

Applications of Multi-Modal Spectroscopic Techniques for the Study of Magnetism in Strongly Correlated Materials

by

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This dissertation by Calvin Bales is accepted in its present form
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Publications

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*Dedicated to all the trans scientists who came before
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INTRODUCTION

The study of magnetism in solid-state materials is a topic of broad interest in condensed matter physics, as magnetic materials present a wealth of possibilities in technological advancements and promising environments for the development of a range of exotic quantum phenomena. Of particular interest are van der Waals materials, materials composed of two-dimensional layers weakly coupled by the van der Waals force, that exhibit antiferromagnetic order. This class of materials has promising applications in the development of spin- and valleytronic devices [1–3], the construction of more efficient transistors [4, 5], and the creation of photodetectors for applications in ultra-fast UV light detection [6, 7]. Since these materials are easy to exfoliate, they also present an ideal platform for studying the nature of magnetism approaching and at the two-dimensional limit and the exotic phenomena that are expected to develop in this limit, such as quantum spin liquids, the quantum spin Hall effect, and the fractionalization of quasiparticles [8].

Many highly effective techniques exist to study magnetism in low-dimensional materials, but as the theories surrounding exotic quantum phenomena become more sophisticated and our desire for more advanced technological devices grows, so does the need to develop an increasingly complete understanding of the magnetic nature of a material. This need for more details motivates the development of new measurement techniques to expand the tools available to us in the study of low-dimensional magnetic systems. This thesis presents two such techniques.

One of these techniques involves measuring the electronic noise of magnetic tunneling junctions to sense magnetic fluctuations in materials in their immediate proximity. This presents unique benefits, as noise fluctuations provide information that is not present in time-averaged values. MTJs are a promising candidate for such sensing, as they can detect changes in magnetism with up to picoTesla sensitivity and are on the order of 50-100 μm in length and width [9–11], making them extremely effective in detecting small changes in local fields with a high level of spatial precision. An array of such devices could be used to probe the nature of spin currents carried through edge states in topological insulators by detecting correlations between local response functions at different positions within a sample [12] or to provide insight into emergent quantum phases of matter, for example, by detecting spin current fluctuations characteristic of quantum spin liquids [13].

Chapter 1 of this thesis will introduce magnetic tunneling junctions (MTJs) and how they work. It will also outline the types of electronic noise present in these devices and the ways in which that noise could be used as a means of detecting magnetic fluctuations and order in materials in their immediate proximity. Chapter 2 presents the measurement set-up and techniques developed to measure the electronic noise of these devices, including the results of tests of several different low-temperature amplifiers. It will also present characteristic measurements of the intrinsic electronic noise of MTJs. Although this project never progressed to the point of using MTJ noise to measure a sample due to a limited availability of MTJs, it presents a strong framework on which future measurements with samples can rely.

The second novel measurement technique presented in this thesis is an expansion of standard nuclear magnetic resonance (NMR) techniques that enables a direct measure of the strength and distribution of spin-spin interactions, named the MSIS (measure of spin interaction strength) technique. The utility of the MSIS technique is demonstrated by its application to the van der Waals antiferromagnetic material

NiPS₃, where two closely coupled ³¹P nuclei are used as a probe of their local environment. These measurements reveal a significant change in the ³¹P -³¹P interaction strength with the onset of magnetic order and a clear coexistence of the interaction strength characteristic of the paramagnetic phase with that of the antiferromagnetic phase through the magnetic transition.

The ability of the MSIS technique to also measure the distribution in the interaction strength makes it highly effective in detecting magnetic fluctuations, since a distribution can reveal effects that are not strong enough to influence the average. In NiPS₃, this allows us to rule out the presence of short-range interactions in the paramagnetic phase, something that was disputed between measurement techniques that probe fluctuations at different energy scales [14–18]. The demonstrated ability of this technique to measure the strength and distribution of the ³¹P -³¹P interaction strength points to its likely utility in the study of other low-dimensional antiferromagnetic materials, as well as in the detection of quantum phenomena characterized by magnetic fluctuations that are expected to arise in such materials.

Chapter 3 outlines the general principles of nuclear magnetic resonance and details the MSIS technique. The derivation of the MSIS model for the specific case of a dipole-like interaction between closely coupled phosphorus nuclei will also be presented. Chapter 4 presents results from standard NMR and MSIS measurements on NiPS₃. The change in ³¹P -³¹P interaction strength with the onset of magnetic order is likely due to a change in the orbital hybridization of the phosphorus atoms and sulfur ligands. Possible explanations for this change in orbital hybridization, which is not a standard characteristic of a magnetic phase transition, as well as the increase in the distribution of the ³¹P -³¹P interaction strength with the onset of magnetic order, are discussed.

The utility of standard NMR for studying magnetic phenomena and order in materials is demonstrated by our NMR measurements on the van der Waals antifer-

romagnetic material CoNb_3S_6 . The nature of the AFM order in this material is not well understood, but since NMR is very sensitive to changes in the local field, our measurements were able to very precisely determine the local field felt at the nuclear site in both the paramagnetic and antiferromagnetic phase. A precise knowledge of the local fields in these phases enables theoretical models to verify possible magnetic orders and provide insight into the structural and magnetic symmetry at the site.

In addition to insight on the magnetic order, an unusual temperature dependence of several characteristics of the NMR spectra was identified. This unusual temperature dependence corresponds closely to the temperature range in which the anomalous Hall effect (AHE) has been detected [19], motivating a thorough analysis of these NMR observables to gain insight into the microscopic origins of the AHE.

Chapter 5 presents results of ^{93}Nb NMR measurements on CoNb_3S_6 . The details of the changes in spectral features over the temperature range in which the AHE coexists with magnetic order will be enumerated. The development of a significant asymmetry in the spectral line shape and the possibility that it has some field dependence is discussed.

Overall, this thesis demonstrates the utility of standard NMR and the MSIS technique in studying low-dimensional magnetic materials, a class of materials of broad interest in the field of condensed matter physics. The results of the application of the MSIS technique to NiPS_3 reveal information on the electronic and magnetic nature of this material that was previously inaccessible by other measurement techniques. Our study of CoNb_3S_6 reveals the potential for standard NMR measurements coupled with detailed theoretical models to provide insight into the nature of a complicated magnetic order. The changes we see in the shape of the spectral line concurrent with the weakening of the AHE could point to the utility of NMR in elucidating the microscopic origins of such exotic phenomena through the detection of characteristic changes in the local environment of the nuclear probes.

Understanding these results and techniques can facilitate the understanding of broader topics in physics. For example, the fundamental principles of the MSIS technique are directly related to the principles of quantum computing, where initializing and controlling spin states enables information to be encoded. Developing techniques to advance the study of magnetism in low-dimensional systems, such as the MSIS technique and using the electronic noise of MTJs as a means of quantum sensing, could contribute to work surrounding technological applications of low-dimensional magnetic materials and could facilitate the detection and study of the exotic phenomena that arise in these materials.

CHAPTER 1

Magnetic Tunneling Junctions and Electronic Noise

One approach to expanding the tools available for studying quantum materials is through the development of a quantum mechanical magnetic camera composed of an array of magnetic tunneling junctions (MTJs) that can provide simultaneous spatial and temporal resolution of ultra-weak magnetic fields. With a large array of highly sensitive MTJs that function over a broad frequency and temperature range, these sensors could function as highly effective probes of quantum materials. For example, they could be used to detect fractional excitations characteristic of quantum spin liquids [13, 20, 21] or to probe spin currents carried through edge states in topological insulators by simultaneously measuring correlations between local response functions at different locations in the sample [12].

