the in-phase and quadrature components as the real and imaginary parts of our signal, Z :

$$Z = x_{\text{phase}} + ix_{\text{quad}}. \quad (5.4)$$

Then we can rewrite Eq. 5.3 in the more succinct form

$$Z = \frac{A}{f - f_0 + i\gamma/2} \quad (5.5)$$

, where $A = -a/2f_0$ is a constant for a given resonance with a given driving force. The magnitude of this signal will be

$$|Z| = \frac{A}{\sqrt{(f - f_0)^2 + (\gamma/2)^2}}. \quad (5.6)$$

By convention, the width of a resonance peak is defined at the half-power point [86, 87], the point at which the magnitude of the response is reduced to $1/\sqrt{2}$ of its maximum. We therefore find that the width of the resonance is simply equal to γ .

The quality factor Q for this system is defined as $Q = f_0/\gamma$. For a crystalline sample, it is typical to find $Q = 1000$ or higher [88]. Indeed, for all of the samples measured in this work we find Q of order 10^3 . Therefore, our previous assumption that we are in the low-damping limit is justified.

The behavior described by Eq. 5.5 is essentially the characteristic response that we are looking for as we sweep the frequency of our driving force. Experimental factors cause some modifications of the measured response, as discussed in Sec. 6.2.

5.3 Elasticity

For a simple mass m on an ideal linear spring, the frequency of the normal mode is given by $\sqrt{k/m}$, where k is the spring constant. The spring constant is a characteristic of the spring that relates the force applied to a spring (F_s) with the distance it is compressed or stretched (x):

$$F_s = kx. \quad (5.7)$$

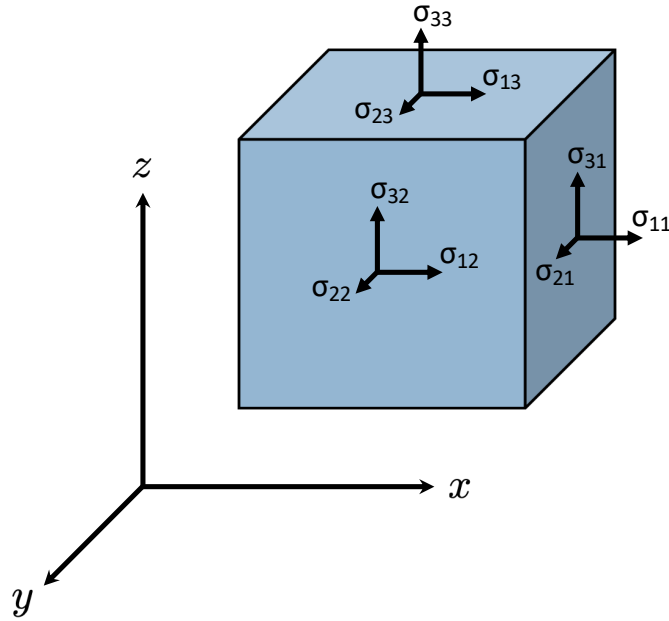


Figure 5.1: An illustration of the components of the stress tensor on an infinitesimal cube.

The equation above, Hooke's law, holds for low values of x ; this is known as the linear-elastic regime.

For continuous three-dimensional objects such as the crystals we measure, deformations can be more complicated than simple linear compression or extension. The analog of Hooke's law for a point in a continuum object is

$$\sigma_{ij} = c_{ijkl}\epsilon_{kl}, \quad (5.8)$$

as long as deformations are small and we remain in the linear-elastic regime. The stress tensor σ and the strain tensor ϵ are related through the elasticity tensor c . We use the Einstein summation convention in Eq. 5.8 and throughout this work. Each index in Eq. 5.8 ranges from 1 to 3, as they refer to Cartesian coordinate directions.

The stress tensor σ specifies the force per unit area applied to a given point in the continuous object ². As illustrated in Fig. 5.1, the first index specifies the direction of the force, while the second index specifies the orientation of the surface that the force is acting upon.

We can see from Fig. 5.1 that if, for example, $\sigma_{23} \neq \sigma_{32}$, this will result in a rotation of the body around the x -axis. Since elasticity specifically concerns deformations of the object, we wish to neglect rigid rotations; therefore, we can see that σ_{ij} must be symmetric [89].

The strain tensor ϵ is the symmetric part of the displacement gradient. Consider a single point in the continuous object, with position $\mathbf{x}$. When the object undergoes some

²Whereas in Part I of this work we used σ to signify electrical conductivity, in Part II we will use it exclusively for stress. It is an unfortunate coincidence that both properties are expressed by the same symbol.

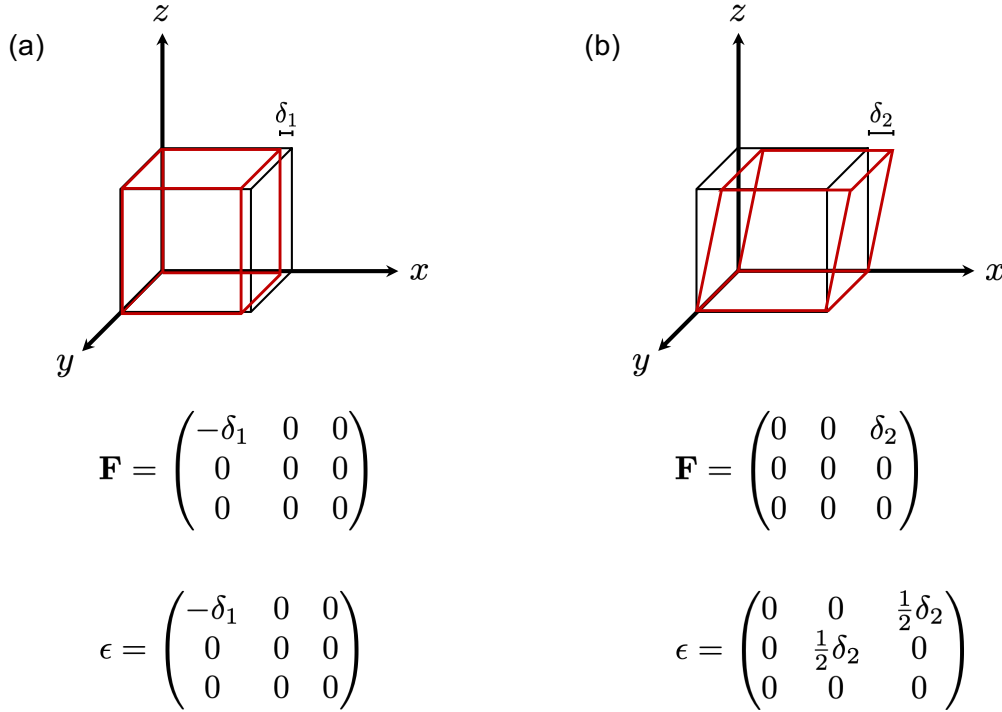


Figure 5.2: Examples of the displacement gradient tensor and the strain tensor for two different deformations of an infinitesimal cube. a) Compression of the cube by δ_1 along x results in a symmetric displacement gradient tensor, which is equal to the strain tensor. b) A simple angular shear of the cube results in a displacement gradient tensor that is not symmetric; this must be symmetrized to obtain the strain tensor.

deformation, we can specify the displacement of that particular point with the displacement vector $\mathbf{u}$. The displacement gradient is defined as

$$F_{ij} = \frac{\partial u_i}{\partial x_j}. \quad (5.9)$$

The strain, being the symmetric part of $\mathbf{F}$, is therefore

$$\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right). \quad (5.10)$$

The strain is explicitly symmetric for the same reason that the stress tensor must be symmetric: to remove the effects of rigid body rotations³. Examples of the displacement gradient tensor and the strain tensor for two different simple deformations are shown in Fig. 5.2.

³The antisymmetric part of the displacement gradient is known as the spin tensor and describes only rigid rotations.

As noted above, for a simple spring the resonant frequency squared will be proportional to the spring constant. Now that we understand elasticity as the analog of the spring constant, it seems clear that the resonant frequencies of a continuous three-dimensional object will depend on its elasticity. In fact, we will find that each resonant frequency squared is proportional to elements of the elasticity tensor. We will detail the exact mathematical relationship between resonant frequencies and elasticity in Sec. 6.3. The key point here is that changes in an object's elasticity will cause corresponding changes in that object's resonant frequencies.

5.3.1 Symmetry and Voigt notation

Both $\boldsymbol{\sigma}$ and $\boldsymbol{\epsilon}$ are rank-two tensors that each have nine elements. However, because they are both symmetric, they each only have six *independent* elements. This allows us to express the stress and strain tensors using Voigt notation, which is a method for representing a symmetric tensor with a reduced rank. In this case, each of our rank-two tensors can now be expressed as a vector:

$$\begin{aligned}\boldsymbol{\sigma} &= (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6), \\ \boldsymbol{\epsilon} &= (\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4, \epsilon_5, \epsilon_6).\end{aligned}\tag{5.11}$$

We have abbreviated each pair of indices into a single index according to the following conventions [89]:

$$\begin{aligned}11 &\rightarrow 1 \\ 22 &\rightarrow 2 \\ 33 &\rightarrow 3 \\ 23, 32 &\rightarrow 4 \\ 13, 31 &\rightarrow 5 \\ 12, 21 &\rightarrow 6\end{aligned}\tag{5.12}$$

The stress components in Voigt notation, σ_m are directly equal to those in tensor notation, σ_{ij} ; for example, $\sigma_1 = \sigma_{11}$ and $\sigma_4 = \sigma_{23} = \sigma_{32}$. However, for reasons that will soon become clear, it is conventional to introduce factors of two for the off-diagonal elements of the strain. So for instance $\epsilon_1 = \epsilon_{11}$, but $\epsilon_4 = 2\epsilon_{23} = 2\epsilon_{32}$.

The elasticity $\mathbf{c}$ is a rank-four tensor with 81 elements. However, because both of the rank-two tensors it relates are symmetric, this brings the number of independent elements down to 36. This allows us to also express c_{ijkl} using Voigt notation. In this case, the indices (ij) are abbreviated as described in Eq. 5.12, as are the indices (kl) . Then we can express $\mathbf{c}$

as a six-by-six matrix:

$$\mathbf{c} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\ c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\ c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66} \end{pmatrix}. \quad (5.13)$$

As a note of caution, these c_{ij} are not actually the components of a second-rank tensor and do not transform as such.

We will use Voigt notation for the remainder of this work. Due to the factors of two we introduced for the vector notation of ***epsilon***, we will find that Eq. 5.8 now takes the analogous form

$$\sigma_i = c_{ij}\epsilon_j, \quad (5.14)$$

where now $i, j = 1, 2, 3, 4, 5, 6$.

By considering derivatives of the free energy, it can be shown that $c_{ij} = c_{ji}$ [89]. Therefore, the number of independent elements of $\mathbf{c}$ is further reduced, from 36 to 21. When we are describing the elasticity of a crystal, the symmetries of the crystal itself will further reduce the number of independent elements of the elasticity tensor. The independent elements of the elasticity tensor are often referred to as elastic moduli.

5.3.2 Elasticity near a phase transition

The elastic moduli are not constant as a function of temperature. This is due to the anharmonicity of the crystal lattice potential, in the same manner that anharmonicity underlies thermal expansion. For many crystalline solids, the behavior of each elastic modulus is well-described by the expression [90]

$$c_{ij}(T) = c_{ij}^{(0)} - s/(e^{t/T} - 1), \quad (5.15)$$

where $c_{ij}^{(0)}$, s , and t are all constants. This function is roughly constant at low temperature and roughly linear, with negative slope, at high temperature. The specific form of Eq. 5.15 comes from an Einstein-oscillator model of the crystal lattice. While the derivation of Eq. 5.15 is not rigorous, this equation accurately describes the temperature evolution of elastic moduli for a wide range of materials [90, 91, 92].

Now consider a system that undergoes a continuous phase transition as a function of temperature, where the phase transition is characterized by a scalar order parameter, Q . Then in the vicinity of the transition temperature T_c , the Landau theory of phase transitions allows us to write the free-energy density as an expansion of even powers of Q :

$$F(Q, T) = F_0(T) + \frac{1}{2}a_2(T - T_c)Q^2 + \frac{1}{4}a_4Q^4 + \dots \quad (5.16)$$

where a_2 and a_4 are taken to be positive constants.

Now we must consider how the free energy of the system will be affected by strain. The elastic energy density due to strain is given by

$$F_e = \frac{1}{2}c_{ij}\epsilon_i\epsilon_j. \quad (5.17)$$

However, the order parameter may also couple to the strain if allowed by symmetry. Let us defined a coupling term $F_c(Q, \epsilon_i)$. Then the free-energy density for the object under strain is given by

$$F(q, T) = F_0(T) + \frac{1}{2}a_2(T - T_c)Q^2 + \frac{1}{4}a_4Q^4 + \frac{1}{2}c_{ij}\epsilon_i\epsilon_j + F_c(Q, \epsilon_i) + \dots \quad (5.18)$$

The order parameter Q will always take a value that minimizes the free energy. Because of the term F_c , applying an external strain to the material will change the value of Q that minimizes the free energy for a given temperature. This change in the order parameter will, in turn, cause a change in the observed elasticity of the material. In short, we expect to see a change in the measured elasticity in the vicinity of a phase transition, in addition to the typical temperature evolution given by Eq. 5.15. We call this change Δc_{ij} . we can determine the expected form of Δc_{ij} as follows [93]:

$$\Delta c_{ij} = -\frac{\partial^2 F_c}{\partial \epsilon_i \partial Q} \chi^{(\epsilon)} \frac{\partial^2 F_c}{\partial \epsilon_j \partial Q}, \quad (5.19)$$

where

$$\chi^{(\epsilon)} = \left(\frac{\partial^2 F}{\partial Q^2} \right)^{-1}_{\epsilon} \quad (5.20)$$

is the ‘clamped’ susceptibility, i.e. the susceptibility with strain held constant.

Consider the case of linear coupling between strain and order parameter: $F_c = \gamma_i Q \epsilon_i$, where γ_i are constant coefficients. Then

$$\frac{\partial^2 F_c}{\partial \epsilon_i \partial Q} = \gamma_i \quad (5.21)$$

and we find

$$\chi^{(\epsilon)} = \frac{1}{a_2(T - T_c) + 3a_4Q^2}. \quad (5.22)$$

In the absence of strain, the value of the order parameter that minimizes the free energy will be:

$$Q = \begin{cases} 0 & \text{for } T > T_c, \\ \sqrt{\frac{a_2(T_c - T)}{a_4}} & \text{for } T < T_c. \end{cases} \quad (5.23)$$

This leads leads to

$$\chi^{(\epsilon)} = \begin{cases} \frac{1}{a_2(T - T_c)} & \text{for } T > T_c, \\ \frac{1}{2a_2(T_c - T)} & \text{for } T < T_c, \end{cases} \quad (5.24)$$

and therefore

$$\Delta c_{ij} = \begin{cases} -\frac{\gamma_i \gamma_j}{a_2(T-T_c)} & \text{for } T > T_c, \\ -\frac{\gamma_i \gamma_j}{2a_2(T_c-T)} & \text{for } T < T_c. \end{cases} \quad (5.25)$$

Note that if either γ_i or γ_j are zero, c_{ij} will have no response at the phase transition. This is vital, because for a given order parameter Q , only certain non-zero γ_i will be allowed by symmetry. The free-energy density has to be symmetric under all of the symmetry operations of the object it describes. This includes crystallographic symmetries but also time-inversion symmetry, gauge symmetry, and more. For the case of linear coupling between strain and order parameter, this means that γ_i must be zero unless ϵ_i and Q belong to the same irreducible representation of the crystallographic point group. This type of symmetry consideration is vital in the elasticity analysis of RUS data, as we will demonstrate in Sec. 8.4.1.

By use of Eq. 5.19, we also find that [93]

$$F_c = \gamma_{ij} Q \epsilon_i \epsilon_j \quad (5.26)$$

leads to

$$\Delta c_{ij} = 2\gamma_{ij} Q, \quad (5.27)$$

while

$$F_c = \gamma_i Q^2 \epsilon_i \quad (5.28)$$

results in

$$\Delta c_{ij} = \begin{cases} 0 & \text{for } T > T_c, \\ -\frac{\gamma_i \gamma_j}{2a_4} & \text{for } T < T_c. \end{cases} \quad (5.29)$$

The responses for these simple forms of $F_c(Q, \epsilon_i)$ are illustrated in Fig. 5.3.

Note that for the above calculations, we have specifically considered a second-order phase transition with a single scalar order parameter. More general versions of Eq. 5.18 and Eq. 5.19 exist [93], but we will not employ them in this work.

Any elastic response to a phase transition, such as those shown in Fig. 5.3, will appear in addition to the smooth evolution in temperature described by Eq. 5.15.

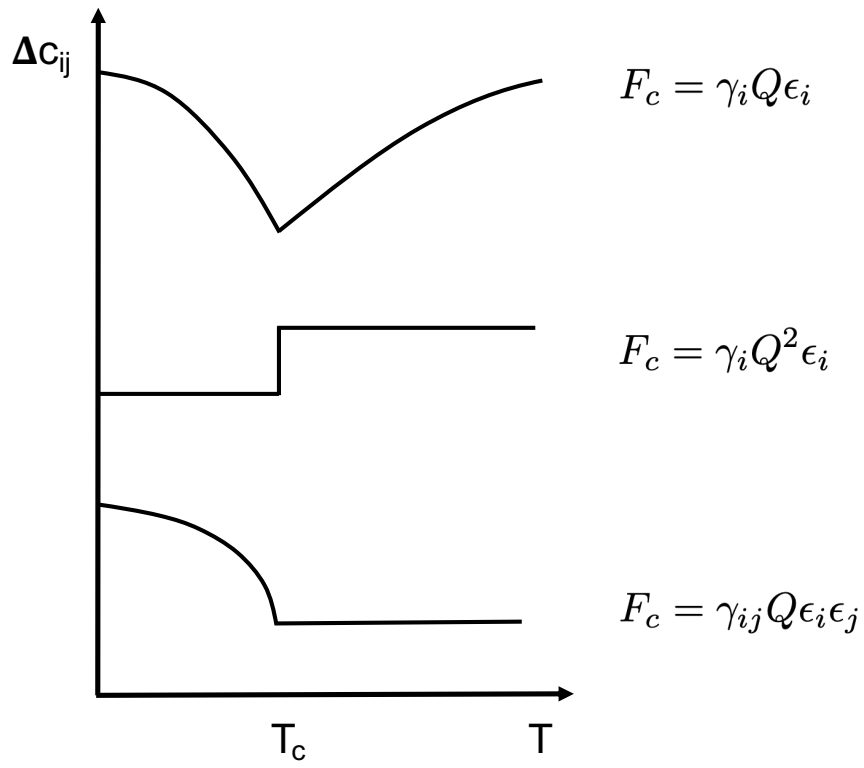


Figure 5.3: The expected change in the elastic modulus c_{ij} due to a second-order phase transition, given various forms of coupling between the order parameter and strain.

Chapter 6

Experimental technique and data analysis

6.1 Experimental setup

The core of an RUS experiment is the ability to vibrate a sample at varying frequencies and the ability to measure the sample’s response to those vibrations. In our setup, this is accomplished through the use of piezoelectric transducers.

We use lithium niobate transducers from Boston Piezo-Optics [94] plated with gold electrodes in a tab-coax configuration, as shown in Fig. 6.2(d). By creating a voltage difference between opposite faces of the disc, we cause the transducer to expand or contract due to its piezoelectric nature. Conversely, if the disc is compressed along its axis, this will lead to a voltage difference between opposite faces of the disc. The “tab” of gold at the top edge of the transducer wraps around the edge of the transducer disc and connects to the opposite face of the disc. We connect one wire to the “tab” of gold and a second wire to the larger pad. These wires can be used to either create or measure a voltage difference between the faces of the lithium niobate disc.

We control and measure these voltage differences with a Zurich Instruments HF2LI lock-in amplifier [95]; Fig. 6.1 is a simple schematic of the measurement setup. One transducer is connected to the lock-in output and receives an AC voltage signal at a specified frequency, causing the transducer to vibrate at that frequency. This will create vibrations of the sample that compress the opposite transducer, thereby generating an AC voltage at the same frequency as the lock-in output. The output frequency of the lock-in amplifier can be smoothly varied, and the sample response recorded as a function of frequency. When a resonance frequency of the sample is approached, there will be a characteristic response in both the in-phase and quadrature signal, as described in Sec. 5.2.

Ideally, the vibrations of the exciting transducer should only reach the pick-up transducer through the sample itself. To reduce other vibrational pathways, both transducers are mounted on blocks of vibration-damping ceramic foam [96] as shown in Fig. 6.2(c). In

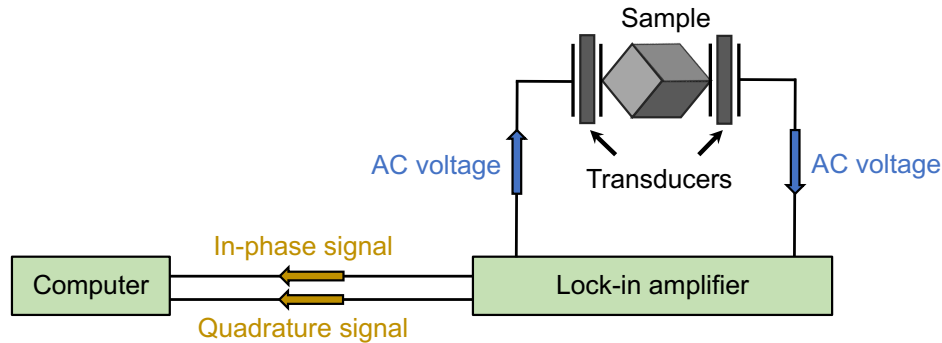


Figure 6.1: A schematic diagram of the experimental setup for gathering RUS data.

this picture, a small crystal is shown held between two lithium niobate transducers, each of which is attached to a block of ceramic foam by epoxy [97]. Each transducer has two small copper wires attached to it by silver epoxy [98]: a ground wire connected to the “tab” gold electrode and a signal wire connected to the larger gold pad. These wires are run through channels in the ceramic foam, then are soldered to coaxial cables that run up to the probe top. The lower block of ceramic foam is fixed in place, while the upper block is attached to a rod that is free to move vertically. This can be seen clearly in Fig. 6.2(b). A condition of RUS measurements is that the sample must be free to vibrate; therefore, the sample is not mechanically attached to the transducers. The only thing keeping the sample in contact with both transducers is the slight weight of the upper foam cube and rod.

The part of our experimental apparatus (or “probe”) that holds the transducers is made of G-10 fiberglass laminate, which damps vibrations more than the stainless steel used for the rest of the probe. The entire probe, held in a ring stand, is shown in Fig. 6.2(a). Besides the two coaxial cables running through the probe for the two lithium niobate transducers, the only other wires in the probe are two twisted pairs leading from the probe top to the sample thermometer. This thermometer is a thin-film resistance temperature sensor [99], visible in Fig. 6.2(c) as a small gold rectangle to the left of the ceramic foam blocks.

In order to gather measurements as a function of temperature, the entire probe is lowered into a helium-flow cryostat [100]. The sample chamber is pumped out, then helium gas is introduced into the cell to provide thermal contact with the sample. Previously, researchers conducting RUS experiments have found that the gas around a sample can provide an unwanted vibrational pathway between the transducers [101]. Therefore, we allow only a small amount of helium gas into the sample chamber. The pressure inside the sample chamber during typical measurements is roughly -28 inHg. The sample thermometer is mounted close by the sample itself, to get as accurate a reading of the actual sample temperature as possible given that the only thermal contact is through the exchange gas.

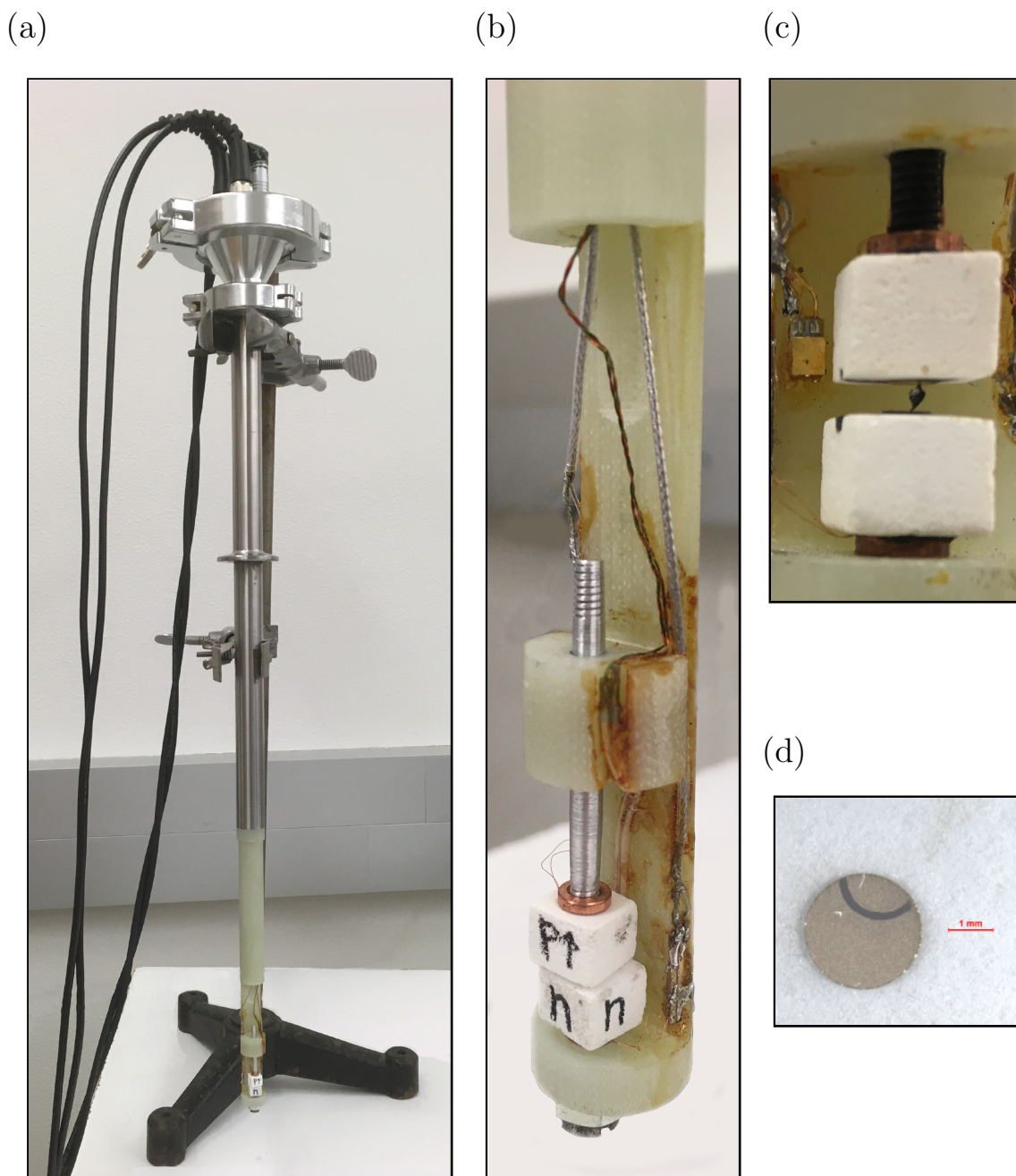


Figure 6.2: Our experimental apparatus for RUS measurements. a) The full RUS probe that is inserted into the flow cryostat. The top is stainless steel and the bottom section is G-10 fiberglass laminate. b) A closer view of the bottom section of the probe, showing that the upper cube of ceramic foam is free to move up and down. c) A crystal is shown mounted between the two lithium niobate transducers, each of which is attached to a cube of ceramic foam. Our temperature sensor is visible to the left of the ceramic cubes. d) One of the lithium niobate transducers used in our RUS measurements, shown with a 1mm scale bar. The transducer is 0.004" thick with a diameter of 0.1". The dark grey crescent on the disc is the lithium niobate itself, the only part not covered by the gold electrodes.

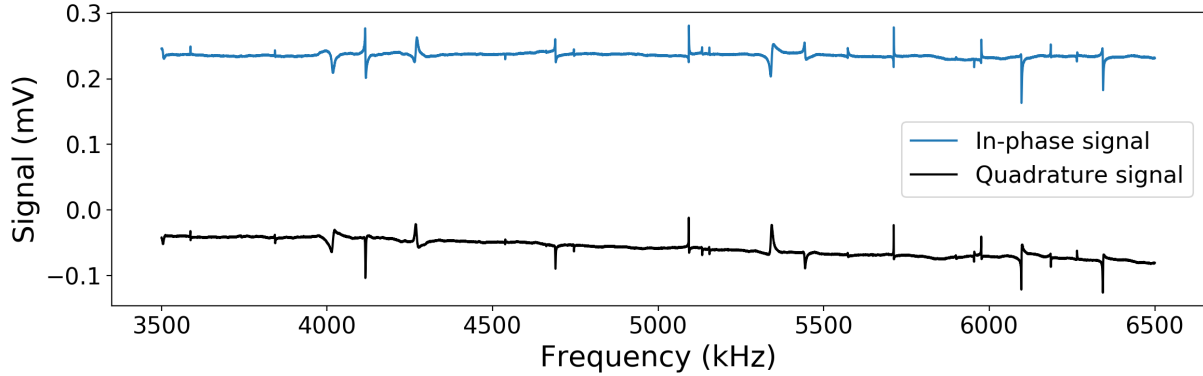


Figure 6.3: The measured RUS signal from a sample of $\text{Fe}_{0.35}\text{NbS}_2$. Data taken at 60 K.

6.2 Fitting resonance frequencies

As derived in 5.2, when the driving frequency f is near a resonant frequency f_0 , we expect a response of the form

$$Z = \frac{A}{f - f_0 + i\gamma/2}, \quad (6.1)$$

, where A is a constant for a given resonance with a given driving force.

Two experimental factors complicate this ideal form. First is the fact that our signal comes on top of a non-zero background, due to resonance responses of the transducers themselves and the rest of the probe. In the vicinity of a resonance, we can use a Taylor expansion to approximate this background to be a constant plus a linear component. Secondly, an arbitrary phase is introduced to the response due to phase shifts in the cables and transducers [102]. Therefore, when fitting a single resonance in our RUS data, we actually use the form

$$Z(f) = Z_0 + Z_1(f - f_0) + \frac{Ae^{i\theta}}{f - f_0 + i\gamma/2}, \quad (6.2)$$

where Z_0 , Z_1 , and θ are constants that do not give any meaningful information about the sample itself. By performing a least-squares fit of Eq. ?? for a given resonance, we can extract its resonant frequency f_0 , full-width half maximum γ , and amplitude A . An example of the RUS data obtained from a frequency sweep is shown in Fig. 6.3. Nearly two dozen resonances appear in the measured frequency range, each of which is approximately described by Eq. 6.2.

To measure resonances as a function of temperature, we typically do not measure at different fixed temperatures. Rather, we slowly vary the temperature while continuously running sweeps of the driving frequency, such that the temperature change during a given frequency sweep is a fraction of a Kelvin. This allows for much faster data collection, although it does increase the uncertainty in temperature. Extracting the exact temperature of a phase transition is not our goal, so this trade-off is acceptable.

In order to track the changes in a resonance's frequency and width as a function of temperature, we go through the initial frequency sweep of the sample and manually select the regions containing Lorentzian responses¹. Our software performs a least-squares fit to Eq. 6.2 in these regions and extracts the initial resonant frequency, width, and amplitude for each resonance. For a given resonance, our peak-tracking software then uses these parameters as initial parameters for a fit of Eq. 6.2 in the subsequent frequency sweep. For each resonance, the software uses a fitting region that is centered around the previous resonant frequency with a fitting window proportional to the resonance width. The program then uses the fit parameters from this sweep as initial fit parameters for the following frequency sweep, and so on through the whole data set. As long as the temperature change is gradual enough, the parameters of the resonance response only change by a small amount from one frequency sweep to the next, so this type of iterative tracking works well. It is possible to run such a tracking program during data acquisition [87], in which case it can be used to sweep frequency in much smaller steps near expected resonances. This is more efficient for data collection but comes with a higher risk of losing track of peaks if they shift too much from one sweep to the next. In this work, we have employed the simpler method of tracking resonances after data collection for a full temperature sweep is done.

Tracking resonant frequencies as a function of temperature gives meaningful information about a sample on its own. As we will see in Sec. 6.3, the frequency of a given resonance is proportional to combinations of the elastic moduli. Therefore, a given frequency can respond to phase transitions in roughly the same manner as an elastic modulus would. By tracking resonance frequencies as a function of temperature, we can observe any phase transition that has an order parameter that couples to strain. Moreover, based on the qualitative response of the frequencies at the phase transition, we can determine the nature of that coupling, as shown in Fig. 5.3. We will make use of this connection in much of our data analysis in Ch. 7 and Ch. 8.

However, even more information can be gleaned by analyzing the elasticity of a sample and how the elements of this tensor change as a function of temperature. By performing this analysis, it is possible to determine the symmetry of the order parameter itself, which places strong constraints on the nature of the ordered phase.

An object's resonant frequencies can be calculated directly if its shape and size, density, and elasticity tensor are known. This is referred to as the “direct problem” or “forward problem,” in contrast to the “inverse problem” of calculating elasticity given an object's resonant frequencies. The inverse problem can not be solved analytically; rather, it relies on repeatedly solving the forward problem with various inputs.

¹This initial peak-finding can also be accomplished through a machine learning algorithm, but the algorithm is not yet as accurate as human analysis

6.3 The forward problem

An efficient procedure for solving the forward problem is described in detail in Ref. [101]. We will outline this method below.

Consider an object that is free to vibrate and has density ρ . If we assume the displacement vector, $\mathbf{u}$, for any point in the object is changing with angular frequency ω as a function of time, then the object's kinetic energy density will be

$$KE = \frac{1}{2} \rho \omega^2 u_i^2. \quad (6.3)$$

Meanwhile, the potential energy density will be

$$PE = \frac{1}{2} c_{ijkl} \frac{\partial u_i}{\partial x_j} \frac{\partial u_k}{\partial x_l}. \quad (6.4)$$

The Lagrangian of the system is then

$$\mathcal{L} = \int_V (KE - PE) dV, \quad (6.5)$$

where we are integrating over the volume of the object.

It can be shown that by minimizing the Lagrangian, we find the sets of u_i that correspond to normal modes of the system, each with an associated resonant frequency $f_i = \frac{\omega_i}{2\pi}$ [101]. In order to solve for the values of ω numerically, it is necessary to use the Rayleigh-Ritz method and expand u_i in a complete set of basis functions $\{\Phi_\lambda\}$:

$$u_i = a_{\lambda i} \Phi_\lambda. \quad (6.6)$$

Then, as derived in Ref. [101], we can solve for the resonances frequencies by solving the following eigenvalue equation:

$$\omega^2 \mathbf{E} \mathbf{a} = \mathbf{\Gamma} \mathbf{a}, \quad (6.7)$$

where we define the matrices $\mathbf{E}$ and $\mathbf{\Gamma}$ as follows:

$$\begin{aligned} E_{\lambda i \lambda' i'} &= \delta_{ii'} \int_V \Phi_\lambda \rho \Phi_{\lambda'} dV, \\ \Gamma_{\lambda i \lambda' i'} &= c_{ij i' j'} \int_V \frac{\partial \Phi_\lambda}{\partial x_j} \frac{\partial \Phi_{\lambda'}}{\partial x_{j'}} dV. \end{aligned} \quad (6.8)$$

As in Ref. [101], we use the basis functions

$$\Phi_\lambda = x^l y^m z^n \quad (6.9)$$

where each basis function is labeled by $\lambda = (l, m, n)$, a set of three non-negative integers. In order to solve Eq. 6.7, we have to use a finite set of basis functions. We limit our set

of basis functions by the condition $l + m + n \leq N$. Then the number of basis functions is $R = 3(N + 3)(N + 2)(N + 1)/6$ and $\mathbf{E}$ and $\mathbf{\Gamma}$ both are matrices of order R . Increasing N makes the eigenvalue calculations more accurate but also increases the computing time. We have used $N = 12$ for the elasticity results in Sec. 8.4.1.

From Eq. 6.7 and Eq. eq:RUSmatrices, we can see that each resonant frequency of the system, $f = \frac{\omega}{2\pi}$, will generally depend on multiple elastic moduli. We can also see that it will be proportional to each elastic modulus as $f^2 \propto c_{ijkl}$. All of the changes in elastic moduli described in the previous chapter—including the typical changes with temperature and the response to a phase transition—are therefore expected in plots of f^2 vs. T as well. They may not follow the exact mathematical formulas that the elastic moduli do, as each resonant frequency squared will depend on linear combinations of the elastic moduli. However, the qualitative behavior of the elastic moduli will be reflected in the resonant frequencies. Because of this, we can draw useful conclusions from RUS data even when the elasticity tensor can not be determined.

Note that calculating the matrix elements in Eq. 6.8 requires performing integrals over the sample volume. It is possible to perform this type of integration for irregularly-shaped samples, for example by using the finite element method [103]. However, this is much more computationally expensive than standard numerical integration and requires a detailed three-dimensional model of the sample. Therefore, when analyzing elasticity it is usually desirable to measure a sample with a simple geometric shape, such as a cylinder or a rectangular parallelepiped.

6.4 The inverse problem

The inverse problem cannot be solved analytically. Rather, the method to find the elasticity tensor is as follows:

1. Define a figure of merit:

$$F = \sum_i w_i (f_i - g_i)^2, \quad (6.10)$$

where $f_i = \omega_i/2\pi$ is the i th calculated frequency from the forward problem, g_i is the i th experimentally measured resonant frequency, and w_i is a weighting factor. Typically $w_i = 1/g_i^2$ so that F reflects the fractional difference between calculated and measured frequencies, but w_i may be set to 0 if the frequency of the i th resonance is not experimentally well-determined.

2. Solve the forward problem using an initial guess for the input parameters and calculate the resultant figure of merit. The input parameters include the elastic moduli, and may also include the sample dimensions if these are not known precisely.
3. Use some method to iterate to a new guess for the input parameters, such that the figure of merit is decreased.

4. Repeat until convergence is achieved. The convergence condition may be a threshold value of F , a threshold value for the amount F is changing with each iteration, or similar.

Note that any minimum found through this type of procedure may be a local minimum, rather than a global minimum, in parameter space. When choosing the initial guess of parameters and the iteration procedure, it is important to make an effort to avoid local minima.

This type of minimization problem arises often, in many different contexts. As such, there are many different algorithms that can be applied to iterate new guesses for the elastic moduli. We have used several of these different methods in our data analysis; we will describe these methods below.

The most commonly-used method for solving the inverse problem in RUS analysis is the Levenberg-Marquardt algorithm, which is laid out in detail in Ref. [101]. The essence of this algorithm is to calculate a numerical gradient of F with respect to the input parameters. When far from the minimum, i.e. when F is large, the method of gradient descent is used: each step in parameter space will be in the direction opposite to the gradient of F . On the other hand, when F is small the algorithm uses Gauss-Newton minimization, which relies on the input parameters being close to the location of the minimum.

Following the method of Ref. [101], we have written software that uses the Levenberg-Marquardt algorithm (LMA) to solve the inverse problem. The user interface of the software is written in python; the most computationally expensive functions, including solving Eq. 6.7, are written in Fortran. The python module `f2py` is used to connect the Fortran code to the user-friendly python program.

A shortcoming of the LMA is that it requires a reasonable initial guess of parameters in order to converge on a global minimum. However, elastic moduli for different materials can range over several orders of magnitude. If the material being studied, or a closely related substance, has not previously had its elasticity experimentally characterized, coming up with a reasonable initial guess can be difficult.

Particle swarm optimization (PSO) is a minimization method that does not rely on an initial guess of parameters. Instead, only constraints on the upper and lower limits for each parameter must be given. The PSO algorithm involves a “swarm” of guesses for the parameters; each guess is thought of as a “particle” in parameter-space. Each particle also starts with a random “velocity” in parameter-space that determine its value for the next iteration. The figure of merit is first evaluated for each particle. Then, based on a combination of the lowest F found by the swarm overall and the lowest F a given particle has found, every particle in the swarm updates its velocity. The particles then each update their positions in parameter space according to their velocity. The process repeats until convergence is achieved. We have built on an existing python PSO module called `pyswarm` [104] to implement PSO for the inverse problem of RUS. We modified `pyswarm` to be fully parallelized, so that the figure of merit for each “particle” could be evaluated independently. This allowed the code to run efficiently across multiple computing cores. All of the PSO

calculations for this work were run on the supercomputing systems of the National Energy Research Scientific Computing Center, a U.S. Department of Energy Office of Science User Facility at Lawrence Berkeley National Laboratory.

6.4.1 Missing modes

One major obstacle in solving the inverse problem is the issue of missing modes. We have defined our figure of merit in Eq. 6.10 such that the i th measured frequencies is compared to the i th calculated frequency. Now imagine the case in which a resonant frequency of the sample is not seen experimentally—for instance, if the transducer that picks up the sample’s vibrations is close to a node of that resonance. In this case, even if we guess precisely the right values of the elastic moduli, we will find a very large figure of merit. We falsely assume we are finding the difference between all of the f_i and g_i when, for example, we may be finding the difference between every f_i and every g_{i+1} beyond the missing frequency. This is demonstrated in Fig. 6.4.