Existing methods of quantum magnetic sensing, such as semiconductor-based Hall effect sensors and diamond nitrogen-vacancy measurement techniques to name two, provide valuable insight into emergent quantum phenomena, but face some drawbacks that can be overcome by MTJs. For example, semiconductor-based Hall effect sensors are compatible with silicon technology, but are far less sensitive than MTJ sensors [22]

and nitrogen-vacancies are incredibly sensitive, but lack the spatial control of MTJs and require an optical readout system [23, 24]. MTJ sensors do not require the same infrastructure for measurement read-out which makes them highly versatile in their potential applications.

An additional motivation for using an array of MTJs to detect quantum phenomena is the unobtrusive nature of the sensors. Changes in the local field of the sample will be detected by an MTJ simply by being in its direct proximity without any need to perturb the system under investigation. In its most passive form, the MTJ sensors can detect a change in magnetic field without even biasing the MTJs, since their resistance can be measured from the thermal noise they produce, noise that exists even in the absence of any applied voltage [25–27].

These sensors do face some drawbacks. For one, the RC constant of the current MTJs only allows them to operate from DC up to around 10 MHz [28]. This presents a significant limitation as the specific value and frequency of the noise due to spin fluctuations is highly dependent on the sample being measured and can vary by orders of magnitude [29], so higher frequency fluctuations remain inaccessible. MTJs are also highly sensitive to electrostatic discharge, making them sensitive to work with and highly susceptible to being destroyed.

In this chapter a brief explanation of what MTJs are and how they work, as well as background information on their dominant noise sources, is discussed. Chapter 2 will outline the details of the experimental set-up and techniques used to begin the realization of MTJ-based quantum property sensors.

1.1 Magnetic Tunneling Junctions

Magnetic tunneling junctions (MTJs) are highly sensitive devices whose resistance changes in the presence of an external magnetic field. Coherent quantum tunneling

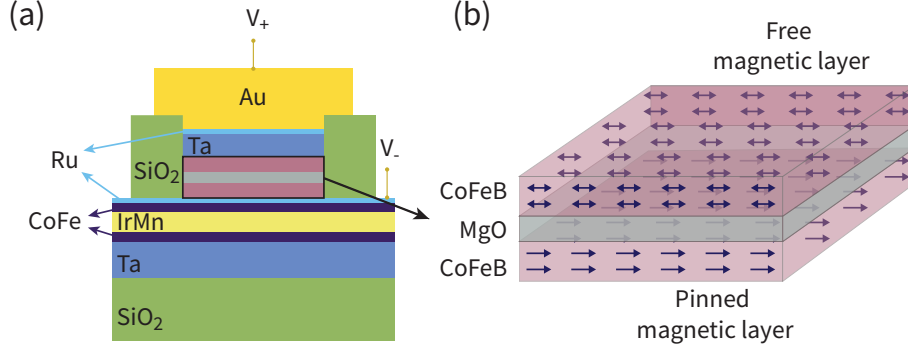


FIGURE 1.1: (a) Structure of an MTJ device and (b) detailed view of the tunneling junction. Adapted from Figure 34.1 in Ref. [30].

occurs between two spin-polarized ferromagnetic electrodes, the rate of which, and thus the resistance of the device, depends on the relative orientation of the magnetization vectors of the two ferromagnetic layers [10, 11, 30]. The physical structure of the MTJs, a brief overview of how tunneling occurs, and the means of characterizing their sensitivity is discussed.

1.1.1 Physical Structure

The physical structure of an MTJ device is shown in Figure 1.1(a). The tunnel junction is composed of two ferromagnetic (FM) electrodes separated by a thin insulating barrier, as shown in Figure 1.1(b). In the devices discussed here, the ferromagnetic electrodes are made of CoFeB and with an insulating barrier of MgO. The top ferromagnetic electrode (the electrode closest to the sample) is called the free magnetic layer because its magnetization vector is free to rotate in response to the presence of an external magnetic field. The bottom ferromagnetic electrode is the pinned magnetic layer as its magnetization vector is pinned in a fixed direction by an adjacent antiferromagnetic (AFM) layer, in this case IrMn, shown in Figure 1.1(a).

IrMn has layered AFM order which makes it a good material for pinning the FM electrode—the magnetization vector of the top layer of the IrMn lies parallel to that of the bottom FM electrode, so if the magnetization vector of the bottom FM electrode were to flip, it would also flip the magnetization of the top layer of IrMn, which

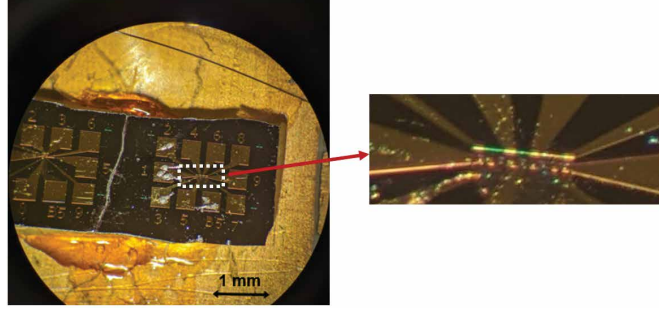


FIGURE 1.2: Photo of an MTJ array mounted on the sample holder and a zoomed in view of the MTJs, denoted on the full photo by the white dashed box.

would require the rest of the IrMn layers to reorient in order to maintain the AFM order, which is not energetically favorable. Thus, the magnetization of the bottom FM electrode remains pinned in a fixed direction. The MTJ structure is mounted on a SiO_2 substrate with gold contacts. The remaining layers of the structure shown in Figure 1.1(a) serve to enhance the magnetic characteristics of the device [30].

A photo of an MTJ array is shown in Figure 1.2. The MTJs are oval in shape with a long axis measuring $\sim 90 \mu\text{m}$ and short axis $\sim 50 \mu\text{m}$. This array only has two active MTJ devices on it, whereas the final quantum mechanical magnetic camera aims to have an array of 100 - 1000 MTJs with a total size of $1 \times 1 \text{ cm}$. These devices are highly sensitive to electrostatic discharge and must be handled with care to avoid destroying the device.

1.1.2 Tunneling Magnetoresistance and MTJ Sensitivity

Magnetic tunneling junctions work according to the principles of tunneling magnetoresistance. This means that as the relative orientation of the magnetization vectors of the two FM electrodes changes, so does the resistance of the device. When the magnetization vectors of both electrodes are parallel, the MTJ has low resistance, and when they are anti-parallel, it has high resistance [31]. This is illustrated in Figure 1.3.