A simple solution is to match the measured and calculated frequencies not by their order, but by their nearness in values. We have chosen to implement a version of the Munkres assignment algorithm². This is a method for minimizing some defined “cost” in a problem involving the assignment of certain “agents” to “tasks”. In our case, the the “agents” are the measured frequencies and we are trying to assign each one a calculated frequency. We designate a cost for each assignment; then the algorithm minimizes the total cost incurred from all of the measured frequencies. We can define the cost as $|f_i - g_j|$ when the calculated frequency f_i is assigned to the measured frequency g_j : a simple measure of the difference between them. However, we make one small modification to this cost function. We want to allow for the possibility of missing frequencies that were not measured, but we do not want the algorithm to be able to ignore a measured frequency. Therefore, we wish to make the cost exorbitantly high if $j > i$. In this case, we add a penalty to the cost of 10 000 times the highest calculated frequency, ensuring that it is well above the cost of any typical assignment. We used these cost functions and an existing python module [105] to implement frequency assignment in our PSO inverse solver. Recently, it has been shown that the use of the Munkres algorithm in combination with PSO is indeed effective in analyzing RUS data with missing modes [106]. When the Munkres algorithm is used, our figure of merit is no longer given by Eq. 6.10. Instead, we use a version that reflects the Munkres assignments of measured and calculated frequencies:

$$F = \sum_j w_j (f_i - g_j)^2, \quad (6.11)$$

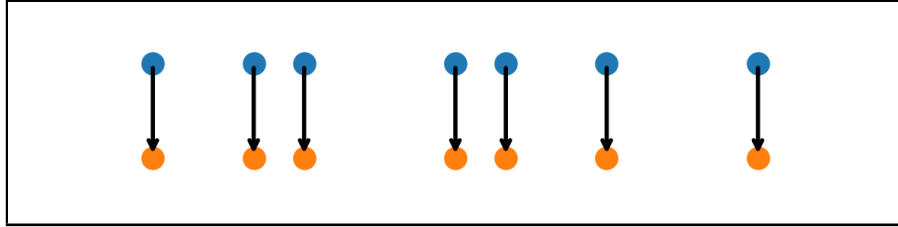
where f_i is the calculated frequency that has been assigned to the given measured frequency g_j .

²The Munkres assignment algorithm is sometimes alternately referred to as the Kuhn-Munkres algorithm or the Hungarian method.

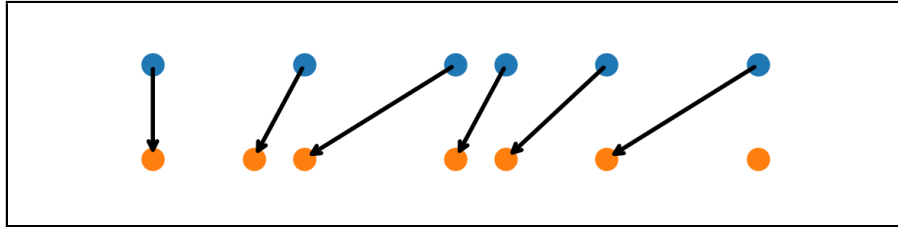
This method of assignment can account for missing modes without the user having to specify where the missing mode might be. If too many missing modes are allowed, the figure of merit may be overly generous even when the measured and calculated frequency spectra are not similar. Therefore, it is important to limit the allowed number of missing modes to a reasonable number. This is easily accomplished by counting the number of calculated frequencies that are in the range of the measured frequencies. If this is above some threshold (e.g, five missing modes) then we revert to using Eq. 6.10 for the figure of merit.

Another method of systematically dealing with missing modes involves a trial-and-error approach, with a maximum number of missing modes specified and the figure of merit calculated for every possible position i of each missing mode [107]. The advantage of the assignment algorithm, in comparison to this approach, is that adding more allowed missing modes or more measured frequencies has a negligible effect on the computation time. With the trial-and-error method, by contrast, the required computing time quickly becomes prohibitive as the number of measured frequencies or missing modes grows.

(a)



(b)



(c)

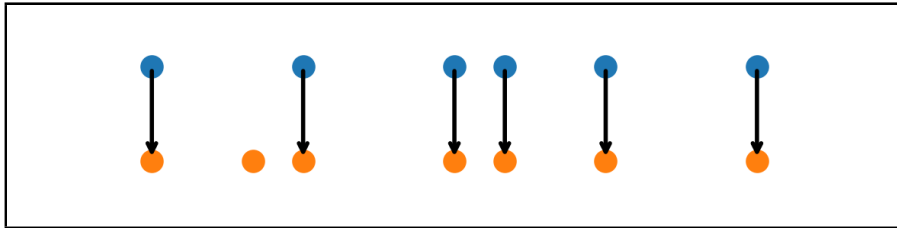


Figure 6.4: An illustration of the use of an assignment algorithm to prevent missing modes from skewing the figure of merit. In each figure, the blue dots represent measured frequencies, the orange dots represent calculated frequencies, and the arrows represent assignment of one to the other. The x -axis represents frequency while the y -axis has no meaning. a) An example with no missing modes, with measured and calculated frequencies matched in order of occurrence (f_1 with g_1 , etc.). In this case, we would find $F = 0$ for the figure of merit. b) As in the previous figure, frequencies are matched in order of occurrence. However, the second measured frequency is missing. In this case, each measured frequency beyond the first is mis-assigned and the figure of merit would be large even though the calculated frequencies are actually correct. c) By using an assignment algorithm, the measured frequencies are matched to the nearest calculated frequencies, and the figure of merit is $F = 0$ as before.

Chapter 7

Study of 100 K behavior in β -Li₂IrO₃

7.1 Introduction to β -Li₂IrO₃

The magnetic honeycomb iridates are a series of polytypes of Li₂IrO₃. The simplest of these is α -Li₂IrO₃, which is composed of two-dimensional layers of honeycombs of edge-sharing IrO₆ octahedra. There is a Li atom in the center of each honeycomb, and these honeycomb layers are alternated with layers of pure hexagonal Li [108]. The other polytypes of Li₂IrO₃ are variations on this structure, but with twists in between the bonds connecting the IrO₆ octahedra. The compound β -Li₂IrO₃ is often called the “hyperhoneycomb” structure, as it does not contain any actual hexagons of IrO₆ octahedra. As shown in Fig. 7.1 the bonds between octahedra still are at the angle of a hexagonal lattice, but due to the twists in bond direction no full hexagon is formed.

All of these polytypes of Li₂IrO₃ involve edge-sharing IrO₆ octahedra, which provide a microscopic mechanism for anisotropic Kitaev magnetic interactions [111]. There are three different possible directions of the bonds between IrO₆ octahedra. The edge-sharing bonding between octahedra leads to an anisotropic spin interaction between neighboring Ir atoms, where they primarily interact through the spin component that is normal to the Ir-O₂-Ir plane [111]. In other words, the component of spin involved in spin-spin interactions for two Li atoms depends on the direction of the Li-Li bond. In these systems, the combination of crystal-field splitting and spin-orbit coupling leads each Ir atom to have an effective total angular momentum of $J_{\text{eff}} = 1/2$.

Consider a two-dimensional honeycomb of spins, each with spin-1/2. If we categorize the three different types of bond direction in the honeycomb as x -links, y -links, and z -links, then the Hamiltonian for an ideal Kitaev system is [112]

$$\mathcal{H} = -J_x \sum_{x\text{-links}} \sigma_j^x \sigma_k^x - J_y \sum_{y\text{-links}} \sigma_j^y \sigma_k^y - J_z \sum_{z\text{-links}} \sigma_j^z \sigma_k^z \quad (7.1)$$

where J_x , J_y , and J_z are coupling strengths and j and k indicate spin sites connected by the specified links. The Kitaev Hamiltonian is exactly solvable: the spins in the system

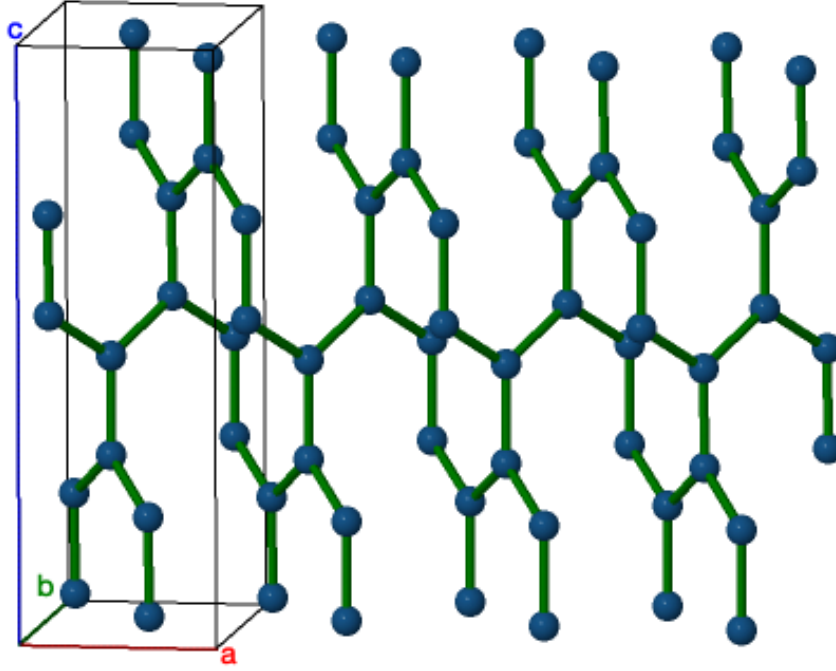


Figure 7.1: The crystal structure and structural unit cell of β - Li_2IrO_3 . This simplified view shows only the Ir atoms (blue balls), each of which is octahedrally coordinated with oxygen. The Ir atoms form chains along the c -axis, with rows of half-hexagons alternately in the $a \pm b$ directions. Structural data taken from Ref. [109] and visualized using Jmol [110].

become fractionalized into Majorana fermions and form a quantum spin liquid (QSL) [112]. The three-dimensional Kitaev model on the hyperhoneycomb lattice has also been shown to have a QSL ground state [113]. It is worth noting that the b -axis of β - Li_2IrO_3 is one of the cardinal directions of the Kitaev Hamiltonian: Kitaev exchange along the c -axis bonds should involve precisely the component of spin that points along the b -axis [114]. Therefore, in the sense of Kitaev interactions, the b -axis of β - Li_2IrO_3 is special.

Experimental measurements of β - Li_2IrO_3 , including resonant magnetic x-ray scattering, have shown that it has a rich phase diagram [114]. Most notably, in the absence of a magnetic field the compound enters an incommensurate magnetically ordered state below 38 K. The presence of long-range magnetic order indicates that β - Li_2IrO_3 is not a Kitaev QSL. One possible explanation for this is that the IrO_6 octahedra are slightly distorted in β - Li_2IrO_3 , which could modify the Kitaev interactions and lead to additional spin-interaction terms in the Hamiltonian [115]. Although it is not a Kitaev QSL, β - Li_2IrO_3 still hosts Kitaev interactions and may exhibit signatures of the Kitaev model above its magnetic ordering temperature of 38 K.

Notably, β - Li_2IrO_3 undergoes a subtle magnetic phase transition at roughly 100 K [116].

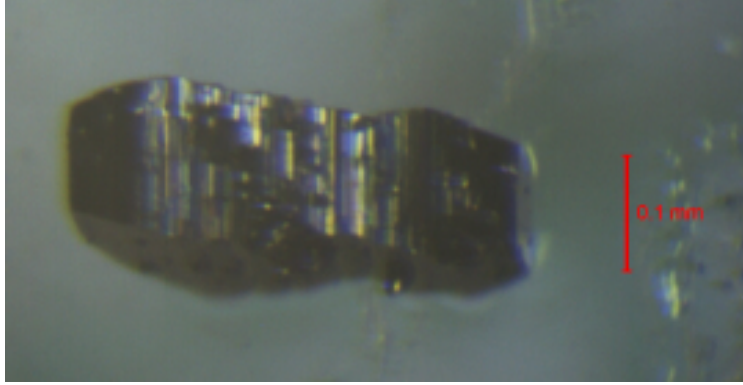


Figure 7.2: The largest crystal of β - Li_2IrO_3 measured in this work, shown with a 0.1mm scale bar.

Below this temperature, the magnetic susceptibility deviates markedly from the expected Curie-Weiss behavior. This feature can only be clearly observed in low magnetic fields, of the order 0.1 T. In measures of magnetization along all three crystal axes, hysteresis also appears below 100 K. Moreover, even in zero field there is a subtle magnetic contribution to the heat capacity of β - Li_2IrO_3 that appears below approximately 100 K, as can be seen through comparison with the nonmagnetic isostructure β - Li_2PtO_3 [116]. At the same temperature as the appearance of these features, β - Li_2IrO_3 undergoes a reordering of its magnetic principal axes. Above 100 K, the largest susceptibility is along the c -axis, while below 100 K, the b -axis susceptibility is dominant [116]. This could be an indication that Kitaev-type interactions begin to dominate at this temperature, given that the b -axis is a cardinal direction for Kitaev interactions in this system.

We have performed RUS measurements on multiple samples of β - Li_2IrO_3 to determine whether any signatures of this phase transition could be observed.

7.2 RUS measurements of β - Li_2IrO_3

The single crystal β - Li_2IrO_3 samples measured in this work were synthesized by Alejandro Ruiz, using the growth method described in Ref. [114]. This material is an electrical insulator and the crystals are shiny, black, and extremely hard and brittle. The as-grown crystals are quite small. We have measured three samples of β - Li_2IrO_3 which we label $\beta 1$, $\beta 2$, and $\beta 3$. The largest sample we measured, $\beta 3$, is shown in Fig. 7.2; it is roughly 400 μm along the c -axis and slightly over 100 microns in the other two dimensions.

One challenge in measuring these samples is their tendency to chip. The vibrations of the driving transducer can cause small cracks to appear, or even cause fragments of the crystal to break off. This change in shape and volume will cause an abrupt change in the resonant frequencies of the sample. An example of this occurring in the sample $\beta 1$ is shown in Fig. 7.3. The change shown in this figure is roughly 50 kHz, or roughly 0.25% of the

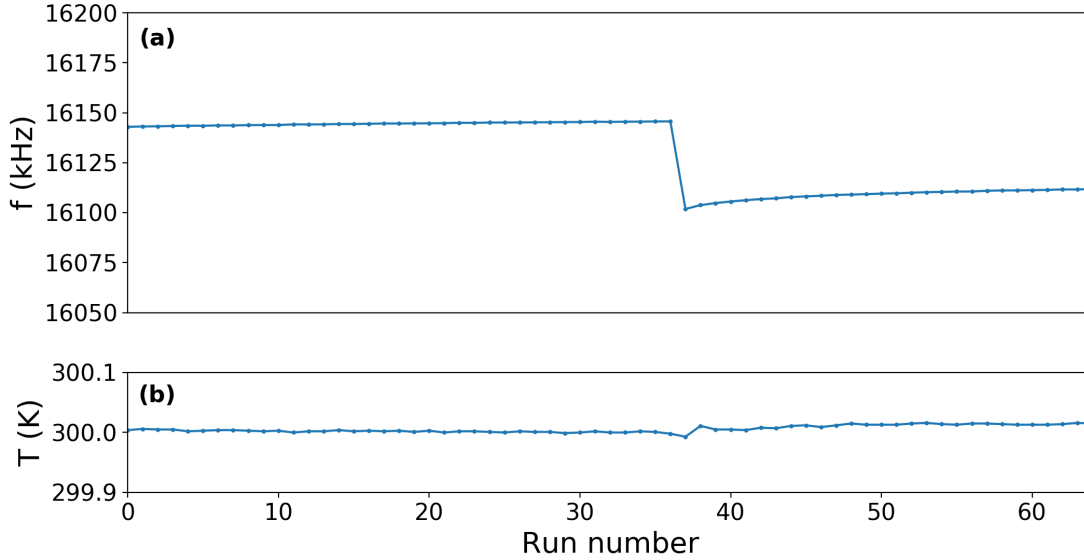


Figure 7.3: The top panel shows the frequency of a resonance as measured in successive frequency sweeps, while the bottom panel shows the temperature at which each measurement was taken. Even though the sample is held at constant temperature, after successive measurements the frequency of the resonance abruptly changes. This is attributed to the sample being damaged by the exciting vibrations, forming a small chip or crack.

initial frequency. As can be seen from Fig. 7.4(b), a change of frequency by 0.25% is quite large and could not be due to a modest fluctuation in temperature. The simplest reasonable explanation is that chipping of the sample is occurring.

Because these samples are quite brittle, they chip often. This made it a challenge to collect continuous data sets across broad ranges of temperature. This is, in part, why we only have low-temperature data (below 70 K) for $\beta 3$ and not the other two samples. We have done our best to use data sets that include minimal chipping. When measuring as a function of temperature, the sudden jump in frequencies due to chipping is qualitatively similar to the expected behavior at certain phase transitions, as shown in Fig. 5.3. However, unlike a phase transition, a chipping event would not be replicated when remeasuring in the same temperature range. As none of the frequency jumps we observed when measuring β - Li_2IrO_3 samples were replicable, we attribute them to chipping.

We have performed RUS measurements on three different samples of β - Li_2IrO_3 . We found that every frequency we were able to measure as a function of temperature evolved smoothly through 100 K, following the expected temperature dependence of elastic moduli. At a phase transition that affects elasticity, the resonance width, γ , should have a maximum due to time-dependent fluctuations of the ordered state near the critical temperature [117]. For the resonances we were able to measure, we also see no signature of an increase in γ corresponding to the 100 K magnetic transition.

In addition to plotting the frequency of each resonance (f) and its width (γ), we often find it helpful to plot the fractional change of each resonance as a function of temperature, f/f_{initial} . Here, f_{initial} is the frequency of the given resonance at the beginning of the plotted temperature sweep. This is helpful since the difference in frequencies between successive resonances is much greater than the change in an individual resonance. Plotting f/f_{initial} for several resonances makes it easier to see when the evolution of multiple resonances across a temperature sweep is similar.

7.2.1 Results: $\beta 1$

Fig. 7.4 shows the temperature evolution of three representative resonant frequencies of $\beta 1$ upon warming the sample from 80 K to 180 K. There is no obvious feature near 100 K that would suggest a strain-coupled phase transition.

As noted in Ch. 5, we expect the elastic moduli to evolve with temperature according to

$$c_{ij}(T) = p_1 - p_2/(e^{p_3/T} - 1), \quad (7.2)$$

where p_1 , p_2 , and p_3 are all constants. We also found in Ch. 6 that for a given resonance, the frequency squared will depend on linear combinations of the elastic moduli. Therefore, it is reasonable to expect that the evolution of f^2 with temperature can also be fit to a function in the form of Eq. 7.2.

In Fig. 7.5, we focus on the middle frequency plotted in Fig. 7.4 and attempt a least-squares fit using a function in the form Eq. 7.2. The best fit is shown in Fig. 7.5(b) and agrees well with the data. In Fig. 7.5(c) we plot $100 \times \frac{f^2 - y}{f^2}$, where y is the fit function; this is the percent difference between the frequency squared and the fit to Eq. 7.2. We see that there is no particular deviation from the expected temperature evolution near 100 K. There is a slight feature at roughly 90 K, but this is attributed to a chip in the sample as it was not replicable in further temperature sweeps.

7.2.2 Results: $\beta 2$

Fig. 7.6 shows the temperature evolution of three resonant frequencies of $\beta 2$ as a function of temperature. The data for $\beta 2$ are not as clean as the data for our other two samples, as can be seen in Fig. 7.6(b): the frequency of each resonance appears to wobble as a function of temperature. When finding the frequency and width of each resonance, we rely on being able to fit the resonance signal using Eq. 6.2. This assumes that our measurement background can be described by a constant term plus a linear term. However, when measuring this sample we saw a background with relatively high curvature. This may account for the lack of consistency in the recorded frequency of each resonance. Even so, we can see that there is not a noticeable feature in either the resonant frequencies or resonant widths near 100 K.

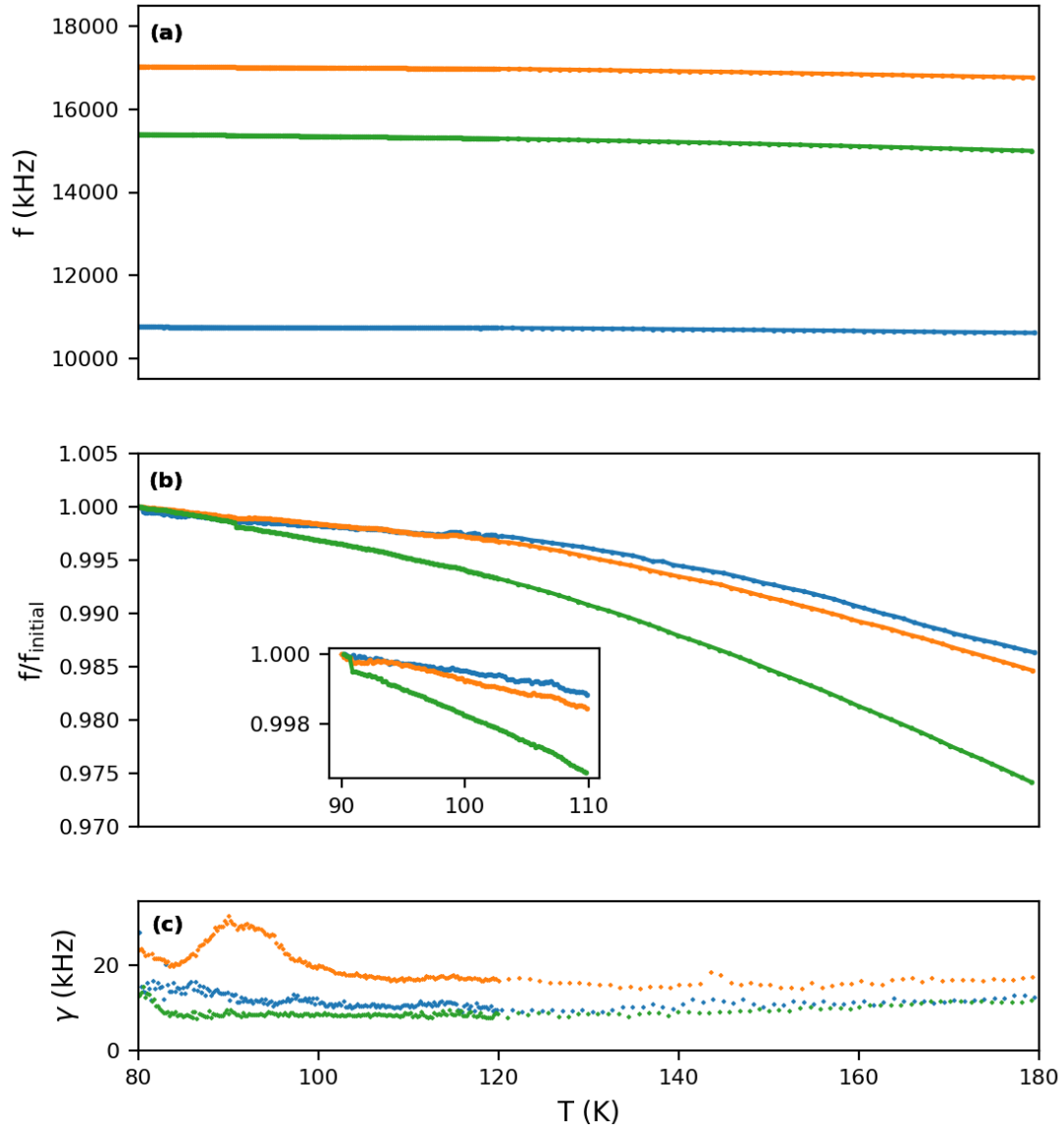


Figure 7.4: Representative RUS data for $\beta 1$. For three resonances we plot a) their frequencies; b) the fractional change in their frequencies; and c) their width, all as a function of temperature. The inset of (b) shows more detail for the data near 100 K.

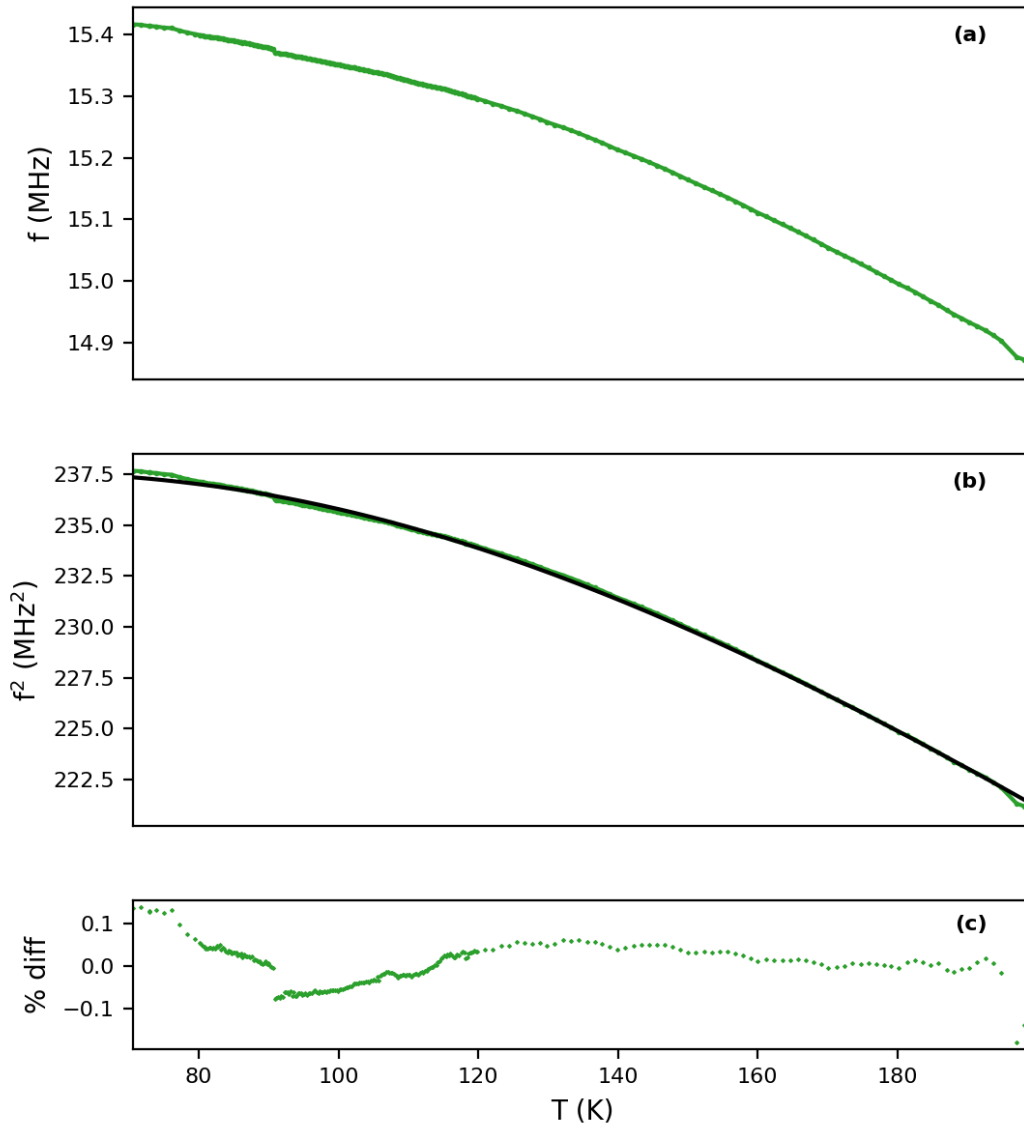


Figure 7.5: a) The temperature evolution of a single resonant frequency of β_1 . b) The squared frequency of the resonance (green) along with the least-squares fit of this data using Eq. 7.2 (black). c) The percent difference between the squared frequency and the least-squares fit, as a function of temperature.

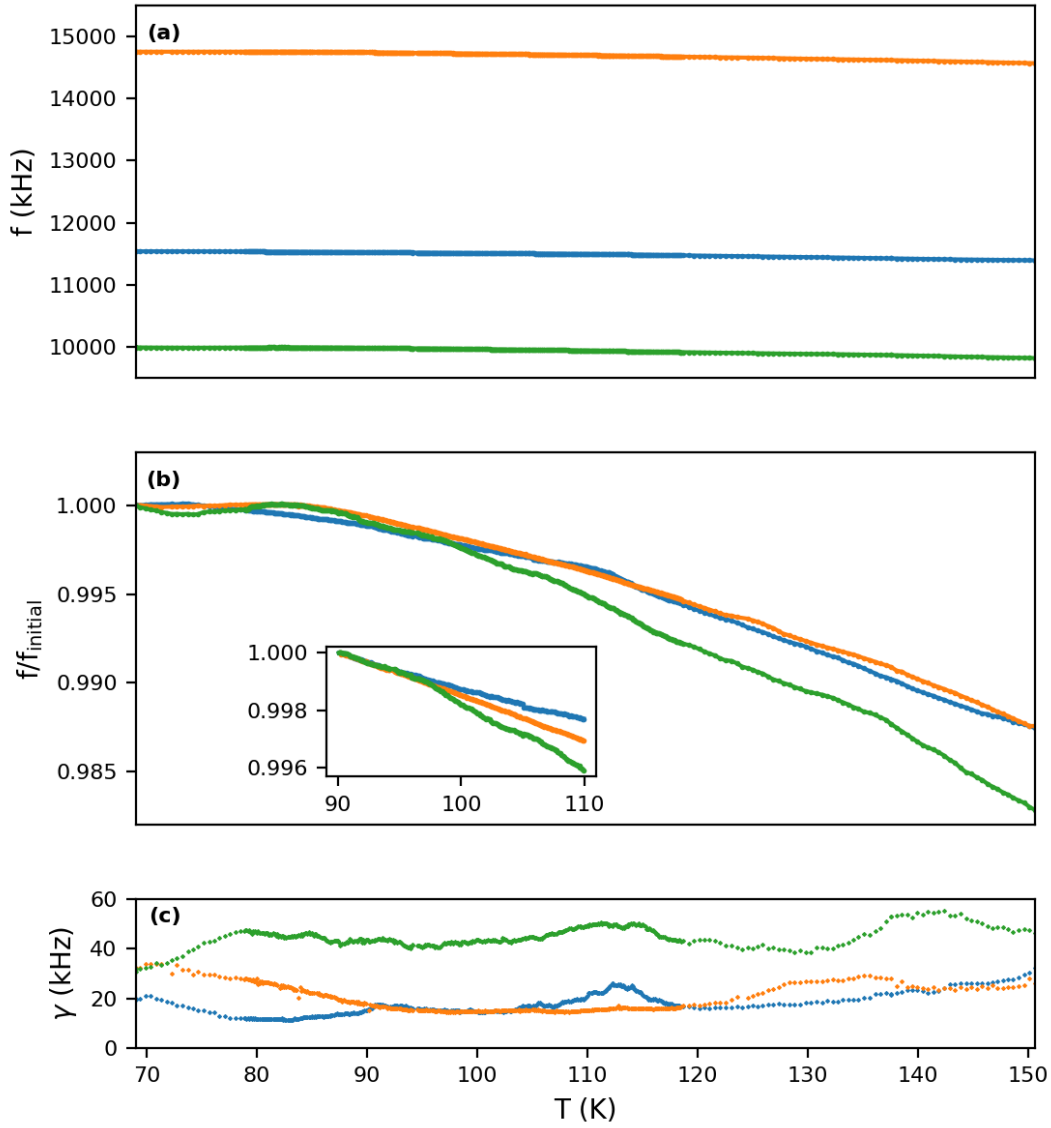


Figure 7.6: Representative RUS data for β_2 . For three resonances we plot a) their frequencies; b) the fractional change in their frequencies; and c) their width, all as a function of temperature. The inset of (b) shows more detail for the data near 100 K.

7.2.3 Results: $\beta 3$

We were able to measure resonances of $\beta 3$ across multiple temperature sweeps, both warming and cooling, and at temperatures down to 5 K. Fig. 7.7 shows the temperature evolution of three representative resonances of $\beta 3$ as a function of temperature, from 90 K to 200 K. As with the previous samples, the resonant frequencies appear to change smoothly through 100 K with no indication of a phase transition and there is not a clear maximum in the resonance widths near 100 K.

Fig. 7.8 shows a fit to the frequency squared of one of these resonances using Eq. 7.2. We see that the best fit agrees extremely well with the data; as shown in Fig. 7.8(c), there is almost no difference between data and fit.

Since we were able to gather data in multiple temperature sweeps of this sample, we can show that the smooth evolution of resonant frequencies through 100 K is highly replicable. In Fig. 7.9, we plot some of the RUS data we collected in the course of seven different temperature sweeps. There are 21 data sets but only 11 distinct resonances shown, since we were able to measure several of the same resonances across multiple warming and cooling cycles. We have plotted the data from 92 K to 108 K, focusing on the region around the 100 K magnetic transition. Once again, we see that the resonant frequencies are evolving as expected with temperature and that there is no feature in the resonant widths near 100 K.

7.3 Discussion and conclusion

There are two different possibilities for the lack of RUS signature for the 100 K magnetic phase transition. The simplest explanation is that the order parameter of this transition does not couple to strain, or couples extremely weakly to the point of undetectability.

The system enters a well-characterized incommensurate magnetic state at 38 K, so it is interesting to compare the resonances' response to this phase transition with the response—or lack thereof—at 100 K. Unfortunately, our low-temperature measurements are of poorer quality due to thermal contraction of the probe, which led to weak contact between the sample and transducer. However, we do have data down to roughly 5 K, as shown in Fig. 7.10. There does appear to be a slight dip in several of the resonances at roughly 38 K, but it is not much greater than other dips in the resonances at other temperatures. Furthermore, there does not appear to be any accompanying maximum in the resonance widths. In Fig. 7.11, we show that the frequency squared of a resonance does deviate from the expected temperature evolution at roughly 38 K; however, there is a deviation of similar magnitude at roughly 180 K, where no magnetic order exists. Therefore, it seems likely that this deviation is due to poor measurement quality rather than an actual elastic response of the system. We can conclude that there is either no elastic response or a weak elastic response to the onset of the incommensurate magnetic phase.

The magnetic behavior of β -Li₂IrO₃ is driven by the electrons that occupy the *d*-orbitals [115]. If the magnetic ordering of these electrons at 38 K does not noticeably influence the

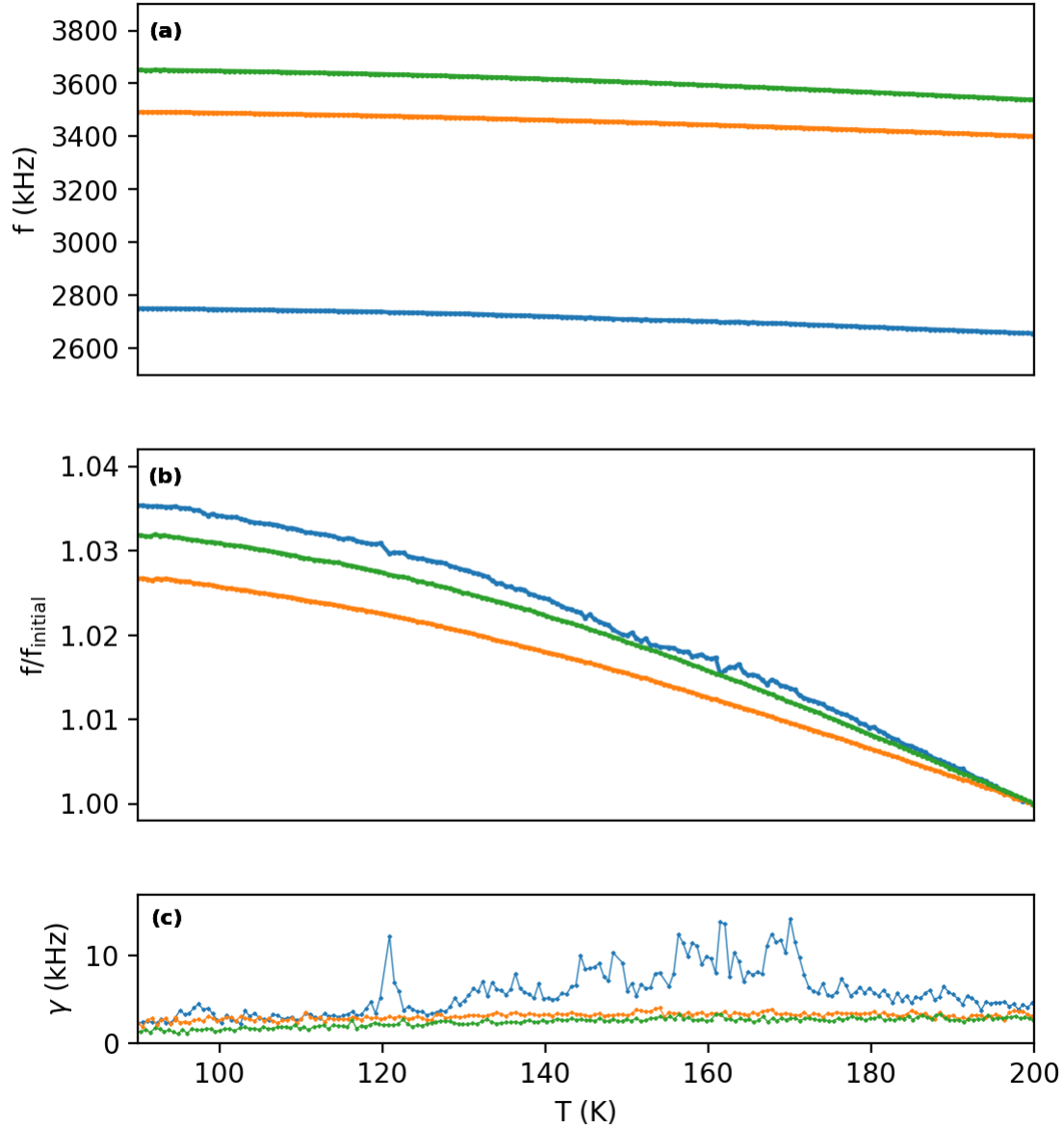


Figure 7.7: Representative RUS data for $\beta 3$. For three resonances we plot a) their frequencies; b) the fractional change in their frequencies; and c) their width, all as a function of temperature. Note that this data was taken while cooling, so f_{initial} is the frequency of each resonance at 200 K.

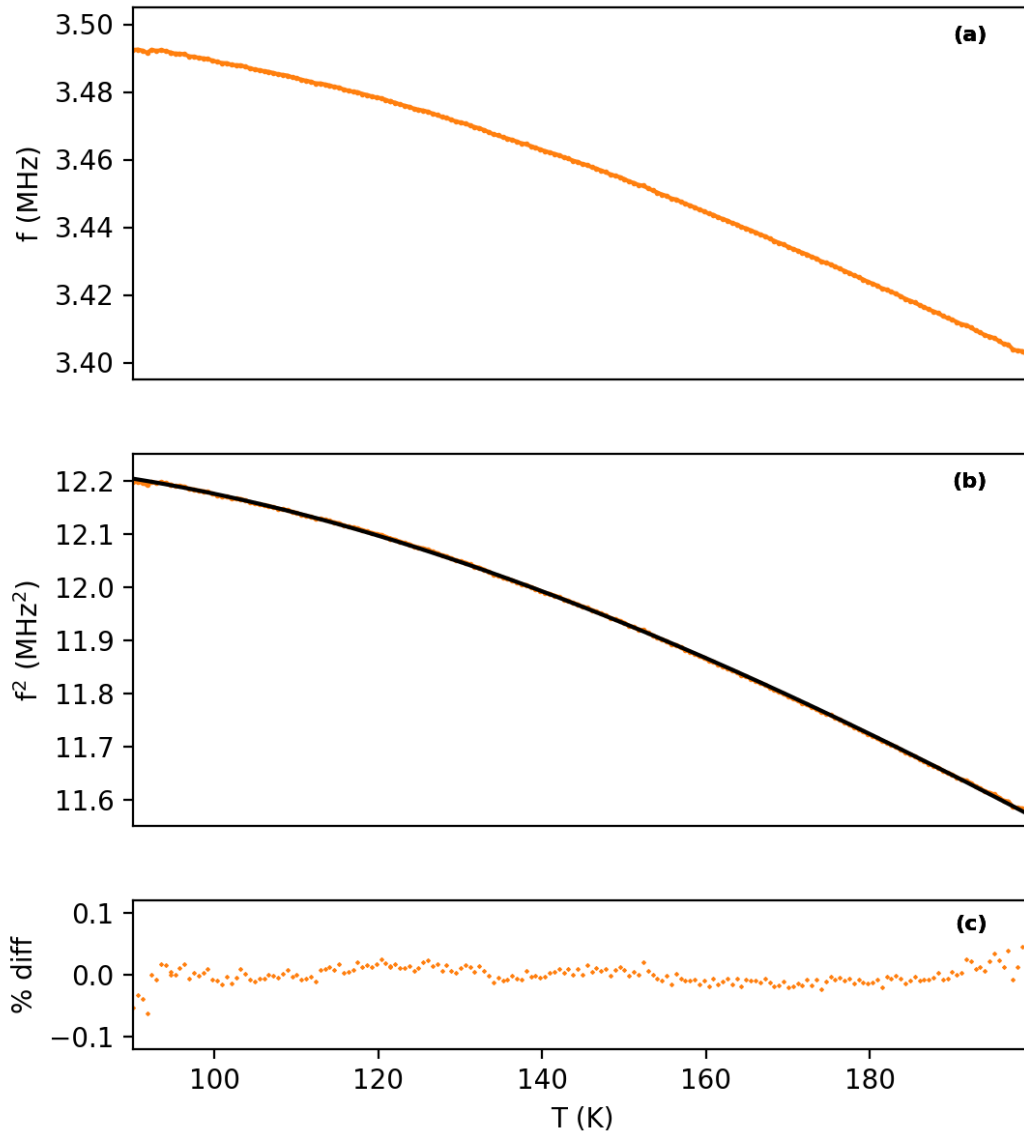


Figure 7.8: a) The temperature evolution of a single resonant frequency of $\beta 3$. b) The squared frequency of the resonance (orange) along with the least-squares fit of this data using Eq. 7.2 (black). c) The percent difference between the squared frequency and the least-squares fit, as a function of temperature.