The bottom panel of Figure 1.3 illustrates why the resistance changes with the

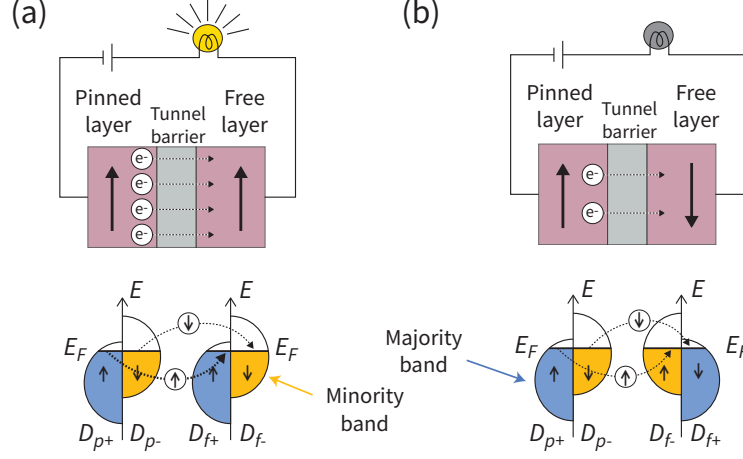


FIGURE 1.3: A circuit diagram showing the magnetic tunneling junction in (a) its low resistance parallel state and (b) its high resistance anti-parallel state. The energy diagrams below the junctions illustrate the energy band transitions of electrons tunneling between aligned and anti-aligned electrodes. $D_{p(f)+}$ and $D_{p(f)-}$ denote the density of states of the majority-spin and minority-spin band of the pinned (free) FM electrodes, respectively, and E_F denotes the Fermi energy. Adapted from Figure 1 in Ref. [31].

relative orientation of the two magnetization vectors. In the parallel state, the electrons in the majority-spin band of both electrodes are aligned, so electrons from the majority-spin band in the pinned layer tunnel into the majority-spin band of the free layer. The same is true for minority-spin band electrons. This creates favorable tunneling conditions, so conductivity is high (resistance is low). When the MTJ is in the anti-parallel state, the converse is true. Majority-spin electrons in the pinned layer have the same orientation as the minority-spins in the free layer, meaning that electrons are tunneling from the majority-spin band in the pinned layer to the minority-spin band in the free layer, and vice versa. These are not favorable tunneling conditions, so the conductance drops and the MTJ is in a high resistance state. The electrode and tunnel barrier materials, as well as the thickness of the tunnel barrier, play a large role in the tunneling magnetoresistance of the MTJ [30–34], but the details of how and why are beyond the scope of this thesis.

The tunneling magnetoresistance is quantified by the tunneling magnetoresistance

ratio (TMR) which is described by the following equation,

$$\text{TMR} = \frac{R_{\uparrow\downarrow} - R_{\uparrow\uparrow}}{R_{\uparrow\uparrow}} \quad (1.1)$$

where $R_{\uparrow\downarrow}$ is the MRJ resistance in the anti-parallel state and $R_{\uparrow\uparrow}$ is the MTJ resistance in the parallel state. Early MTJs exhibited $\text{TMR} \sim 200\%$ [35], with newer MTJs reaching $\text{TMR} \sim 500\%$ at room temperature and $\text{TMR} \sim 1000\%$ at cryogenic temperatures [31, 36].

A larger tunneling magnetoresistance is desired for MTJ-based quantum sensors, as a higher TMR yields larger sensitivity. The sensitivity of the MTJs is characterized by the following equation,

$$S_0 = \frac{1}{R_0} \frac{\Delta R}{\Delta H} \quad (1.2)$$

where $R_0 = (R_{\uparrow\downarrow} + R_{\uparrow\uparrow})/2$ and ΔR is the change in MTJ resistance in response to a change in external field ΔH . The sensitivity is given in units of $\%/Oe$ and for a typical MTJ is around $1.5\%/Oe$. However, the MTJs proposed to be used for the quantum mechanical magnetic camera have a sensitivity of $775.4\%/Oe$ and a detectable field limit of $30 \text{ pT}/\sqrt{\text{Hz}}$ at 10 kHz [11].

1.2 Electronic Noise

The lower limit for measuring small-amplitude signals is the noise floor. Noise in this case refers to random fluctuations in current or voltage that produce spurious signals and is present in all conducting materials. Noise can originate from different physical processes and can carry valuable information that is not present in time-averaged signals. Three dominant sources of noise present in magnetic tunneling junctions are $1/f$ noise, thermal noise, and shot noise [37].

Noise is characterized by a noise power spectral density, which is the noise power

per unit bandwidth, given in units of voltage squared per frequency (V^2/Hz). It can also be expressed as the noise amplitude spectral density, which is the square root of the noise power spectral density and has units of $V/\sqrt{\text{Hz}}$.

1.2.1 $1/f$ Noise

At low frequencies, the dominant noise sources is $1/f$ noise, also known as flicker or pink noise. As the name suggests, $1/f$ noise is inversely proportional to signal frequency. In general,

$$S_V(f) \propto \frac{1}{f^\beta}, \quad (1.3)$$

where β is close to unity and the proportionality constant depends on the circuit component. For example, in a resistor, $S_V(f) = KV_0^2 R_0/f$ where V_0 and R_0 are the average voltage and resistance, respectively, and K is a constant specific to the resistive material [38].

In magnetic tunneling junctions, the $1/f$ noise takes the form,

$$S_V(f) = \alpha \frac{V^2}{Af}, \quad (1.4)$$

where α is a constant based on the materials used in the junction and called the Hooge parameter, A is the junction area, and V is the voltage applied across the sensor [30]. The Hooge parameter is an experimentally determined value with units of m^{-2} that depends on various MTJ parameters, including the resistance-area product, tunneling magnetoresistance ratio, parallel versus anti-parallel configuration, and biasing conditions [39, 40]. It can vary from values on the order of $1 \times 10^{-10} \text{ } \mu\text{m}^{-2}$ to values on the order of $1000 \times 10^{-10} \text{ } \mu\text{m}^{-2}$. In MTJs, the $1/f$ noise originates from the trapping of electrons at defects in the barriers. When the electrons become immobilized, the flow of charge carriers is slowed, causing a disruption in the transmission of electrons through the junction, which appears as noise $1/f$ [37].

Experimentally, $1/f$ noise can be removed from a measurement by applying a low-pass filter, although this also filters out any contributions to the desired signal below the filter bandwidth. To remove only the $1/f$ noise and not the signal, the $1/f$ noise proportionality constant can be determined by calibration so that it can be subtracted from the signal after acquisition. The suppression of intrinsic $1/f$ noise in MTJs is best addressed in the fabrication stage, which is beyond the scope of this work. In studying MTJs, the Hooge parameter can provide information on the device since it depends on various MTJ parameters, but at this stage it is not the focus of our noise measurements for the purpose of quantum sensing.

1.2.2 Thermal Noise

Thermal noise, also known as Johnson-Nyquist noise, is a frequency-independent noise source present in all conducting materials due to the random thermal fluctuation of charge carriers [25–27]. This noise arises naturally from the fluctuation-dissipation theorem which states that if a process dissipates energy through heat, the reverse process is also possible, *i.e.* thermal fluctuations near the Fermi energy in a conducting material induce Brownian motion in the charge carriers [41]. The noise arising from such fluctuations is described by the following equation,

$$S_R(T) = 4k_B T R, \quad (1.5)$$

where k_B is the Boltzmann constant, T is the temperature of the conducting material, and R is its resistance.