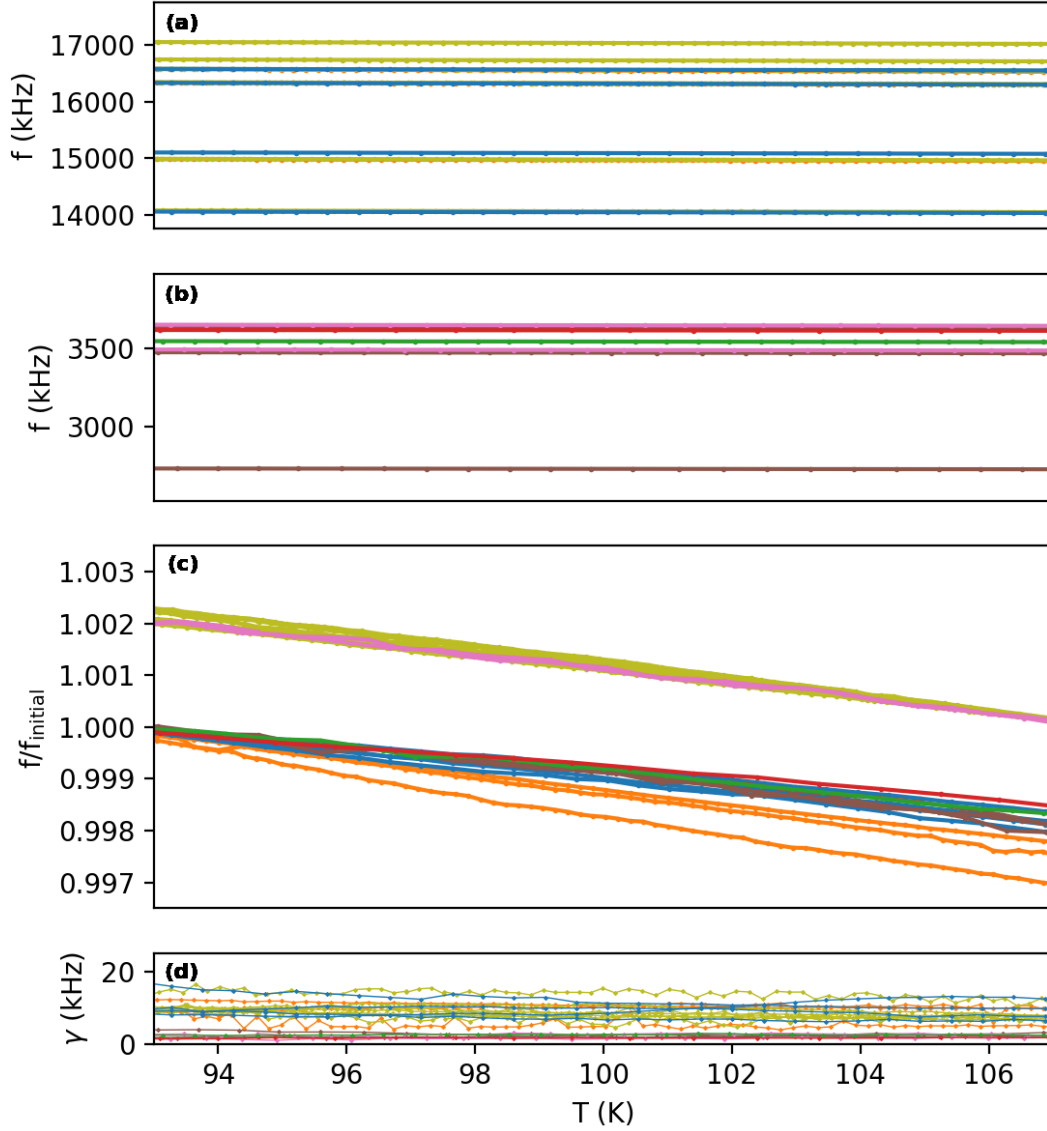


Figure 7.9: RUS data for 11 distinct resonances of $\beta 3$. For the resonances measured in each temperature sweep, we plot a)–b) their frequencies; c) the fractional change in their frequencies; and d) their width, all as a function of temperature. Data of the same color are from the same temperature sweep. We have separated (a) and (b) into two subplots due to the large difference in frequency between the lowest and the highest resonances measured. Note that for data taken while cooling, f_{initial} is the frequency of each resonance at 108 K; for data taken while warming, f_{initial} is the frequency of each resonance at 92 K.

elasticity of the system, they must not influence the mechanical bonding of the system. This could be an explanation for the lack of RUS signature at 100 K as well.

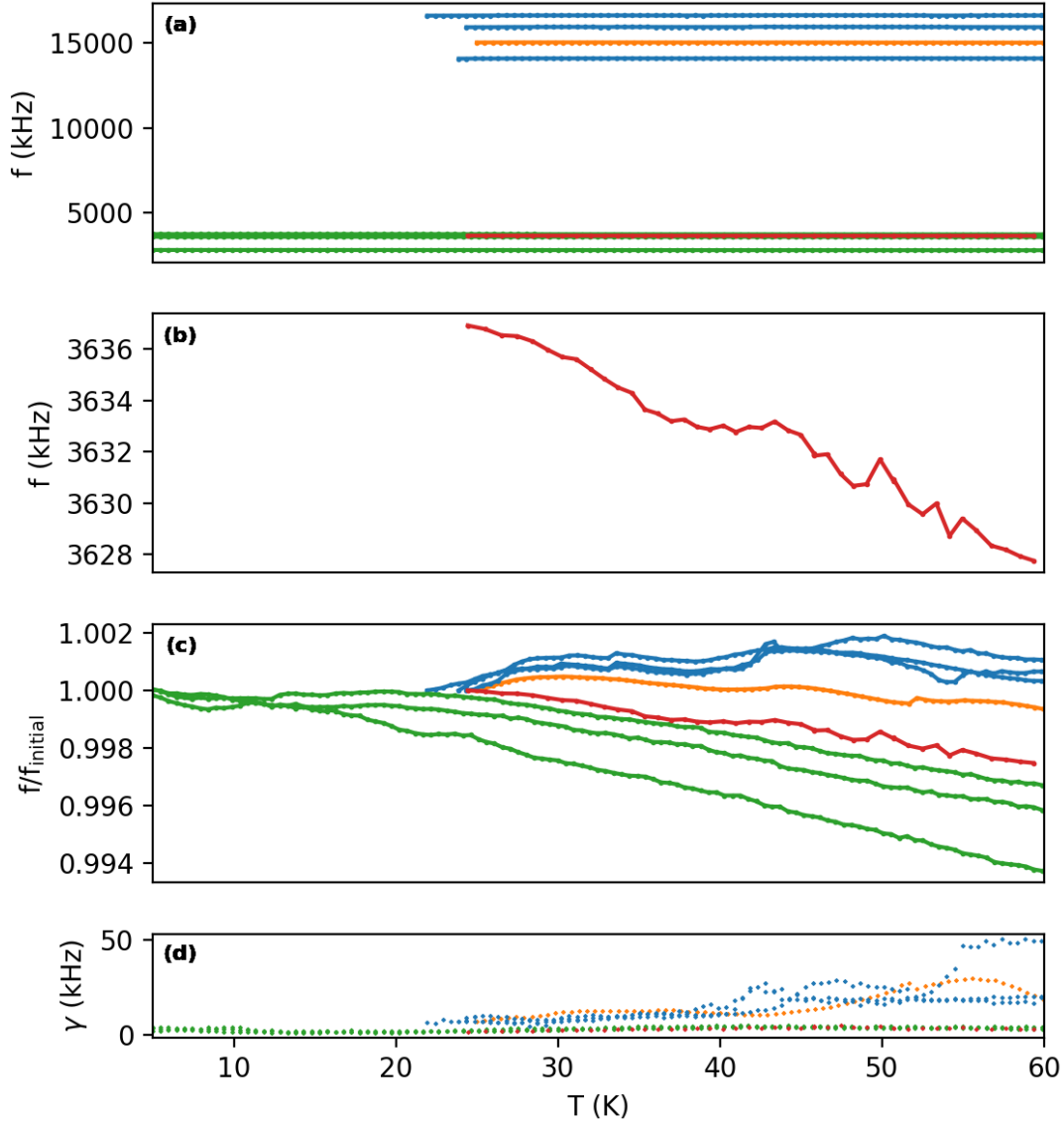


Figure 7.10: Representative low-temperature RUS data for β_3 , taken over the course of four different temperature sweeps. For seven distinct resonances we plot a) their frequencies; c) the fractional change in their frequencies; and d) their width, all as a function of temperature. In subplot b) we show the frequency of one resonance in greater detail. Data of the same color are from the same temperature sweep.

As an alternate explanation, we must keep in mind that absence of evidence is not evidence of absence. We have not determined the elasticity tensor for $\beta\text{-Li}_2\text{IrO}_3$. We have

merely measured a selection of the resonant frequencies of three different sample. Even for β 3, the sample on which we were able to gather the most data, we only gathered clean data for 11 distinct resonances passing through 100 K. Each resonance frequency squared depends on a linear combination of the elastic moduli, c_{ij} . It is possible, though perhaps unlikely, that there is an element of the elasticity tensor of β -Li₂IrO₃ that *does* couple to the order parameter of the 100 K transition, but that the frequencies we measured all have a weak dependence on that particular c_{ij} . As the crystal structure of β -Li₂IrO₃ is orthorhombic [114], it will have nine independent elastic moduli in the absence of magnetic order [89]. The only way to definitively show that none of these nine are affected by the phase transition would be to actually determine the elasticity tensor as a function of temperature. However, as mentioned in Ch. 6, determination of the elasticity tensor typically requires a sample with a simple geometric shape such as a rectangular parallelepiped. For many crystals, this can be achieved through manual cutting and polishing. Due to the small size of as-grown β -Li₂IrO₃ crystals and their brittleness, fashioning a sample into a regular geometric shape would be a difficult undertaking.

We conclude that there is no detectable RUS signature of the 100 K magnetic phase transition in β -Li₂IrO₃. Given this phase's subtle contribution to heat capacity and its disappearance at fields above 0.5 T [116], characterizing the order that drives the phase transition remains a challenge.

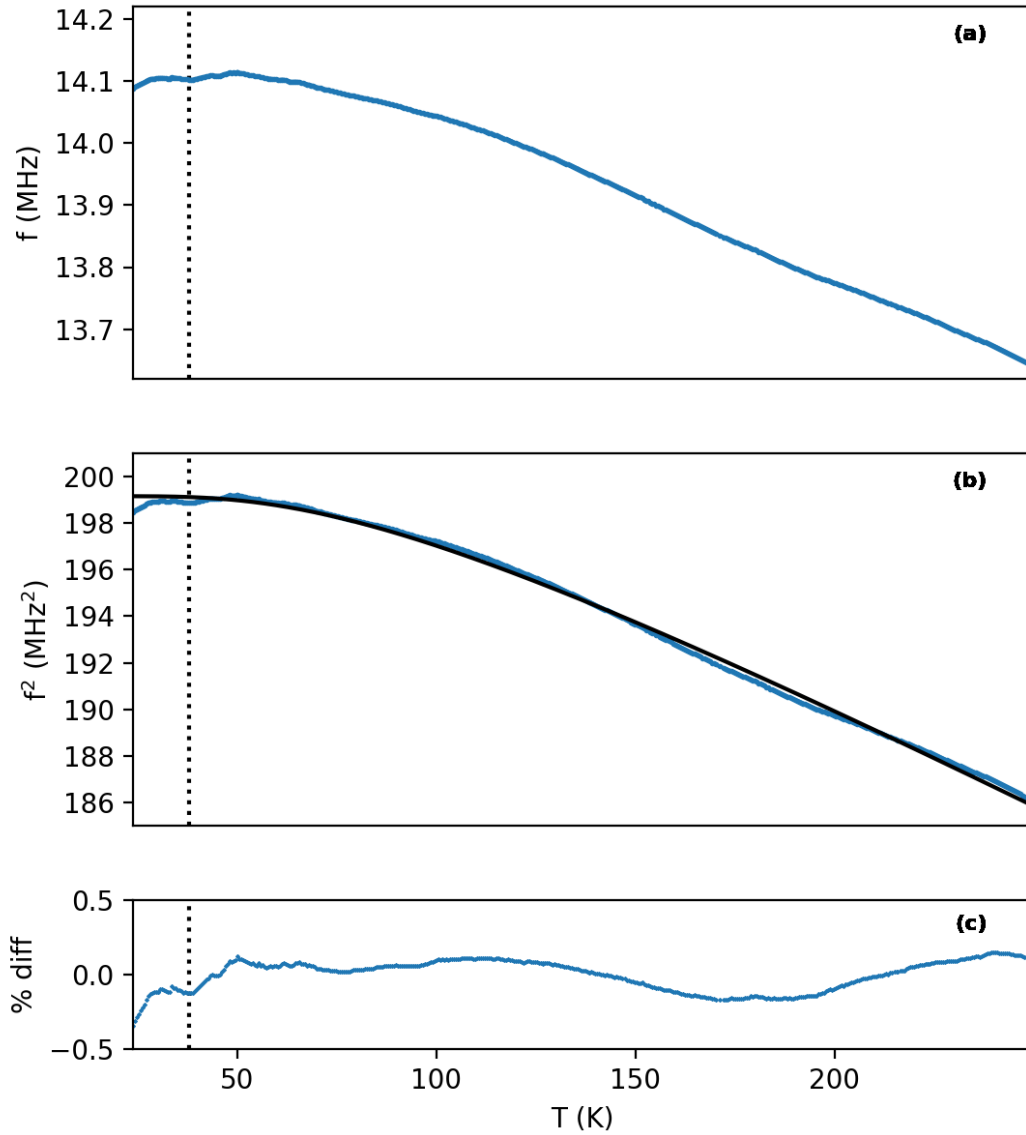


Figure 7.11: a) The temperature evolution of a single resonant frequency of $\beta 3$ down to roughly 24 K. b) The squared frequency of the resonance (blue) along with the least-squares fit of this data using Eq. 7.2 (black). c) The percent difference between the squared frequency and the least-squares fit, as a function of temperature. On all three plots, there is a dashed vertical line at 38 K, indicating the onset of the incommensurate magnetic state.

Chapter 8

Magnetic transitions in Fe_xNbS_2

8.1 Introduction to Fe_xNbS_2

The transition metal dichalcogenide NbS_2 is a hexagonal crystal consisting of two-dimensional layers that are weakly bonded to each other through van der Waals interactions. Bulk crystals are known to exist in two different polytypes, known as 2H and 3R, with different patterns of interlayer stacking. The crystal structure of 2H- NbS_2 is shown in Fig. 8.1. By incorporating iron in between the layers of the 2H phase, it is possible to form a range of materials with the formula Fe_xNbS_2 . When $x = 1/3$, the material forms the stoichiometric compound FeNb_3S_6 . It is also possible to grow crystals of Fe_xNbS_2 with $x < 1/3$ or $x > 1/3$, corresponding to vacancies in the iron sites of FeNb_3S_6 or excess iron between NbS_2 layers, respectively.

These iron-intercalated compounds are of both scientific and technological interest, primarily due to their electrically switchable antiferromagnetic (AFM) order. By applying current pulses to a crystal of Fe_xNbS_2 , it is possible to switch the crystal between a high-

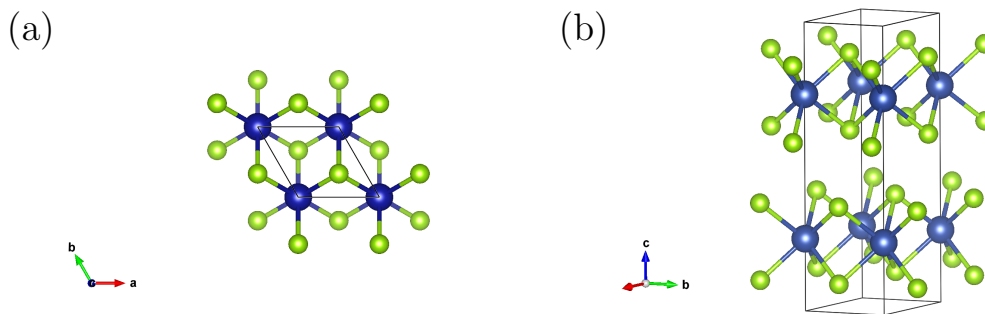


Figure 8.1: The crystal structure of 2H- NbS_2 , as viewed a) along the c -axis and b) from the side. The Nb atoms (blue balls) are each bonded with six S atoms (green balls), forming two-dimensional layers of NbS_2 . The atomic structure was visualized using the software package VESTA [118].

resistance state and a low-resistance state. The mechanism for this switching involves the current pulse reorienting AFM domains in the crystal [119]. Therefore, the resistance can therefore only be switched in the AFM phase, which persists to roughly 45 K (for $x = 0.33$). If it persisted to room temperature, this type of electrically controlled AFM switching could be used as the basis for ultrafast and highly stable memory storage [119]. Understanding the nature of the antiferromagnetism in Fe_xNbS_2 is crucial to determining whether the same switching behavior may be possible at room temperature in a different material.

From measurements of heat capacity and magnetism, we know that crystals with intercalation near the stoichiometric value of $x = 1/3$ undergo two distinct AFM transitions as a function of temperature, one at approximately 44 K and one at roughly 42 K [120]. For crystals with $x = 0.35$, both AFM transitions are still present, though with slightly different transition temperatures than the near-stoichiometric compounds. But in addition to antiferromagnetism, these over-intercalated samples start to freeze into a spin glass state at roughly 15 K. Under-intercalated crystals with $x = 0.31$ also show two AFM transitions and spin glass behavior. However, for these samples the spin glass is believed to onset at approximately the same temperature as the lower AFM transition. There is strong evidence to suggest that the existence of the spin glass facilitates the AFM switching for both $x = 0.31$ and $x = 0.35$, greatly enhancing the magnitude of the resistance switching in these compounds [120]. It is worth noting that the spin glass in the over-intercalated system and the spin glass in the under-intercalated system are two distinct spin glass phases, with differences in their magnetic texture and dynamics.

We have performed RUS measurements on a series of Fe_xNbS_2 samples with $x = 0.31$, $x = 0.33$, and $x = 0.35$. By tracking the resonant frequencies of these samples as a function of temperature, we are able to see evidence of not only the AFM transitions in these compounds but also the spin glass transitions. For $x = 0.33$, which is close to the stoichiometric value, we have also prepared and measured a sample in the rectangular parallelepiped geometry in order to determine its elasticity. By analyzing the changes in the elasticity tensor at the upper AFM transition, we can place new constraints on the nature of the higher-temperature AFM order. Furthermore, to our knowledge this is the first experimental measurement of the elasticity of an intercalated transition metal dichalcogenide.

All of the single crystals of Fe_xNbS_2 we studied were grown by Eran Maniv and Shannon Haley, using chemical vapor transport as described in Ref. [119]. The level of intercalation of each batch of synthesized crystals was confirmed using energy dispersive X-ray spectroscopy.

8.2 Results: $\text{Fe}_{0.35}\text{NbS}_2$

The results of our RUS measurements of a sample of $\text{Fe}_{0.35}\text{NbS}_2$ are shown in Fig. 8.3. We show the data gathered across two different temperature sweeps, with nine distinct resonances measured. The vertical lines in Fig. 8.3 mark the freezing temperature of the spin glass at 15 K and the two AFM transitions at 37 K and 45 K, respectively. These temper-

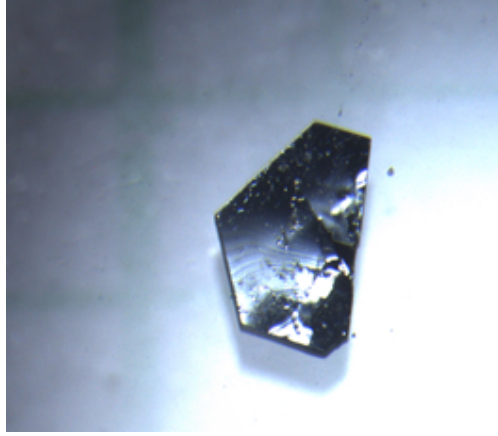


Figure 8.2: An as-grown crystal of $\text{Fe}_{0.33}\text{NbS}_2$ on millimeter graph paper.

atures were estimated based on magnetism and heat capacity measurements of crystals of the same intercalation [120].

There is clearly a kink in the frequencies at the lower AFM transition, accompanied by a maximum in the resonance widths as expected at a phase transition. The upper AFM transition is much more subtle. There appears to be a slight kink in the evolution of the resonant frequencies with temperature and no obvious maximum in the resonance widths. As for the onset of the spin glass, it is marked by a broad maximum in the resonance widths, which is the expected response at the freezing temperature [121].

We know from measurements of magnetization that both AFM transitions are continuous phase transitions. Therefore, based on the response of the resonant frequencies to these transitions, we should be able to determine the nature of the coupling between strain and the AFM order parameters. By comparison with Fig. 5.3, we can see that we do not have a coupling of the form $F_c = \gamma_i Q^2 \epsilon_i$, as this would result in an abrupt jump in the frequencies. However, it is difficult to distinguish whether the responses we see here correspond to $F_c = \gamma_i Q \epsilon_i$ or $F_c = \gamma_{ij} Q \epsilon_i \epsilon_j$. The transitions are in close proximity to each other and are relatively broad. Moreover, the elastic response at the phase transitions is subtle in comparison to the background temperature evolution of the resonant frequencies. We will see in Sec. 8.4 that the coupling of both AFM transitions in $\text{Fe}_{0.33}\text{NbS}_2$ is of the form $F_c = \gamma_i Q \epsilon_i$, which makes it likely that this would be the form of F_c for the over-intercalated system as well.

Fig. 8.4 shows the data for just one resonance as a function of temperature. With the data plotted on this scale, it is easier to see the subtle kink in the frequency at approximately 45 K. There also appears to be a small hump in the resonance width at roughly 45 K that is obscured due to its proximity to the local maximum at 37 K.

In measurements of the heat capacity and magnetism of $\text{Fe}_{0.35}\text{NbS}_2$, it is similarly the case that the lower AFM transition has a stronger experimental signature than the upper AFM signature [120].

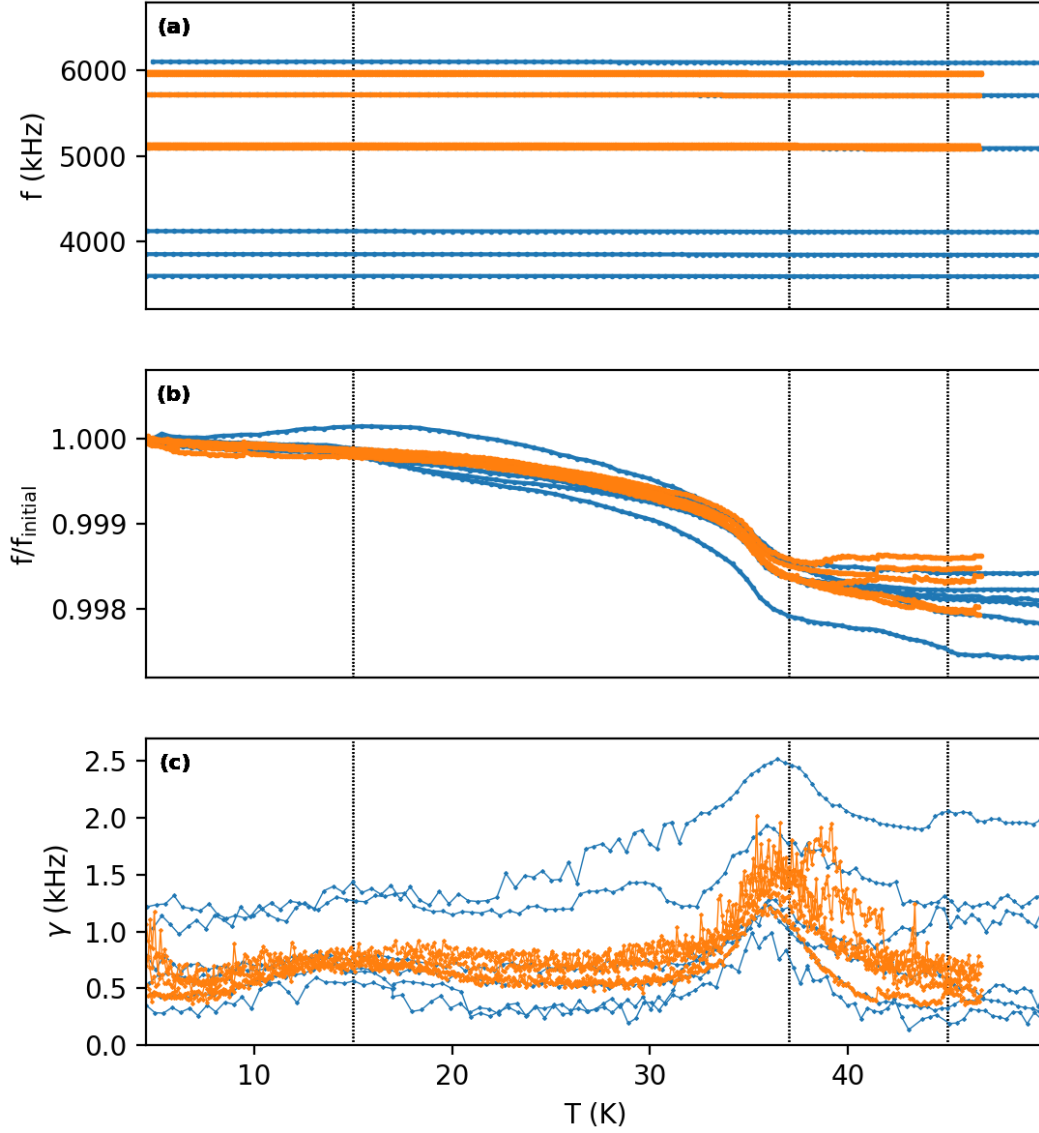


Figure 8.3: RUS data for nine distinct resonances in a sample of $\text{Fe}_{0.35}\text{NbS}_2$, gathered across two different temperature sweeps. For each resonance measured in each temperature sweep, we plot a) their frequencies; b) the fractional change in their frequencies; and c) their width, all as a function of temperature. Data of the same color are from the same temperature sweep. The vertical lines indicate the spin glass onset at roughly 15 K, the lower AFM transition at roughly 37 K, and the upper AFM transition at roughly 45 K.

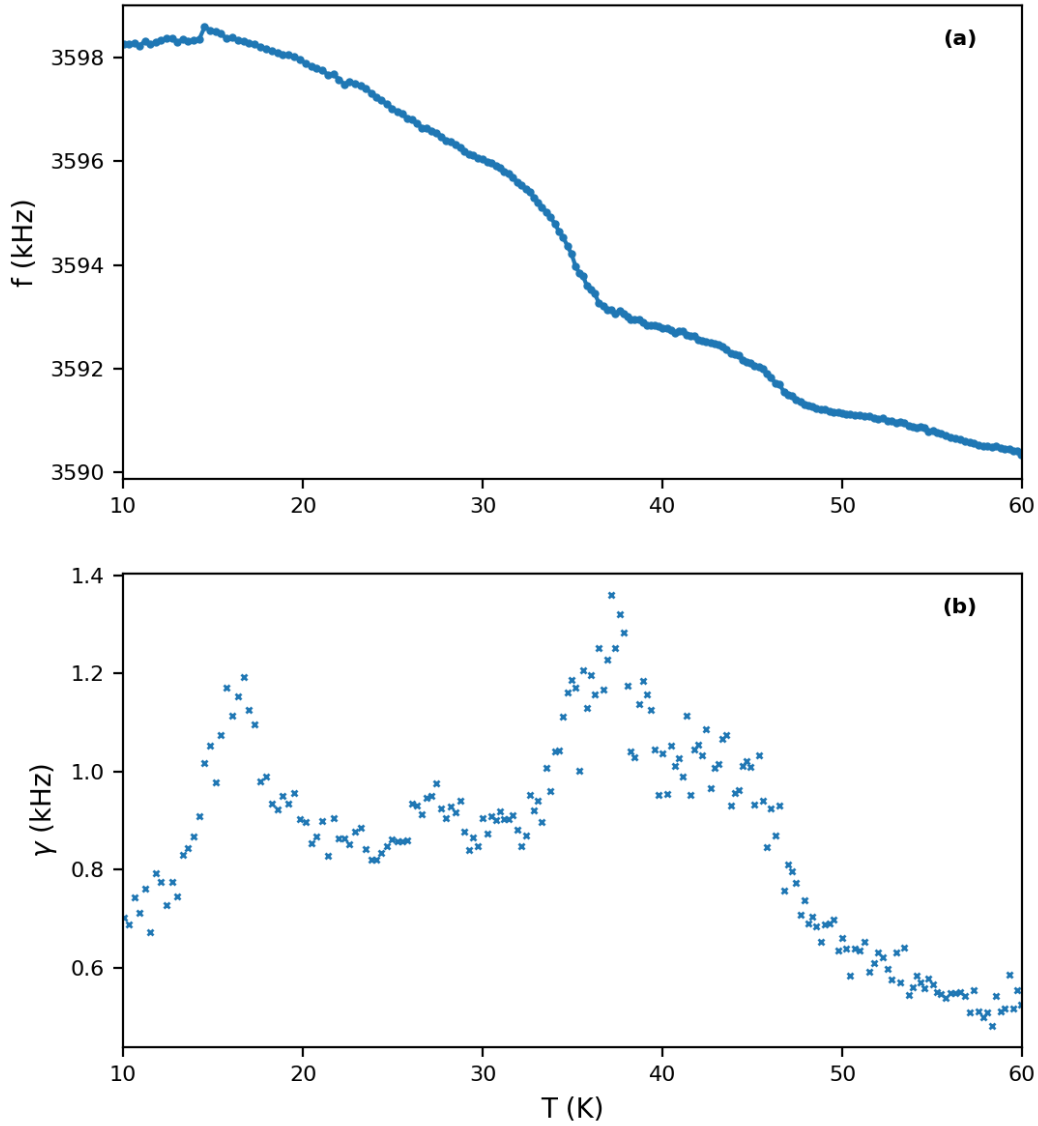


Figure 8.4: RUS data for one resonance of $\text{Fe}_{0.35}\text{NbS}_2$, showing a) its frequency and b) its width as a function of temperature. With the data plotted on this scale, it is easier to see the clear maximum in the resonance width at roughly 15 K, as well as the subtle kink in the frequency at roughly 45 K.

8.3 Results: $\text{Fe}_{0.31}\text{NbS}_2$

Representative RUS data for a sample of $\text{Fe}_{0.31}\text{NbS}_2$ are shown in Fig. 8.5. In this case, all four of the resonances shown were measured in a single temperature sweep. The vertical lines in Fig. 8.5 mark the lower AFM transition at roughly 37 K and the upper AFM transition at roughly 43 K. As before, these temperatures were estimated based on magnetism and heat capacity measurements of crystals of the same intercalation [120]. Based on those same measurements, the spin glass freezing temperature is estimated to be roughly 37 K as well.

We see clearly in the RUS data that the lower AFM transition is marked by a maximum in the resonance widths and a kink in the resonant frequencies. As for the upper AFM transition, it is difficult to determine whether it has any signature in our RUS data. There is a change in slope of the frequencies slightly above 43 K. However, this may be a softening related to the 37 K transition, assuming that the order parameter of the lower AFM transition is linearly coupled to strain.

The most interesting feature of our data is a second maximum in the resonance widths at approximately 28 K, accompanied by a very subtle change in slope of the resonant frequencies. The most likely explanation is that this is the true freezing temperature of the spin glass. The reported freezing temperature of approximately 37 K was determined by comparing field-cooled and zero-field-cooled magnetism measurements. As can be seen in Ref. [120], it is difficult to pinpoint the temperature at which these two curves diverge. A freezing temperature of 28 K still seems consistent with the magnetism data in Ref. [120]. Compared to measurements of magnetism, the RUS results give a less ambiguous signature at the spin glass freezing temperature of $\text{Fe}_{0.31}\text{NbS}_2$. Given that the spin glass is thought to play an important role in the AFM switching behavior of Fe_xNbS_2 , an accurate determination of the freezing temperature is necessary for rigorous investigation of the switching mechanism.

8.4 Results: $\text{Fe}_{0.33}\text{NbS}_2$

For $x = 0.33$, we wished to not only measure the resonant frequencies and widths as a function of temperature, but also determine the elasticity tensor as a function of temperature. As explained in Ch. 6, determining elasticity is much more computationally efficient if the sample has a simple geometric shape. Therefore, we have polished a sample of $\text{Fe}_{0.33}\text{NbS}_2$ into a rectangular parallelepiped, as shown in 8.6. In order to achieve a cuboid shape we used lapping paper, a right-angle block, and a polishing jig, employing similar techniques to those described in Ref. [122]. We polished the sample on lapping paper with successively smaller grains of silicon carbide, finishing with 3 μm grains. Scratches from the 3 μm grains are visible on the surface of the crystal. However, these surface-level scratches should not meaningfully impact our elasticity analysis; recall that the normal modes we are measuring have wavelengths on the order of the sample size.

Throughout this work, we have shown plots of the frequencies and widths of various

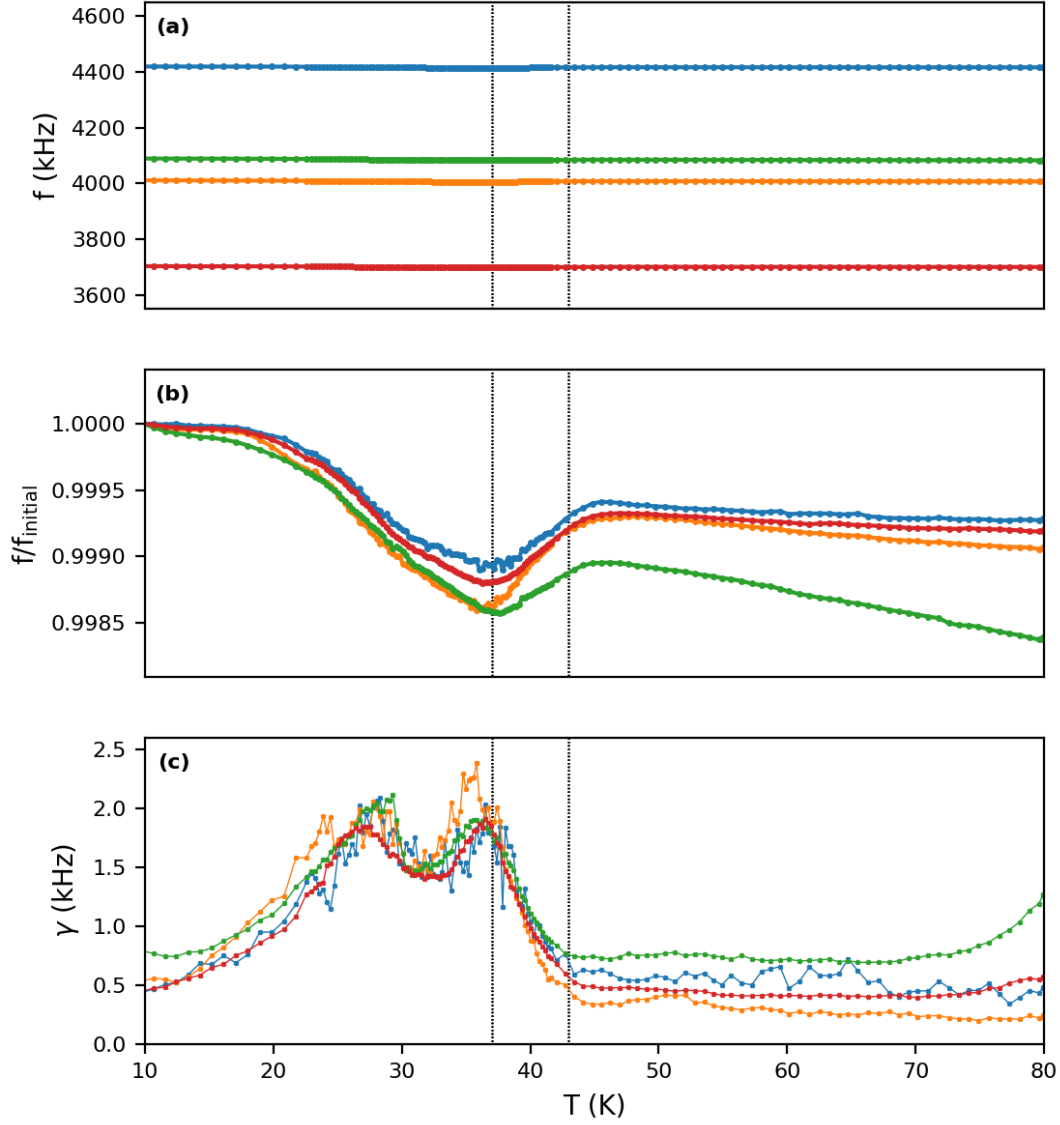


Figure 8.5: Representative RUS data for a sample of $\text{Fe}_{0.31}\text{NbS}_2$. For four different resonances we plot a) their frequencies; b) the fractional change in their frequencies; and c) their width, all as a function of temperature. The vertical lines indicate the lower AFM transition at roughly 37 K and the upper AFM transition at roughly 43 K.

resonances without showing the raw data from which these values were extracted. In order to elucidate this step in the data analysis, in Fig. 8.7 we show the actual signal measured in our RUS probe for data taken at successive temperatures. We are showing only a small subsection of a much broader frequency sweep to highlight the resonant frequency at approximately 6480 kHz. The red curve at the bottom of the plot shows the data recorded at

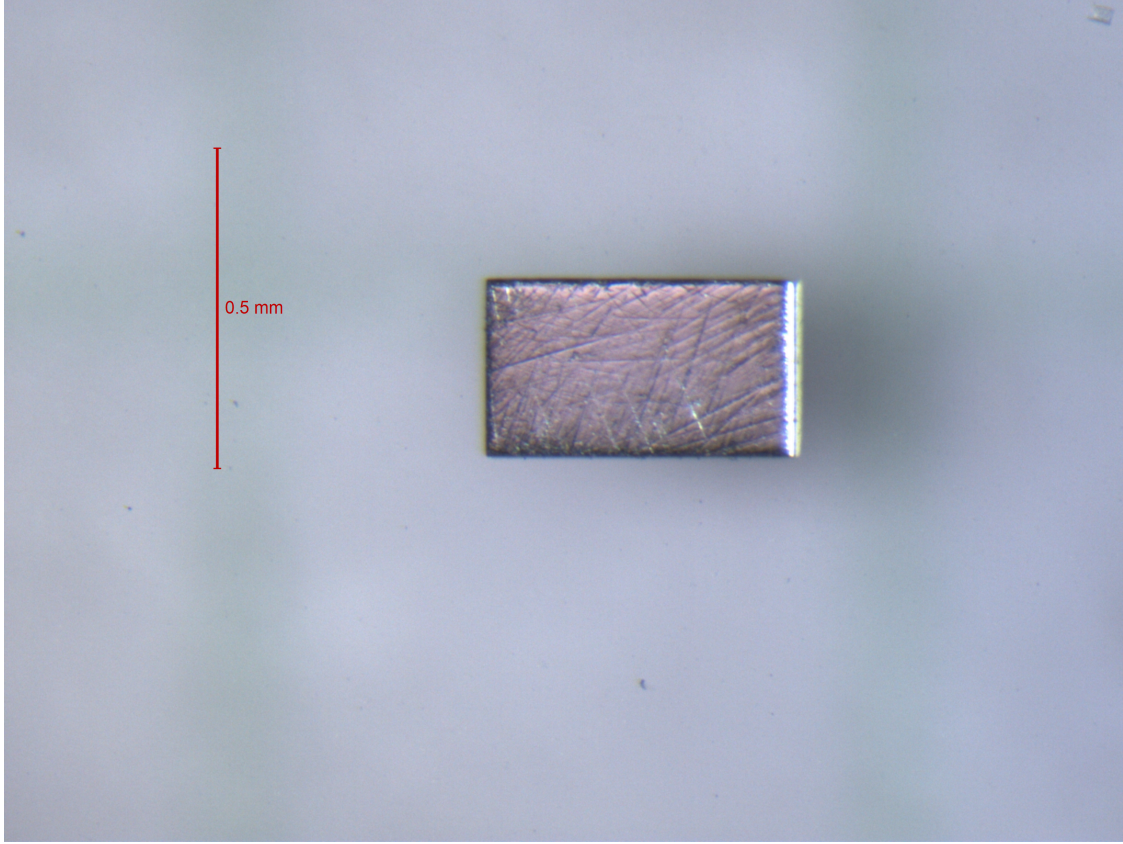


Figure 8.6: A rectangular parallelepiped crystal of $\text{Fe}_{0.33}\text{NbS}_2$ on millimeter graph paper, with a 0.5mm scale bar. This rectangular parallelepiped was formed by polishing the crystal shown in Fig. 8.2.

roughly 55 K. Data taken at successively lower temperatures are offset upwards by a constant amount so that the evolution of the resonance with temperature can be seen. The two AFM transitions in $\text{Fe}_{0.33}\text{NbS}_2$ are clearly visible. They are marked by a kink in the frequency as a function of temperature; moreover, from this raw data we can see that the resonance broadens significantly at both AFM transitions.

We fit the resonance at each temperature to the expected Lorentzian response given in Eq. 6.2. From these fits, we extract the resonant frequency and resonant width as a function of temperature, as shown in Fig. 8.8.

This is just one of the many resonances that was measured in this particular temperature sweep. In total, we measured 43 different resonances. In Fig. 8.9, we plot the data extracted for 15 different resonances from 55 K down to 10 K.