Thermal noise measurements have been shown to be a reliable way of extracting relevant physical parameters from a system. It is a well-developed method of thermometry [42, 43] and has been used to measure the Boltzmann constant with a high degree of precision [44]. For the purposes of quantum sensing using magnetic

tunneling junctions, thermal noise is used as a precise means of measuring the MTJ resistance, which changes in the presence of local magnetic fields. Therefore, fluctuations in the thermal noise at a given frequency would indicate the presence of magnetic fluctuation at that frequency, creating a change in the local field, and thus resistance and thermal noise of the MTJ.

1.2.3 Shot Noise

Shot noise, also known as Poisson noise, is noise that arises due to the discrete nature of charge carriers. It originates from charge carriers crossing barriers in a random and uncorrelated way which can be modeled by a Poisson distribution. The power spectral density due to shot noise can be described by,

$$S_I = 2eI, \quad (1.6)$$

where e is the charge of the an electron and I is the average DC current through the device. The factor of two is introduced to account for the identical contribution of both positive and negative frequencies [38, 39].

The actual shot noise measured can be suppressed compared to the value calculated from Eq. (1.6). This difference is characterized by the Fano factor,

$$F = S/2eI, \quad (1.7)$$

where S is the measured shot noise. The presence of correlated electrons means that the carrier crossings are no longer completely Poissonian, which leads to a reduction of the shot noise ($F < 1$). Different barriers have different Fano factors: ballistic barriers have $F = 0$, diffusive barriers have $F = 1/3$, and tunnel barriers have $F = 1$ [30, 45]. In some cases, the shot noise can even be enhanced due to instabilities caused by interactions [46]. In most MTJs, the Fano factor depends on the relative orientation

of the magnetization vectors of the free and pinned ferromagnetic layers and is usually around 1, but has also been found to be suppressed in some MTJs [39, 47].

With the exception of measurements taken at very low temperatures, the noise of a MTJ biased with voltage V will contain both shot noise and thermal noise. These two noise sources can be described in a single equation of the form,

$$S_V = 2eRV \coth \left(\frac{eV}{2k_B T} \right), \quad (1.8)$$

where R is the MTJ resistance, e is the charge of an electron, k_B is the Boltzmann constant, and T is the temperature of the MTJ.

Shot noise provides information that is not present in time-averaged values and is a powerful tool in the detection of fractional charges in materials. Shot noise measurements have been used to study fractional charges in the fractional quantum Hall regime [48, 49] and to detect Cooper pairs in superconducting-normal junctions [50]. In the fractional quantum Hall regime, the electron charge e in Eq. (1.6) becomes $e^* = e/q$ where e^* denotes the effect charge of the carriers and $1/q$ is the fractional filling factor. For the case of Cooper pairs in a superconducting-normal junction, $e^* = 2e$. This motivates the desire to measure the MTJ shot noise as a means of detecting evidence of fractional excitations characteristic of quantum entangled states which could lead to the detection of emergent phenomena such as quantum spin liquids.

CHAPTER 2

Measuring MTJ Noise

In order to realize magnetic sensing by means of detecting changes in the electronic noise of a magnetic tunnel junction (MTJ), a measurement system capable of measuring such small signals over a wide frequency bandwidth was designed. Each component of the measurement circuit was carefully considered in order to minimize the systematic noise and preserve the desired MTJ noise. This chapter will cover the details of the measurement set-up as well as specifics about the probe and strategies implemented to mitigate systematic noise.

2.1 Measurement Set-Up

The measurement set-up used to measure the electronic noise of MTJs is shown in Figure 2.1. The components of the circuit diagram that are highlighted in blue sit at the foot of the probe to be cooled to cryogenic temperatures. The rest of the components, as shown in the photo in Figure 2.1, remain at room temperature. There are three main components of the measurement system: the spectrum analyzer, the voltage bias circuit for the MTJ, and the amplifiers.

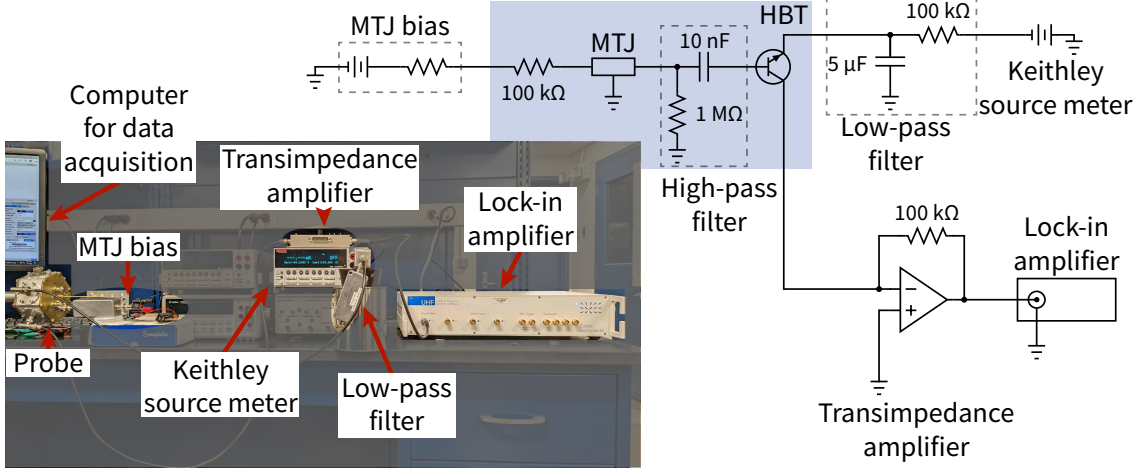


FIGURE 2.1: Circuit diagram showing the experimental set-up used to measure the MTJ noise. The region highlighted in blue represents the part of the circuit that sits at the base of the probe. The photo shows the room temperature components of the system. This is the set-up for an HBT-based low-temperature amplifier, but the set-up for other low-temperature amplifiers is similar.

2.1.1 Spectrum Analyzer

A Zurich Instruments UHFLI 600 MHz bandwidth lock-in amplifier was used as the spectrum analyzer. This lock-in amplifier allows for precise measurements of signals across a range of frequencies and has a built-in noise measurement feature, which allows for noise spectra to be measured with ease. The basics of lock-in detection and its application to noise measurements are outlined below.

Principles of Lock-In Detection

Lock-in amplifiers utilize a homodyne detection scheme and low-pass filters to isolate a signal at a specific frequency ω_s from a noisy signal. It does this by mixing the incoming signal with a reference signal at a known frequency ω_r . The mixing of the two signals creates a new signal with two frequency components, one at the difference between the reference frequency and the signal frequency ($\omega_- = \omega_r - \omega_s$), and a second at the sum of the two frequencies ($\omega_+ = \omega_r + \omega_s$). By applying a low-pass filter to the resulting signal, only the ω_- component survives. The bandwidth of the low-pass filter determines the range about the reference signal that is measured. For example,

a low-pass filter with a cutoff frequency near zero will only allow signals within a very small bandwidth of the reference frequency to survive, since $\omega_r = \omega_s$ returns a signal at $\omega_- = 0$. This process of mixing a signal from the system under investigation with a reference signal is called “demodulation” or “phase-sensitive detection” where the reference frequency is the demodulator frequency.

The lock-in amplifier adds another degree of sophistication to this process by mixing the measured signal with the reference signal *and* a 90° phase-shifted copy of the reference signal. This is called “dual-phase demodulation” or “quadrature detection” and allows both the amplitude and the phase (relative to the reference) of the signal to be determined. This is easiest to understand by looking at the math behind the process.

Consider a complex signal that is a sum of two vectors with magnitude $\sqrt{2}R$ rotating in the complex plane at the same frequency ω_s but in opposite directions, *i.e.* a sinusoidal wave:

$$V_s(t) = \sqrt{2}R \cos(\omega_s t + \theta) = \frac{\sqrt{2}}{2}R \left(e^{-i(\omega_s t + \theta)} + e^{i(\omega_s t + \theta)} \right). \quad (2.1)$$

We can define the reference signal at frequency ω_r as

$$V_r(t) = \sqrt{2} \cos(\omega_r t) - i\sqrt{2} \sin(\omega_r t) = \sqrt{2}e^{-i\omega_r t}. \quad (2.2)$$

Mixing these two signals returns

$$Z(t) = V_s(t)V_r(t) = R \left(e^{i[(\omega_s - \omega_r)t + \theta]} + e^{-i[(\omega_s + \omega_r)t + \theta]} \right). \quad (2.3)$$

After applying a low-pass filter to keep only the difference between the two signals, what remains is

$$Z(t) = R e^{i[(\omega_s - \omega_r)t + \theta]}, \quad (2.4)$$

and if $\omega_s = \omega_r$ then,

$$Z(t) = R e^{i\theta} = R (\cos \theta + i \sin \theta), \quad (2.5)$$

which returns the amplitude R and phase θ of the signal. The real part of $Z(t)$ is the in-phase component ($\Re(Z) = R \cos \theta = X$) and the imaginary part is the quadrature component ($\Im(Z) = R \sin \theta = Y$) [51].

Noise Measurements

The Zurich UHFLI 600 MHz lock-in amplifier has a noise floor below $8 \text{ nV}/\sqrt{\text{Hz}}$ with a 10 mV input range and $1 \text{ M}\Omega$ input impedance. The MTJ noise is on the order of $10 \text{ nV}/\sqrt{\text{Hz}}$, so the signal needs to be amplified before it is input into the lock-in in order to ensure the signal sits well above the instrument’s noise floor.

The Zurich Instruments’ LabOne Instrument Control Software has a built-in “Noise Amplitude Sweep” procedure. This procedure sweeps the demodulator frequency over a desired frequency range and collects multiple data samples at each frequency. The standard deviation of the samples at each frequency is calculated and returned as the noise amplitude spectral density ($\text{V}/\sqrt{\text{Hz}}$) at that frequency.

There are various lock-in parameters that can be tuned to increase the precision of the noise measurement. The cutoff frequency of the low-pass filter applied directly after mixing the signal with the reference is set by the lock-in time constant τ_c . A long time constant corresponds to a low cutoff frequency, and a short time constant corresponds to a high cutoff frequency. The goal of a noise amplitude sweep is to determine the noise at the reference frequency, so the signal of interest is the $\omega_- = 0 \text{ Hz}$ signal that comes from the mixer. In general, a low cutoff frequency will improve the precision of the measurement as it will filter out more of the contributions from noise at frequencies not equal to the reference frequency. However, a low cutoff frequency comes at the expense of measurement time since a longer time constant is necessary. The “Noise Amplitude Sweep” procedure has an “auto-bandwidth” setting

that adapts the time constant/bandwidth of the low-pass filter as the frequency is swept to optimize between measurement time and precision. The “auto-bandwidth” setting was found to be optimal for our measurements.

The wait time between a change in the sweep frequency and the first measurement at that frequency also affects the precision of the noise measurement. The wait time, also called the settling time, is the amount of time required for the new sweep parameter to reach the desired accuracy. The settling time is determined by the time constant of the filter and the desired accuracy and set to whichever value is larger. When using the “Noise Amplitude Sweep” procedure, the measurement precision can be set to “low”, “high”, or “very high”, which changes the settling time to achieve the desired precision. This means that the measurement time increases with increased precision. For initial measurements to ensure that the measured signal is of the expected order of magnitude, “low” precision is sufficient, but “high” or “very high” precision is recommended for actual data acquisition.

2.1.2 MTJ Voltage Bias

In order to measure the shot noise of the MTJs, a voltage bias must be applied to the device. We initially used a Keithley 2400 source meter to apply a voltage bias, since it allows for easy control of the applied voltage and simultaneous measurement of the current being drawn, but quickly found that the Keithley introduced significant noise into the measurement. To mitigate the noise, we replaced the Keithley with a battery and resistor. Although this was effective in eliminating the input noise from the bias voltage source, it introduced a new problem which was accurately determining the voltage applied to the MTJ. This may seem like a trivial problem, except that the MTJ resistance changes when a voltage is applied to it. To circumvent this problem, we measured the voltage of the battery and used the Keithley to apply the same voltage to the MTJ through the bias resistor used with the battery while simul-

taneously reading out the current. Since the resistance of the bias resistor remains constant across all measurements, it is a normal thin film resistor that remains at room temperature even when the MTJ is cooled, this proved to be an effective means of determining the MTJ resistance. The Keithley source meter was disconnected from the measurement circuit before taking data.

2.1.3 Amplifiers

As mentioned above, the MTJ noise must be amplified above the noise floor of the lock-in amplifier to be read. One possible solution to this problem is to use more resistive MTJs to increase the electronic noise above the noise floor of the lock-in without amplification. This proves to be a poor solution as increasing the resistance of the MTJs also increases the RC roll-off of the MTJ-probe system, which limits the accessible frequency range of the MTJ sensors. Therefore, amplification of the signal is necessary.

There are two amplifiers shown in the circuit diagram in Figure 2.1. One is a low-temperature heterojunction bipolar transistor (HBT)-based amplifier, and the other is a room-temperature transimpedance amplifier (TIA). The transimpedance amplifier is necessary when the HBT low-temperature preamp is used to convert the current gain from the HBT into a voltage gain which is ultimately what is measured. Without the HBT low-temperature preamp, the transimpedance amplifier in the circuit diagram in Figure 2.1 can be replaced by any low-noise room-temperature preamplifier.

The MTJ Johnson noise measurements in Figure 2.2 were taken using a room-temperature Stanford Research Systems SR560 low-noise preamplifier and no low-temperature amplifier. The measurements are in good agreement with the expected noise values, denoted by the dashed lines, and calculated with Eq. (1.5), however there are a few limitations introduced by the room-temperature amplifier. One clear

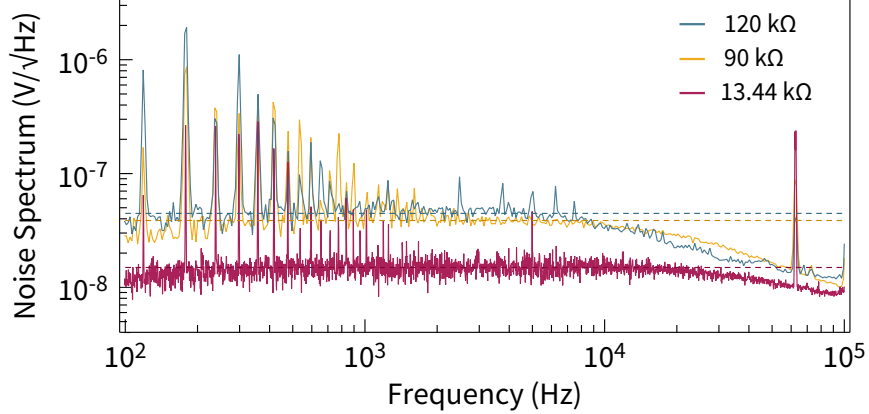


FIGURE 2.2: Johnson noise spectra of three MTJs with different resistances measured at room temperature using the lock-in amplifier and a room-temperature amplifier. The dashed lines represent the expected Johnson noise for each resistance calculated using Eq. (1.5). The 13.44 kΩ MTJ noise measurement appears noisier than the other two because more points are taken over the same frequency range.