From magnetism measurements of $\text{Fe}_{0.33}\text{NbS}_2$, we know that the AFM transitions are both second-order transitions. By comparing Fig. 8.9 with the calculated responses shown in Fig. 5.3, we can see that both phase transitions also have order parameters that are coupled linearly to strain. In other words, the form of the coupling term is $F_c = \gamma_i Q \epsilon_i$ for

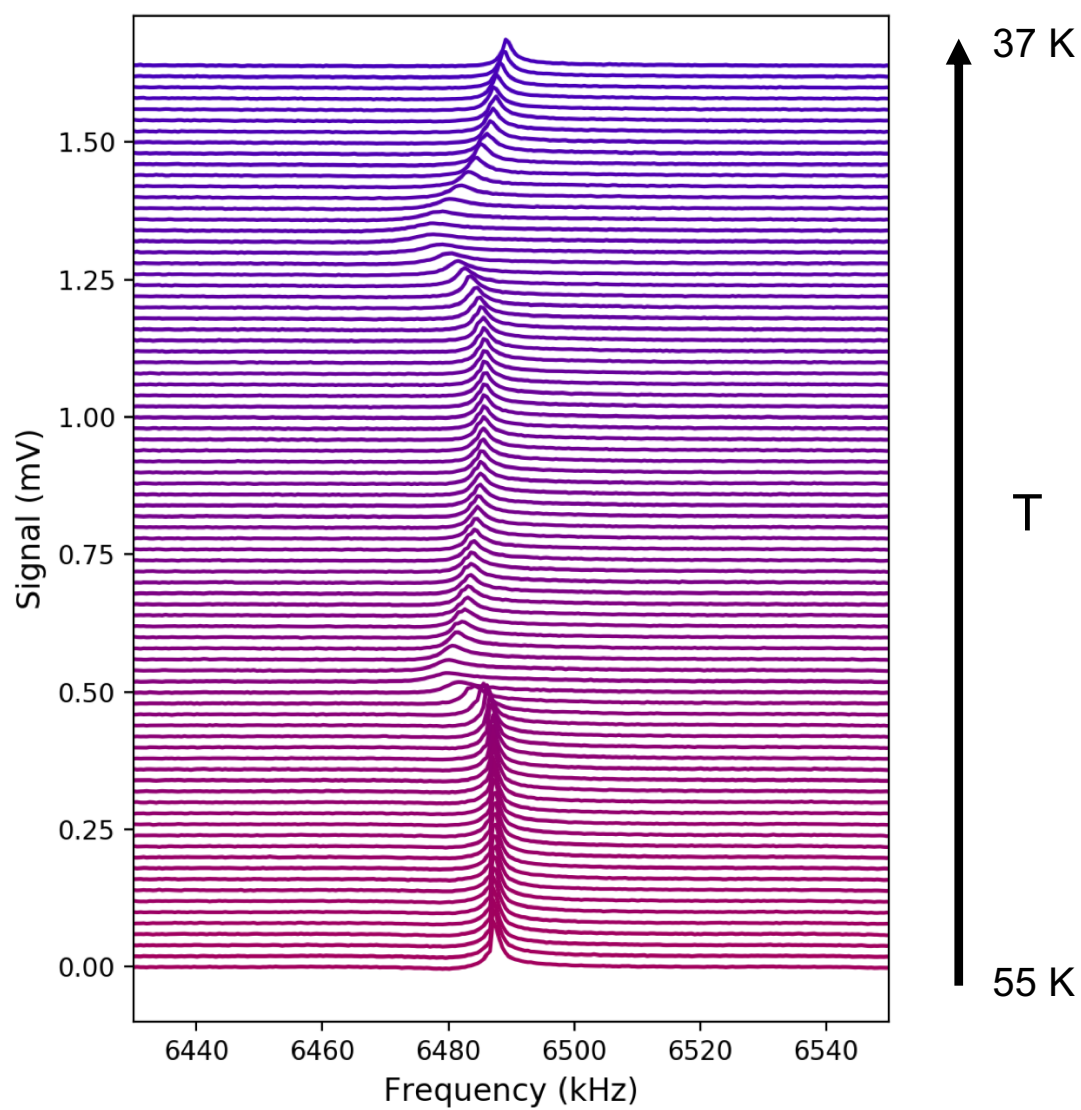


Figure 8.7: RUS signal versus frequency for measurements at successively lower temperatures, from roughly 55 K to 37 K. Each frequency sweep is offset by a constant amount for clarity.

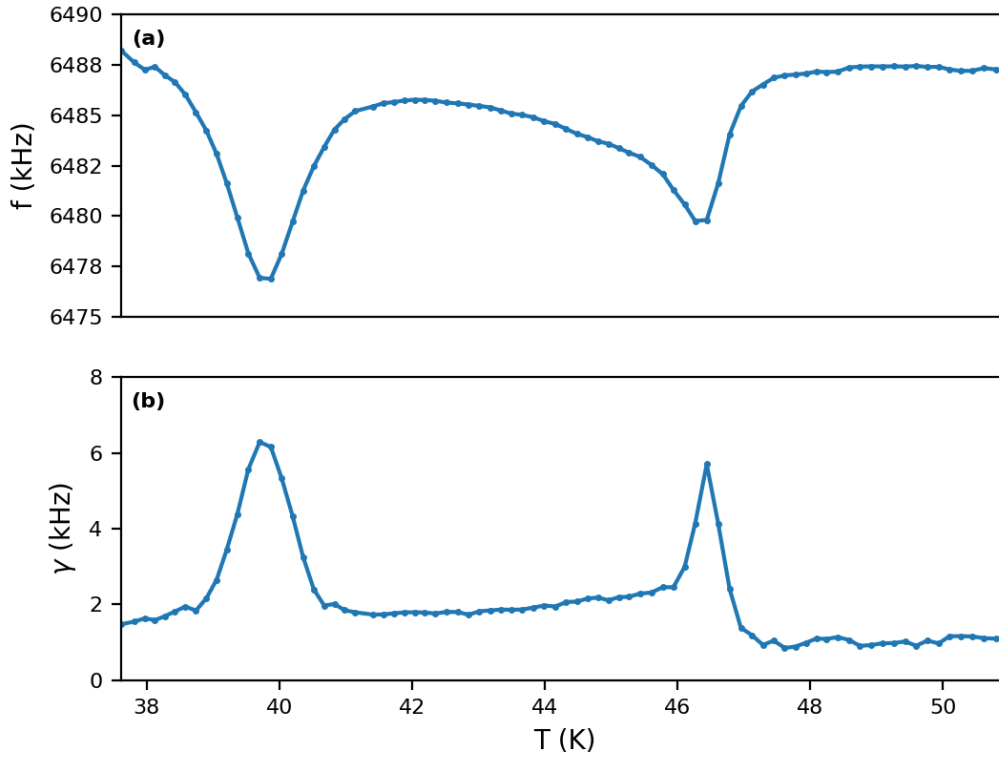


Figure 8.8: a) The frequency and b) the width of a single resonance of $\text{Fe}_{0.33}\text{NbS}_2$ as a function of temperature.

both AFM transitions.

8.4.1 Determining the elasticity of $\text{Fe}_{0.33}\text{NbS}_2$

As described in Ch. 5, the elasticity tensor has at most 21 independent elements, but the number of independent elements may be reduced due to crystal symmetries. In the case of a hexagonal crystal such as $\text{Fe}_{0.33}\text{NbS}_2$, we find that there are only five independent terms in the elasticity tensor [89]. The elasticity of $\text{Fe}_{0.33}\text{NbS}_2$ will be fully described by the moduli $c_{33}, c_{23}, c_{12}, c_{44}$, and c_{66} .

The elasticity of a small number of transition metal dichalcogenides has been studied experimentally; these include 2H-TaSe₂, 2H-NbSe₂, and WS₂ [123, 124]. However, in the case of 2H-TaSe₂ and 2H-NbSe₂ only the Young's modulus was determined, rather than the full elasticity tensor; in the case of WS₂, the elasticity tensor could only be determined up to a constant of proportionality. For the iron-intercalated transition metal dichalcogenides, we know of no prior determinations of elasticity. Therefore, we did not have an accurate initial guess for the elastic moduli. As described in Ch. 6, the LMA method of solving the inverse problem is only useful given a reasonable initial guess of the elasticity.

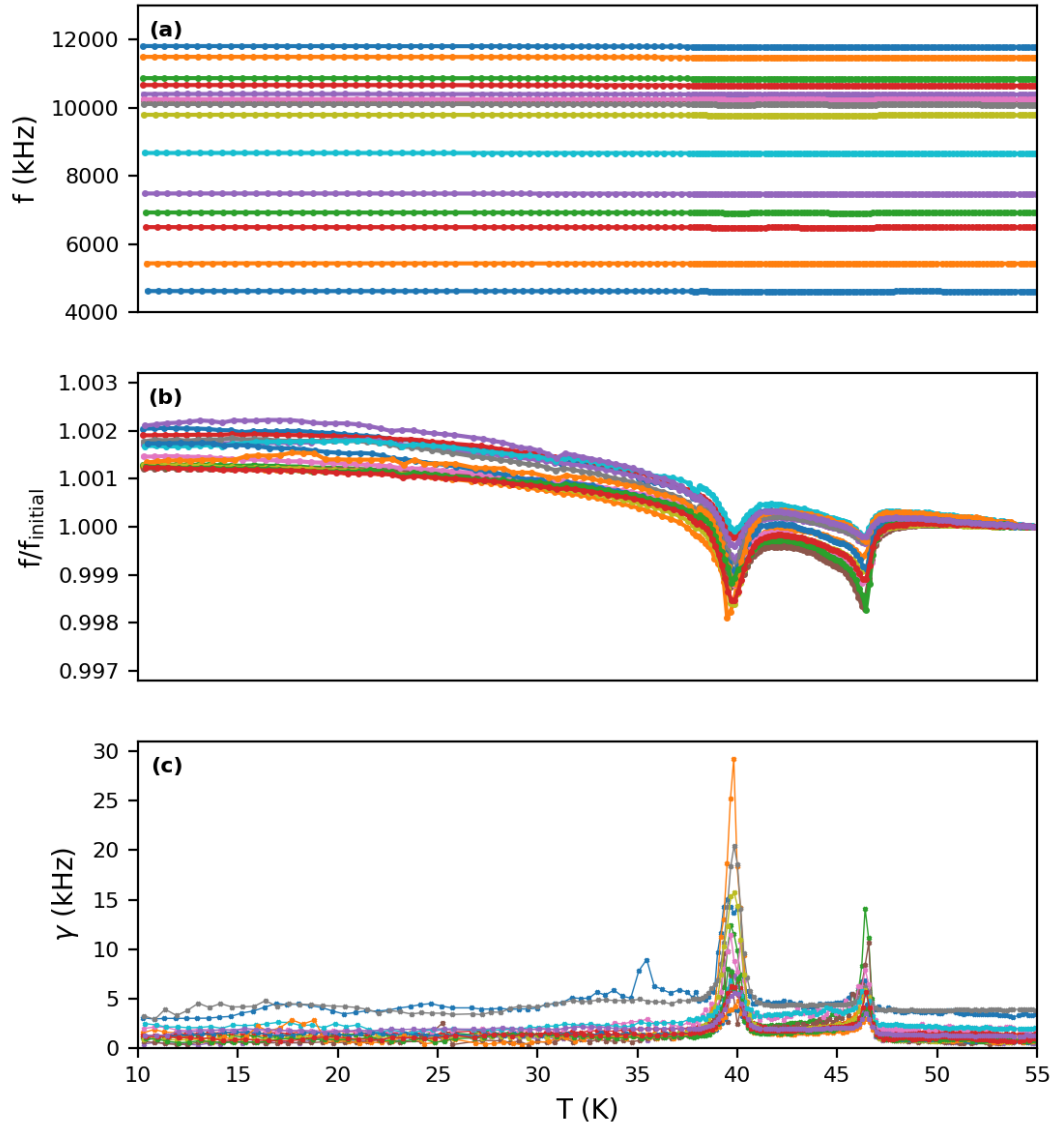


Figure 8.9: For 15 of the resonances measured in a single temperature sweep of $\text{Fe}_{0.33}\text{NbS}_2$, we plot a) their frequencies; b) the fractional change in their frequencies; and c) their width, all as a function of temperature.

Additionally, we did not have any intuition for the number of missing modes that might be in the range of frequencies we measured (recall, a missing mode is a natural resonance of the sample that is not observed in the RUS signal). Missing modes often arise when one of the transducers contacts the sample near a node of a particular resonance. We measured the sample several times at room temperature with slightly different positions on our transducers, which allowed us to find several of these “missing” modes. Even so, we suspected we had missing modes remaining—and this suspicion turned out to be correct.

Therefore, for our first determination of the elasticity of $\text{Fe}_{0.33}\text{NbS}_2$, we used PSO in combination with the Munkres assignment algorithm. This allowed us to search a broad range of parameter space while also allowing for the possibility of missing modes in our data set. The best fit to our data showed that we were missing several modes, including the two lowest-frequency resonances of the sample. Unfortunately, these were below the lowest frequency at which we measured when collecting this data set. However, we later re-measured the sample at room temperature and were indeed able to see these modes at the predicted frequencies. Through the use of the Munkres algorithm, we also became aware of several missing modes that were actually present in our data set but so faint that we had initially overlooked them.

In addition to fitting the elastic moduli, we also used the PSO procedure to determine our sample’s dimensions. The longest dimension of our sample is roughly $456.8\ \mu\text{m}$, as measured in a scanning electron microscope. However, we had some difficulty in accurately measuring the other two dimensions. Therefore, we fixed the longest dimension at $456.8\ \mu\text{m}$ and treated the other two dimensions as free parameters. We found the other two dimensions to be approximately $266.4\ \mu\text{m}$ and $66.3\ \mu\text{m}$, respectively, which is consistent with the estimations of the dimensions we obtained from the scanning electron microscope.

For the resonances measured at 55.4 K, we found the best figure of merit with parameters as follows:

$$[c_{33}, c_{23}, c_{12}, c_{44}, c_{66}] = [193.6, -101.0, 93.5, 45.6, 72.1]\ \text{GPa}. \quad (8.1)$$

We have estimated the error in these elastic moduli using the method described in Ref. [101]. We find that the c_{66} is determined to within roughly 0.1% and c_{44} is determined to within roughly 0.8%. We therefore take the values of the shear moduli, c_{44} and c_{66} , in Eq. 8.1 to be accurate determinations of these moduli. However, the other three moduli can change by factors of over 100% without significantly affecting the figure of merit of the fit. In other words, there is a broad range of values for these moduli that give an equally good agreement between the measured and calculated frequencies, so we cannot make any claims regarding the values of c_{33} , c_{23} , or c_{12} . Fortunately, as we will explain below, c_{44} and c_{66} are the most important moduli with respect to the AFM transition.

In Fig. 8.10, we show a comparison between the resonant frequencies we measured at 55.4 K and those calculated using the sample dimensions and elastic moduli we determined. As mentioned above, the two lowest-frequency modes of the sample were below the minimum frequency we measured for this data set. We accounted for these two missing modes when

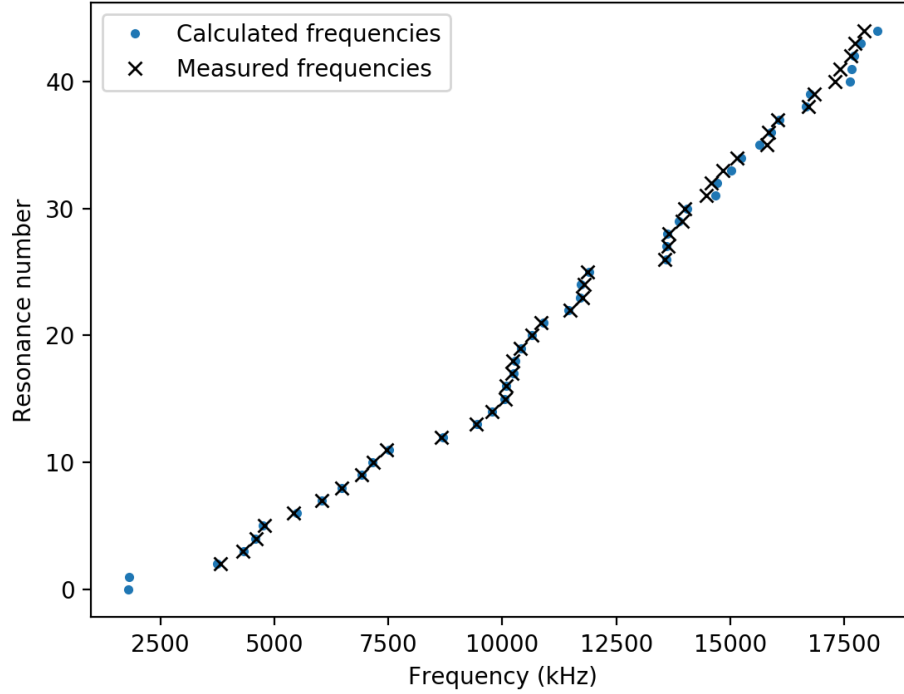


Figure 8.10: The first 43 measured resonant frequencies of $Fe_{0.33}NbS_2$ at 55.4 K compared to the frequencies calculated using the values in Eq. 8.1. Note that the measured frequencies begin at resonance number 2, as we determined that we were missing the two lowest-frequency modes in our measurement.

performing the fit, which is why the first two calculated frequencies do not have corresponding measured frequencies. We are showing the first 45 calculated frequencies of the sample, along with the first 43 measured frequencies. Note that when performing our fit to find the elastic moduli, we only used the first 24 measured frequencies of the sample—we did not fit for the frequencies above 11900 kHz. We can see that our fit has predictive power, as it reproduces the approximate frequencies of all 43 measured resonances, even though it was only fit using the first 24.

Our reason for only using the first 24 measured frequencies in our fit was a pragmatic one: a higher order of matrices is needed to calculate successively higher frequencies, as explained in Sec. 6.3. In order to accurately calculate the frequencies near 17000 kHz, we would need to use $N = 16$ at least. We have chosen to only use $N = 12$ as the cutoff for our basis functions, since it is much more computationally efficient. We can see that the fit between measured and calculated frequencies becomes worse as the frequency increases.

Once we had a result of the elasticity at this initial temperature, as well as the locations of our missing modes, we were able to use the LMA to determine the elasticity as a function of temperature. The results for the shear moduli are shown in Fig. 8.11. Due to the large

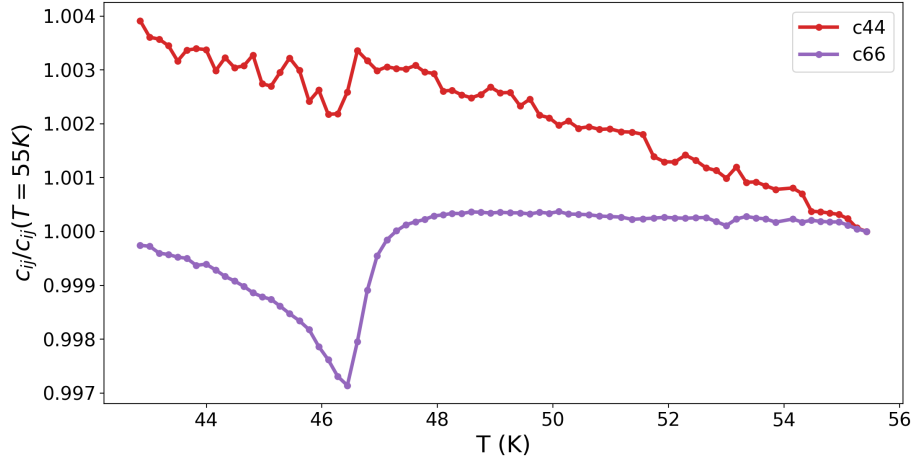


Figure 8.11: The evolution of c_{44} and c_{66} across the upper AFM transition of $\text{Fe}_{0.33}\text{NbS}_2$. Each modulus is plotted as a fraction of its value at 55 K.

error bars for the other three moduli, it is not meaningful to consider how they change with temperature, and so we have not plotted them.

As we can see, c_{44} increases steadily, while c_{66} shows a sharp feature at the upper AFM transition. As described above, this is a continuous phase transition with the coupling between strain and order parameter given by $F_c = \gamma_i Q \epsilon_i$.

Since the coupling term F_c appears in the free energy density of this material, it must be the case that F_c obeys all of the symmetries of the system, i.e. it must be A_1 -like. Given the form of F_c we have determined, this is only possible if the order parameter Q belongs to the same irreducible representation as the element of strain ϵ_i that it is coupled to. Table 8.1 shows the character table for D_6 , the point group of $\text{Fe}_{0.33}\text{NbS}_2$. Table 8.2 shows how order parameters of different irreducible representations will lead to responses in different elements of c_{ij} at the phase transition.

D_6	E	$2C_6(z)$	$2C_3(z)$	$C_2(z)$	$3C'_2$	$3C''_2$	Quadratic functions
A_1	+1	+1	+1	+1	+1	+1	$x^2 + y^2, z^2$
A_2	+1	+1	+1	+1	-1	-1	-
B_1	+1	-1	+1	-1	+1	-1	-
B_2	+1	-1	+1	-1	-1	+1	-
E_1	+2	+1	-1	-2	0	0	(xz, yz)
E_2	+2	-1	-1	+2	0	0	$(x^2 - y^2, xy)$

Table 8.1: The character table for point group D_6 .

Irr. rep. of Q	Quadratic functions	Allowed coupling	Allowed Δc_{ij}
A_1	$x^2 + y^2, z^2$	$\gamma_1 Q(\epsilon_1 + \epsilon_2), \gamma_3 Q\epsilon_3$	$\Delta c_{11} = \Delta c_{12}, \Delta c_{33}, \Delta c_{13}$
A_2	-	-	-
B_1	-	-	-
B_2	-	-	-
E_1	(xz, yz)	$\gamma_4 Q(\epsilon_4, \epsilon_5)$	Δc_{44}
E_2	$(x^2 - y^2, xy)$	$\gamma_6 Q(\epsilon_1 - \epsilon_2, \epsilon_6)$	Δc_{66}

Table 8.2: The elements of c_{ij} that may be affected if the order parameter belongs to each irreducible representation of D_6 , given that there is linear coupling between the order parameter and strain. The column labeled “Allowed coupling” shows the linear coupling terms that are allowed by symmetry, while the column “Allowed Δc_{ij} ” shows the elastic moduli that will be affected by such coupling terms.