limitation is the noise introduced by the amplifier, most notably the 60 Hz spikes at low frequencies. The SR560 also has a limited bandwidth of < 1 MHz, so the noise spectra in Figure 2.2 are only measured up to 100 kHz. However, the initial deviation of the measured noise from the expected value is due to the RC roll-off of the MTJ-probe system, highlighting the need for lower resistance MTJs to achieve a sensor capable of detecting fluctuations at frequencies in the MHz range. Since Johnson noise is proportional to resistance, lower resistance means lower Johnson noise, so amplifying the noise as close to the source (MTJs) as possible will minimize signal loss and amplify just the MTJ noise without amplifying noise from other elements in the measurement circuit that may be introduced to the signal before it is measured. This calls for the need to implement a low-noise, wide-bandwidth preamplifier that operates at cryogenic temperatures.

2.2 Low-Temperature Preamplifiers

Implementing a preamp at the foot of the probe, directly next to the MTJ, serves to amplify only the MTJ noise and minimize signal loss between the sample and the

read-out. The goal is to have an amplifier that is operational from the millikelvin temperature range up to room temperature, can amplify signals that range in frequency from a few kilohertz up to a few gigahertz, and introduces a minimal amount of noise into the signal. Many highly effective cryogenic preamplifiers have been designed [52–55], but none meet all the criteria outlined above. The most notable barrier is in the accessible bandwidth; existing cryogenic amplifiers have bandwidths either from DC up to several MHz or that sit fully in the GHz range without overlap. To investigate whether a cryogenic amplifier with a bandwidth ranging from DC up to the GHz range is possible while also maintaining low noise, several transistor-based low-temperature amplifiers were tested.

2.2.1 Heterojunction Bipolar Transistor

The first low-temperature amplifier we implemented was a heterojunction bipolar transistor (HBT)-based amplifier. These amplifiers were made by collaborators at the Sandia National Laboratory Center for Integrated Nanotechnologies and the details of their design can be found in Ref. [56]. The HBT is a current amplifier; its gain is determined by the ratio between the collector current and the base current. As we are more interested in measuring the voltage for purposes of obtaining the voltage spectral density, a transimpedance amplifier was implemented at the room temperature stage to convert the current gain into a voltage gain. HBTs work well as low-temperature amplifiers as they have low $1/f$ noise and can achieve a higher gain with the same applied power relative to high-electron mobility transistors (HEMTs).

HBT Basics

Bipolar transistors are semiconducting current-controlled devices that consist of two p - n junctions. They have three terminals, an emitter that emits charge carriers, a collector that collects the charge carriers, and a base between the emitter and the collector that controls the number of charge carriers that pass between them. These

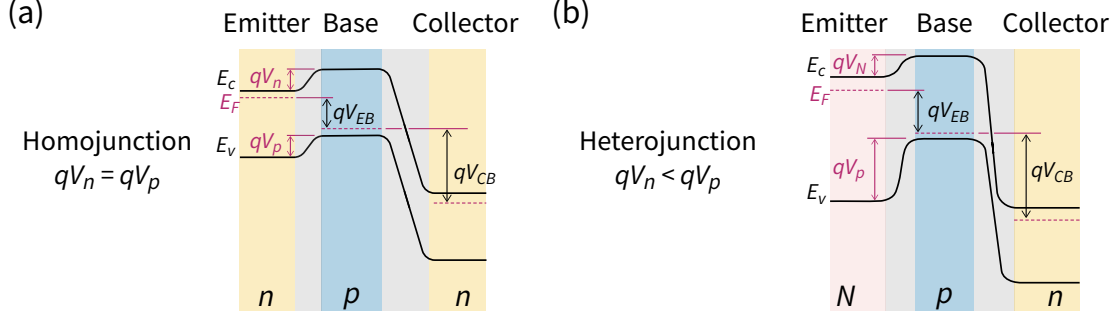


FIGURE 2.3: Band diagrams of (a) a homojunction bipolar junction transistor and (b) a heterojunction bipolar transistor. E_c denotes the conduction band, E_F the Fermi level, and E_v the valence band. q is the charge of an electron, $V_{n(p)}$ is the potential barrier for electron (hole) injection, and V_{EB} and V_{CB} are the emitter-base and collector-base voltage differences respectively. The grey region between the p - n junctions is the depletion region. Adapted from a figure in Ref. [57].

transistors can be npn -type or pnp -type. In the npn -type transistor, the emitter and collector are both n -type semiconductors doped with an excess of electrons and the base is a p -type semiconductor doped with holes. In the pnp -type transistor, the emitter and collector are p -type semiconductors and the base is a n -type semiconductor. At the interface between the n - and p -type semiconductors, there is an insulating region with no mobile charge carriers called the depletion region. The bipolar transistor used for the purposes on these experiments is a npn -type transistor, so what follows will focus on that type.

When the p - n junction is forward (reverse) biased, a positive (negative) voltage is applied to the p side with respect to the n side which shrinks (widens) the depletion region and decreases (increases) the potential difference across the depletion region. A bipolar transistor is considered to be in “active mode” when the base-emitter junction is forward-biased ($V_{BE} > 0$) and the base-collector junction is reverse-biased ($V_{CB} < 0$). In this configuration, a large number of electrons travel from the emitter, through the base and to the collector, with only a small number of holes flowing from the base to the emitter [58].

Referencing Figure 2.3, V_n (V_p) represents the potential barrier that electrons

(holes) must overcome to travel between the emitter and the base. In a homojunction bipolar transistor, commonly referred to as a bipolar junction transistor, the transistor is made of a single material such that $V_n = V_p$. Changing the voltage across the emitter-base junction V_{BE} changes the potential barrier which also changes the flow of carriers, *i.e.* the current, through the transistor, so bipolar transistors are a voltage-controlled current source which makes them useful for amplification.

In a heterojunction bipolar transistor, the emitter is made from a semiconductor with a wider band gap than the base, as shown in Figure 2.3(b). The wider band gap of the emitter means that the barrier to electron injection is smaller than the barrier to hole injection ($V_p > V_n$), which makes the injection of electrons across the emitter junction preferential and limits the injection of holes. A change in the barrier height exponentially changes the carrier injection, so a small change in the barrier height can drastically change the transport of electrons and holes through the base-emitter junction [57]. The limitation of hole mobility through the base makes HBTs effective amplifiers, as we will see in the next section.

HBT Amplification

Since the emitter and collector current are controlled by a relatively small base current, it is straightforward to see how HBTs would be useful as current amplifiers whose gain β is simply the ratio between the collector and base current, $\beta = I_C/I_B$. The HBT amplifier circuit shown in Figure 2.1 has the HBT in a common-emitter configuration, where a small input signal from the MTJ is applied to the base and the amplified signal is read out through the collector. The voltage bias applied through the emitter sets V_{BE} and the 160 Hz high pass filter between the MTJ and the base prevents the DC bias applied to the MTJ from changing V_{BE} .

The collector current consists entirely of electrons injected at the emitter that

aren't lost to recombination in the base, so

$$I_C = B I_{E_n} \quad (2.6)$$

where B is the base transport factor which quantifies the fraction of electrons that make it across the base and I_{E_n} is the emitter current due to negative charge carriers (electrons). The total emitter current also includes the current due to positive charge carriers, $I_E = I_{E_n} + I_{E_p}$ and the emitter injection efficiency is defined as,

$$\gamma = \frac{I_{E_n}}{I_{E_p} + I_{E_n}}. \quad (2.7)$$

The current transfer ratio is,

$$\frac{I_C}{I_E} = \frac{B I_{E_n}}{I_{E_p} + I_{E_n}} = B\gamma \equiv \alpha \quad (2.8)$$

which quantifies the current amplification between the emitter and the current which should be close to one ($\alpha \lesssim 1$) since most injected electrons should participate in the collector current so that $B \approx 1$ and $\gamma \approx 1$.

The base current is determined by the rate at which holes are lost from the base by injection across the emitter junction and the rate of electron recombination with holes in the base since lost holes must be resupplied by the base current I_B . The fraction of electrons that are lost to recombination in the base is $(1 - B)$, so the base current is,

$$I_B = I_{E_p} + (1 - B)I_{E_n}. \quad (2.9)$$

We can now write the amplifier gain as,

$$\beta = \frac{I_C}{I_B} = \frac{B I_{E_n}}{I_{E_p} + (1 - B)I_{E_n}} = \frac{B [I_{E_n}/(I_{E_p} + I_{E_n})]}{1 - B [I_{E_n}/(I_{E_p} + I_{E_n})]} = \frac{B\gamma}{1 - B\gamma} = \frac{\alpha}{1 - \alpha}, \quad (2.10)$$

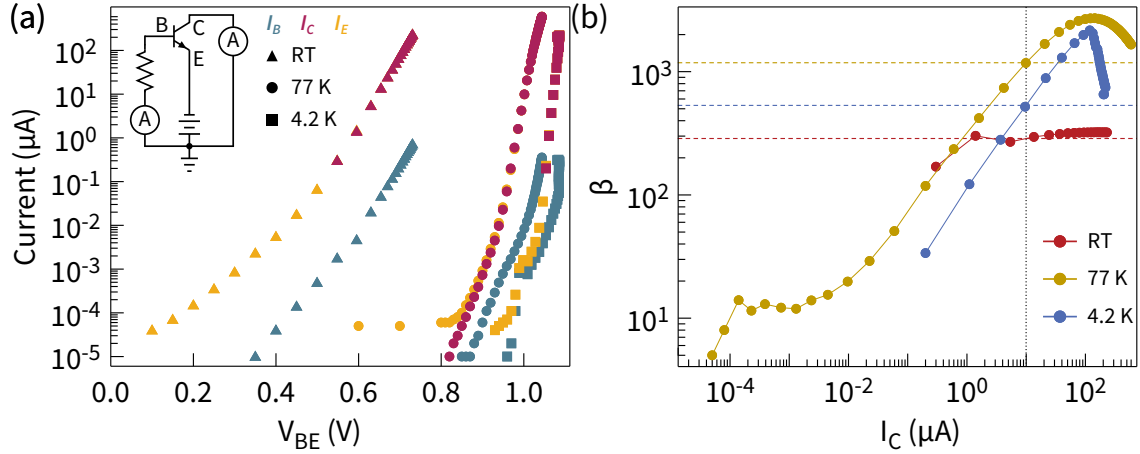


FIGURE 2.4: (a) Gummel plot for the HBT amplifier circuit measured at room temperature (RT $\sim$ 298 K), 77 K, and 4.2 K. I_B is the base current, I_C is the collector current, and I_E is the emitter current. The circuit diagram in the inset shows the set-up used to measure the Gummel plot. The resistor on the base is a 1 M Ω resistor. (b) The HBT gain β as a function of collector current at room temperature, 77 K and 4.2 K.

from which it is clear that limiting the hole mobility across the emitter junction by application of a heterojunction will increase the gain achievable by the HBT.

HBT Gain Calibration

The HBT gain must be carefully characterized as it depends on many intertwined variables, as is evident in Eq. (2.10). The gain of our HBT amplifier was calibrated using the circuit in the inset of Figure 2.4(a). A voltage was applied through the emitter to set V_{BE} with a Keithley source meter that also served to measure the current drawn. The resistor between the base and the ammeter is a 1 M Ω resistor that is not necessary to calibrate the HBT gains but is on the HBT amplifier chip between the contact pad and the base, so it could not be avoided.

Figure 2.4(a) is the Gummel plot with data at room temperature (298 K), in liquid nitrogen (77 K), and in liquid helium (4.2 K). This plot shows the base current I_B , collector current I_C , and emitter current I_E for a set of applied base-emitter voltages V_{BE} . This provides a visual representation of the gain β as a function of V_{BE} and allows the gain for a given V_{BE} to be easily calculated. The voltage applied by the

Keithley is $V_K = V_{BE} + I_B(1 \text{ M}\Omega)$.

The gain as a function of the collector current I_C is shown in Figure 2.4(b). We represent the gain calibration as a function of collector current because the base current will be set in part by the output signal from the MTJ, so the only way to determine the gain for a set of data is to measure the collector current and to know what the associated gain is based on the calibration. It was determined that $I_C = 10 \text{ }\mu\text{A}$ was a good operating point for the HBT amplifier, as it provides an appropriate amount of gain without itself introducing an abundance of noise. As denoted by the dashed lines in Figure 2.4(b), $\beta_{298 \text{ K}} = 286$, $\beta_{77 \text{ K}} = 1180$, and $\beta_{4.2 \text{ K}} = 531$.

Transimpedance Amplifier

A Femto DLPCA-200 transimpedance amplifier (TIA) was used with the HBT low-temperature amplifier to supply current to voltage amplification. Its gain is determined by the ratio of the input current to the output voltage which is set by the feedback resistor. A higher resistance feedback resistor provides a larger transimpedance gain; however, the frequency bandwidth of the TIA is inversely proportional to the resistance, so a higher gain comes with the trade-off of reducing the operational frequency range of the measurement system. A transimpedance gain of $100 \text{ k}\Omega$ provided an adequate voltage gain for these measurements without limiting the bandwidth of the measurement system. The Femto DLPCA-200 was operated in low-noise mode with DC coupling and $\times 1 \text{ V}$ gain.

With the transimpedance gain set to $100 \text{ k}\Omega$, the voltage gain due to the HBT-TIA amplifying system is determined by:

$$A_V = g_m R_{TIA}, \quad (2.11)$$

where g_m is the transconductance of the HBT and R_{TIA} is the collector resistance. The

transconductance is the derivative of the output current with respect to a change in input voltage, $g_m = dI_{out}/dV_{in}$. From the HBT Gummel plots, the transconductance was found at each temperature to be $g_m^{289\text{ K}} = 369 \pm 1.6\text{ }\mu\text{A/V}$, $g_m^{77\text{ K}} = 1166 \pm 7.4\text{ }\mu\text{A/V}$, and $g_m^{4.2\text{ K}} = 2062 \pm 40.5\text{ }\mu\text{A/V}$. Since $R_{TIA} = 100\text{ k}\Omega$, the resulting voltage gains are $V_{gain}^{298\text{ K}} = 36.9$, $V_{gain}^{77\text{ K}} = 116.6$, and $V_{gain}^{4.2\text{ K}} = 206.2$.