We can see that a response in c_{66} is only allowed if the order parameter belongs to the irreducible representation E_2 . Referring to Table 8.1, we see that an order parameter that is E_2 -like will break all of the point group symmetries of the system except for the identity and the C_2 symmetry about the z -axis.

Note also that the moduli c_{33} , c_{23} , and c_{12} will only respond to a phase transition if the order parameter of that transition belongs to the irreducible representation A_1 . In other words, the order parameter must preserve every symmetry of the point group. However, for an AFM transition this will not be the case. Therefore, the fact that we cannot determine the temperature evolution of these three moduli does not actually affect our symmetry analysis.

Another factor we have not yet considered is time-reversal symmetry. The free energy must preserve every symmetry of the system, not just the point group symmetry. Given the form of F_c for this system, it must be the case that the order parameter and the strain have the same behavior under time-reversal symmetry. As strain is time-reversal symmetric, the order parameter must be as well [107]. This is possible for an AFM order parameter as long as time-reversal combined with a translation brings the crystal back to its original state [125].

Fig. 8.12 shows one possible AFM ordering that satisfies all of these constraints on the symmetry of the order parameter. Note that the structure shown is the stoichiometric compound $Fe_{1/3}NbS_2$. The sample we have measured, with $x = 0.33$, has a slightly lower iron concentration, so it will have vacancies on a small fraction of the iron sites shown in 8.12. The AFM ordering shown in Fig. 8.12 breaks every symmetry of point group D_6 except for the identity and the C_2 rotational symmetry about the z -axis. It can also be seen that time reversal plus a diagonal translation of the lattice will leave the system unchanged. The magnetic ordering shown is magnetic group $P_{B2_12_12}$ in the BNS notation,

While we have strictly limited the type of AFM order that can exist in the high-

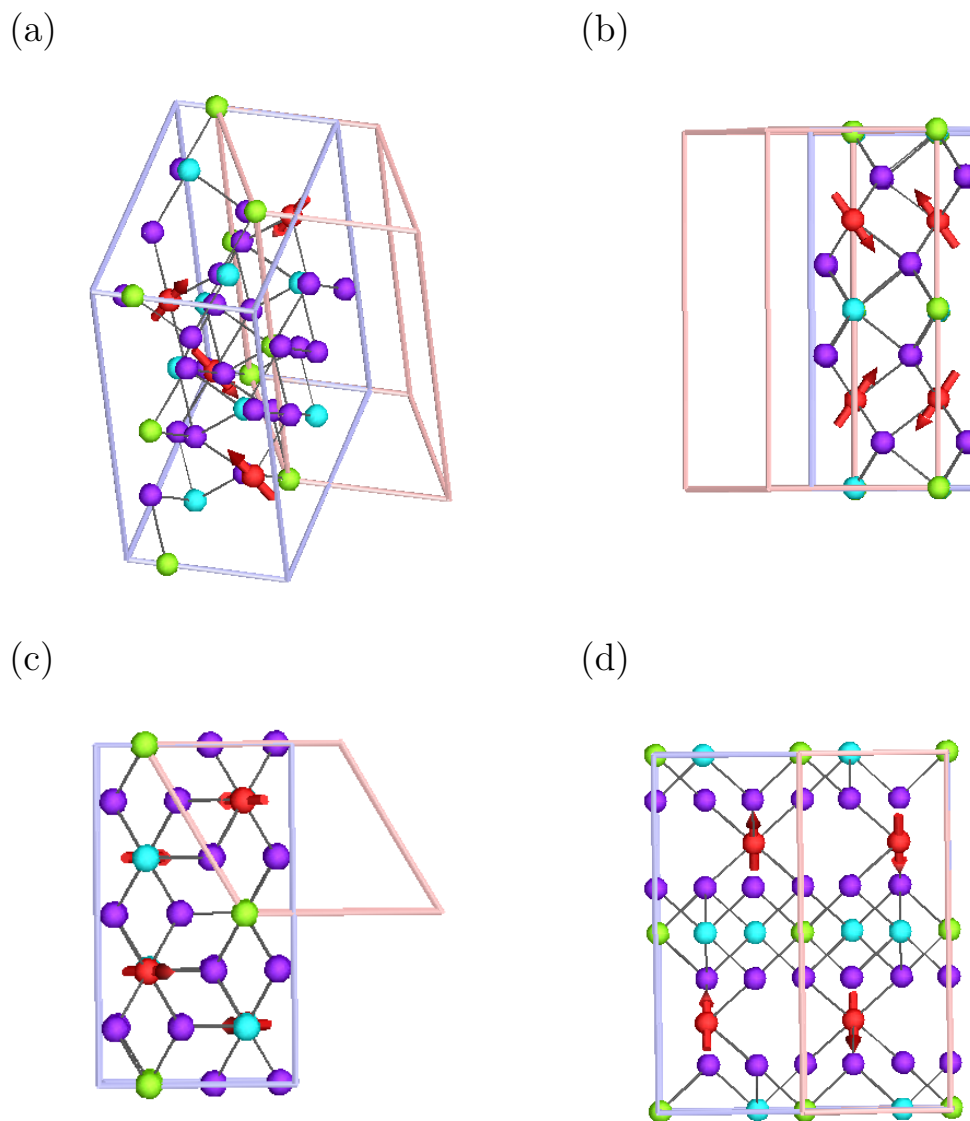


Figure 8.12: An illustration of one type of AFM ordering that satisfies the constraints that have been found through RUS analysis. The pink cage represents the original hexagonal unit cell, while the blue cage represents the new orthorhombic unit cell of the AFM phase. The Fe sites (red balls) are shown with arrows indicating the spin direction; each Nb atom (green/blue balls) is bonded with 6 S atoms (purple balls). a) Isometric top view; b) view along b -axis of the orthorhombic unit cell; c) view along the c -axis of the orthorhombic unit cell; d) view along the a -axis of the orthorhombic unit cell. This magnetic structure was calculated using ISODISTORT and visualized using ISOVIZ [126, 127].

temperature AFM phase, we have not made any conclusions about the lower-temperature AFM phase. Doing so will be an important next step of this analysis. However, it will come with new challenges. The paramagnetic state of $\text{Fe}_{0.33}\text{NbS}_2$ is hexagonal, so it only has five independent elastic moduli. If the high-temperature AFM ordering causes the crystal to become orthorhombic, this increases the number of independent elastic moduli to nine. Moreover, because hexagonal crystals have isotropic in-plane elasticity, we did not have to determine the angle of the crystal axes with respect to the axes of our rectangular parallelepiped. For an orthorhombic system, we will have to determine the angle of the crystal axes with respect to the sample axes, as this angle will affect the resonant frequencies of the sample.

8.5 Conclusion

We have used RUS to study the magnetism of Fe_xNbS_2 at three different intercalation levels: $x = 0.31, 0.33$, and 0.35 . For $\text{Fe}_{0.35}\text{NbS}_2$, our results were quite consistent with magnetism and heat capacity measurements. On the other hand, for $\text{Fe}_{0.31}\text{NbS}_2$ we determined that the freezing temperature for the spin glass state is approximately 28 K, rather than the value of 37 K that was extracted from analysis of the magnetization. An accurate determination of the freezing temperature is necessary in order to analyze the effects of the spin glass state on the AFM switching.

From the RUS data of $\text{Fe}_{0.33}\text{NbS}_2$, we demonstrated that both AFM transitions have a coupling between strain and order parameter of the form $F_c = \gamma_i Q \epsilon_i$. We determined the values of the shear moduli for $\text{Fe}_{0.33}\text{NbS}_2$, the first such determination for an intercalated transition metal dichalcogenide. We were able to analyze the elastic response of the upper AFM transition and determine that the order parameter is E_2 -like and must be symmetric under time-reversal. These symmetry constraints highly restrict the possible magnetic ordering that can exist in the higher-temperature AFM state of $\text{Fe}_{0.33}\text{NbS}_2$.

Appendix A

ADMR: Supplementary

A.1 Details of the vectorized form of the Shockley-Chambers tube integral

Our vectorized equation varies from the equation derived in Ref. [16] in two significant ways.

First, the authors of Ref. [16] consider a circular in-plane Fermi surface, with the result that ω has no azimuthal dependence. Therefore, they can simplify the integral in the exponential in Eq. 2.34:

$$\int_{\varphi_0}^{\varphi} \frac{d\varphi'}{\omega\tau} = \frac{\varphi - \varphi_0}{\omega\tau} \quad (\text{A.1})$$

whereas we must keep the integral in its unsolved form. The authors of Ref. [16] define

$$\begin{aligned} \lambda_+[j] &\equiv \int_{M_j}^{M_{j+1}} d\varphi_0 \exp[ik_F \tan(\theta) \cos(\varphi_0 - \phi + \pi/2 - \xi)] e^{(\varphi_0 - M_j)/\omega\tau}, \\ \lambda_-[j] &\equiv \int_{M_j}^{M_{j+1}} d\varphi_0 \exp[-ik_F \tan(\theta) \cos(\varphi_0 - \phi + \pi/2 - \xi)] e^{(M_j - \varphi_0)/\omega\tau}, \\ \lambda_{\text{init}}[j] &\equiv \int_{\varphi_0}^{M_{j+1}} d\varphi \exp[-ik_F \tan(\theta) \cos(\varphi - \phi + \pi/2 - \xi)] e^{(M_j - \varphi)/\omega\tau}. \end{aligned} \quad (\text{A.2})$$

Given the difference described above, we have defined

$$\begin{aligned}
\lambda_{\varphi_0}[j] &\equiv \int_{\mathbf{M}_j}^{\mathbf{M}_{j+1}} d\varphi_0 \frac{f(\varphi_0)e^{-iG(\varphi_0)}}{\cos(\gamma(\varphi_0))} \exp\left(\frac{-1}{\omega_0\tau \cos(\theta)} \int_{\varphi_0}^{\mathbf{M}_j} \frac{d\varphi'}{\cos(\gamma(\varphi'))}\right), \\
\lambda_{\varphi}[j] &\equiv \int_{\mathbf{M}_j}^{\mathbf{M}_{j+1}} d\varphi \frac{f(\varphi)e^{iG(\varphi)}}{\cos(\gamma(\varphi))} \exp\left(\frac{-1}{\omega_0\tau \cos(\theta)} \int_{\mathbf{M}_j}^{\varphi} \frac{d\varphi'}{\cos(\gamma(\varphi'))}\right), \\
\lambda_{\text{init}}[j] &\equiv \int_{\varphi_0}^{\mathbf{M}_{j+1}} d\varphi \frac{f(\varphi)e^{iG(\varphi)}}{\cos(\gamma(\varphi))} \exp\left(\frac{-1}{\omega_0\tau \cos(\theta)} \int_{\mathbf{M}_j}^{\varphi} \frac{d\varphi'}{\cos(\gamma(\varphi'))}\right).
\end{aligned} \tag{A.3}$$

Note that the authors of Ref. [16] have defined ω such that it includes a factor of $\cos(\theta)$. The integrands of Eq. A.2 do not include the terms $\frac{f(\varphi)}{\cos(\gamma(\varphi))}$ because these terms are equal to unity for the Fermi surface in Ref. [16]: $f(\varphi) = 1$ because the Fermi surface has a simple cosine interlayer warping and $\cos(\gamma(\varphi)) = 1$ because the in-plane Fermi surface is circular. Beyond that, there are several cosmetic differences between the definitions in Eq. A.2 and Eq. A.3. In Eq. A.3 we have used $G(\varphi) \equiv ck_F(\varphi) \tan(\theta) \cos(\varphi - \phi)$, where c is the interlayer lattice spacing. The term in the exponentials of Eq. A.2 appears slightly different: the authors have written k_F in units of c^{-1} and they have some additional terms in the argument of the cosine due to the coordinate systems they use to define φ or φ_0 (the quasiparticle's azimuthal position) versus ϕ (the azimuthal direction of the applied magnetic field). The signs of $G(\varphi)$ and $G(\varphi_0)$ are also reversed in Eq. A.2 vs. Eq. A.3; since we end up taking the real part of our result in Eq. 2.38, this is inconsequential. Finally, we have chosen to integrate with respect to φ rather than φ_0 for the integral in λ_{φ} because we believe this more accurately depicts the role it plays as compared to the original integral in Eq. 2.34. Since λ_{φ} is only evaluated on its own and not as part of any double integration, this makes no difference to the mathematical result and is purely cosmetic.

The second major difference between our vectorized equation and that of Nowojewski *et al.* is that they consider a specific case: a system with four MB junctions for which the change in k_z^0 through Bragg diffraction can only take two values, which they call $\pm\Delta k_z$. We have written an equation that allows for an arbitrary number of MB junctions for which the change of k_z^0 at the j^{th} MB junction is denoted $\Delta k_z^{(j)}$ and may be a different value for each MB junction (see Sec. 2.7 for information on calculating each $\Delta k_z^{(j)}$). This affects how the vector called $\mathbf{x}$ in Ref. [16] must be defined. Nowojewski *et al.* have defined

$$\mathbf{x}_n[j] \equiv \lambda_-[j]e^{-in\Delta k_z} + d_j(p\mathbf{x}_n[j^*] + q\mathbf{x}_{n\pm 1}[j']) \tag{A.4}$$

where $D_j \equiv e^{-(\mathbf{M}_{j+1}-\mathbf{M}_j)/\omega\tau}$ represents the exponential damping as a quasiparticle travels across the segment of the Fermi surface in question and $q = 1 - p$. Whereas the authors of Ref. [16] write out every term of $\mathbf{x}_n[j]$ explicitly, we've used j^* and j' to indicate the MB junctions at which the quasiparticle arrives if it undergoes magnetic breakdown or Bragg diffraction, respectively, after traversing the section from $\mathbf{M}_j$ to $\mathbf{M}_{j+1}$.

Whether the final term in Eq. A.4 is $\mathbf{x}_{n+1}[j']$ or $\mathbf{x}_{n-1}[j']$ depends on whether the value of k_z^0 changes by $+\Delta k_z$ or $-\Delta k_z$ when the quasiparticle Bragg diffracts from junction $\mathbf{M}_{j+1}$.

The authors of Ref. [16] only need one value of n to track these changes to k_z^0 . We consider the general case of arbitrary and independent $\Delta k_z^{(j)}$, each of which is tracked by n_j , the number of times the quasiparticle has Bragg-diffracted from the j^{th} MB junction. Therefore, we define $\mathbf{x}$ as follows:

$$\mathbf{x}_{\{n_i\}}[j] \equiv \boldsymbol{\lambda}_\varphi[j] e^{-ic \sum n_i \Delta k_z^{(i)}} + D_j(p\mathbf{x}_{\{n_i\}}[j^*] + q\mathbf{x}_{\{n'_i\}}[j']) \quad (\text{A.5})$$

where $D_j \equiv \exp\left(\frac{-1}{\omega\tau \cos(\theta)} \int_{\mathbf{M}_j}^{\mathbf{M}_{j+1}} \frac{d\varphi'}{\cos(\gamma(\varphi'))}\right)$ represents the exponential damping as a quasiparticle travels across the segment of the Fermi surface in question. We use $\{n_i\}$ to refer to the set of n for all MB junctions and we use $\{n'_i\}$ to refer to the set $\{n_i\}$ that has had the element n_{j+1} increased by 1. If the quasiparticle Bragg-diffracts after traversing the section between $\mathbf{M}_j$ and $\mathbf{M}_{j+1}$, then we need to increment n_{j+1} , which counts the number of times Bragg diffraction has occurred from junction $\mathbf{M}_{j+1}$.

Once these changes are accounted for, the derivation follows the same steps as Ref. [16] to arrive at Eq. 2.38.

A.2 In-plane transport simulations for $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$

In addition to calculating σ_{zz} for $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$, we can use the same methods as detailed in the main text to calculate the in-plane components of the conductivity tensor [46]. Neglecting the weak interlayer warping of our system, we find $v_x(\varphi) = \frac{\hbar}{m^*} k_F^\parallel(\varphi) \cos(\varphi - \gamma)$ and $v_y(\varphi) = \frac{\hbar}{m^*} k_F^\parallel(\varphi) \sin(\varphi - \gamma)$. Here γ is the angle between v_F and a vector pointing radially outward towards the Fermi surface, and it is given by

$$\gamma(\varphi) = \tan^{-1} \left[\frac{\partial}{\partial \varphi} [\log k_F(\varphi)] \right], \quad (\text{A.6})$$

as described in Ref. [38]. The procedure is then nearly identical to that for σ_{zz} , though slightly simplified by the fact that the $\Delta k_z^{(j)}$ terms are not involved in the in-plane calculations. We can calculate in-plane conductivity exactly, whereas we can only calculate σ_{zz} up to a constant of proportionality since we do not know the value of $t_\perp$.

Rather than calculating the in-plane transport terms and fitting them to experimental data, we want to see what predictions we can make for in-plane transport based on our analysis of the interlayer transport. We fit the points from Fig. 3.6 text to analytical functions: a second-order polynomial in temperature for $1/\omega_0\tau$, and a function of the form $\frac{c_1}{T} e^{-c_2/T}$ for B_0 , as we expect that at higher temperatures B_0 must decrease due to weakening antiferromagnetic correlations.

Using these analytical functions of our temperature-dependent parameters, we are able to calculate the in-plane transport of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ at any temperature—though such calculations should be interpreted with care because we are extrapolating to higher temperatures using information that comes from 50 K and below. We can compare these calculations to

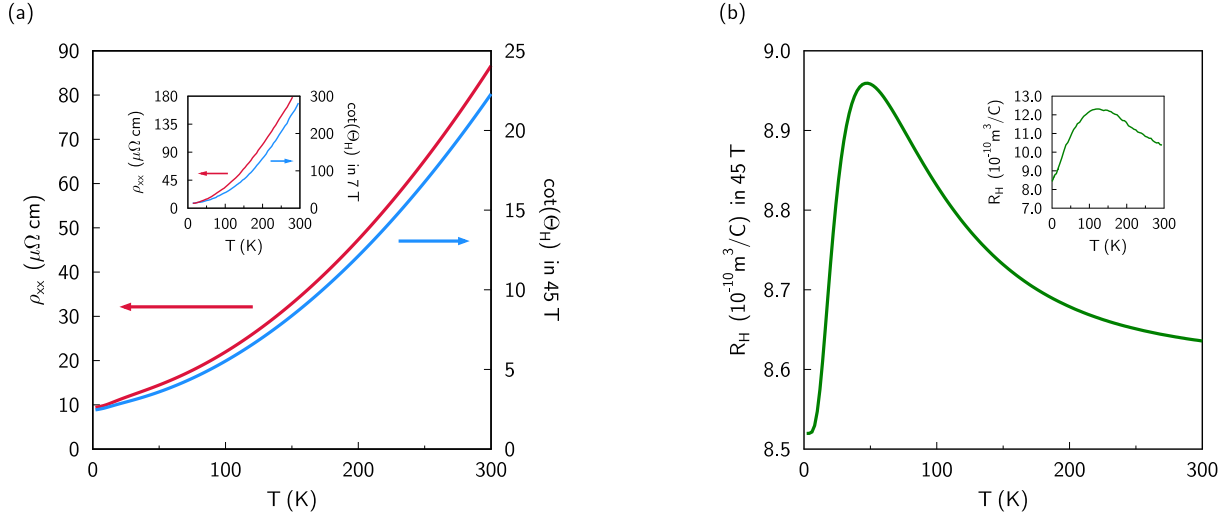


Figure A.1: Simulations of in-plane transport for $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ compared to experimental data taken from Ref. [128]. (a) Calculated values for the in-plane resistivity and for the cotangent of the Hall angle in a 45-T field plotted versus temperature (inset: data at 7 T). (b) Calculated values of the Hall coefficient as a function of temperature in a 45-T field (inset: data at unspecified field).

data taken from comparable samples by Mackenzie *et al.* [128], as shown in Fig. A.1. Note that the data presented in these figures come from a sample with T_c of 15 K, the same critical temperature as the sample whose ADMR data we have analyzed.

Our simulations of in-plane transport are qualitatively similar to experimental data, though they do not agree quantitatively, especially the Hall angle and Hall coefficient. The temperature at which the Hall coefficient reaches a maximum is determined by the temperature at which B_0 is greatest. It is important to note that in the magnetic breakdown model, where B_0/B plays an important role, we do not have Drude-like resistivity: ρ_{xy} is not directly proportional to the magnetic field. Therefore, we would have to use Hall data taken at 45 T to truly make a meaningful comparison. We cannot simply lower the magnetic field strength in our calculations to match the field at which data was taken, as we only have information on B_0 for a 45-T field. It has been proposed that antiferromagnetism in the cuprates is enhanced by an applied magnetic field [129, 130] and therefore we cannot assume that the value of B_0 at lower fields matches that at 45 T.

These results do not definitively support or contradict the magnetic breakdown model, but are shown in the spirit of sharing the results of our explorations. Given that we do not know the dependence of B_0 on B , it seems unlikely that such in-plane calculations can yield strong evidence for or against the suggested model unless new in-plane transport data are taken at 45 T.

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