Viability of HBT Preamps

An example of MTJ shot noise measured with the use of an HBT preamp near the device compared to MTJ shot noise measurements taken with only a room temperature amplifier are shown in Figure 2.5(a) and (b). In Figure 2.5(c) and (d), the measured value, averaged over the shaded frequency range in (a) and (b), is compared to the expected value calculated with Eq. (1.8). These plots clearly show that the accuracy of the measurement is better when the signal is amplified with an HBT preamp than when no low-temperature amplifier is used.

Despite the clear improvement in the accuracy of the measurement, the data in Figure 2.5 also show some drawbacks of the HBT amplifiers. The most significant drawback is the limited bandwidth due to the HBT which has a cutoff frequency of 500 kHz and transimpedance amplifier which has a cutoff frequency of 400 kHz. The low frequency noise with the HBT preamp also persists to higher frequencies than without the HBT preamp, overall limiting the frequency range over which the MTJ shot noise can be measured. The HBT circuit used for these measurements was not optimized for high-frequency applications [56], so some changes to the HBT amplifier circuit could yield a higher bandwidth. For example, replacing the 100 k Ω shunt resistor with a 10 k Ω shunt resistor could increase the bandwidth to 1 MHz. This does not address the limited bandwidth of the TIA, so a TIA with a higher frequency cutoff would also need to be implemented.

HBTs are low-noise amplifiers, which is a useful characteristic when considering

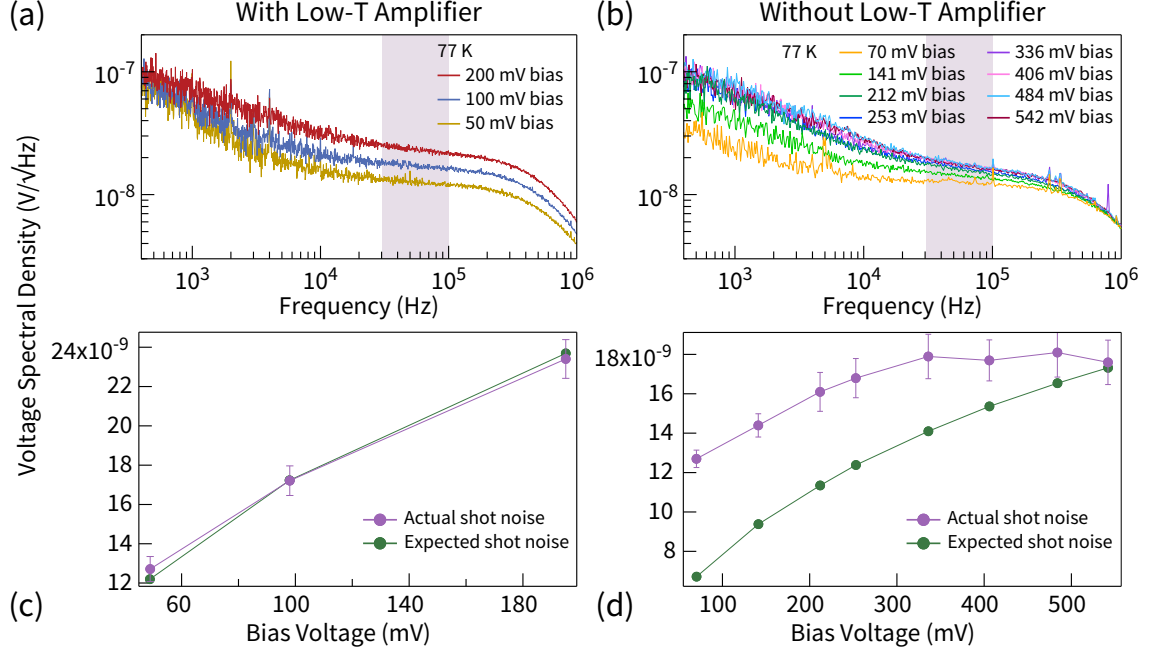


FIGURE 2.5: (a) Shot noise of a 9 kΩ MTJ measured with a low-temperature amplifier and (b) shot noise of a 3 kΩ MTJ measured without. (c) and (d) show the measured shot noise averaged over the shaded frequency range in (a) and (b) compared to the expected values calculated from Eq. (1.8). All measurements were taken at 77 K.

their viability for applications in measuring MTJ noise. There are several contributions to the total noise of the HBT-TIA amplifier: shot noise introduced by the base and collector current, Johnson noise proportional to the input resistance of the HBT, and noise of the TIA. The TIA noise is given in the Femto DLPCA-200 datasheet and should be multiplied by the resistance of the feedback resistor and normalized by the voltage gain to obtain its contribution to the total system noise. A color map showing the ratio of the MTJ noise to the HBT-TIA noise with a range of MTJ resistances and bias voltages is shown in Figure 2.6. The solid color regions in the plots in (a) and (b), $T = 298$ K and $T = 77$ K respectively, represent regions where the MTJ noise is less than the noise introduced by the amplifiers. This region disappears completely in (c) where $T = 4.2$ K, which highlights the significant decrease in HBT noise when operated at cryogenic temperatures.

Overall, HBT-based amplifiers are a good option for low-temperature amplifica-

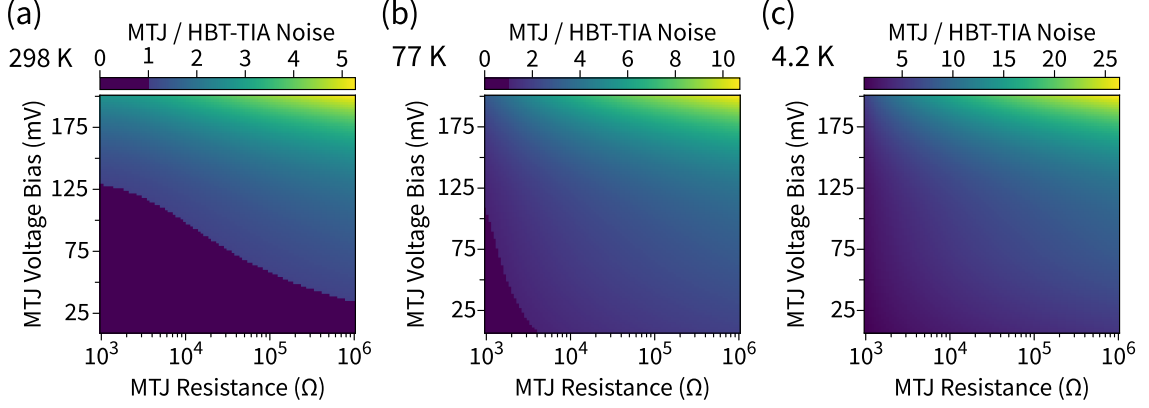


FIGURE 2.6: MTJ shot noise normalized by the HBT-TIA amplifier system noise for various MTJ resistances and bias voltages at (a) 298 K, (b) 77 K, and (c) 4.2 K. The solid color regions in (a) and (b) represent ranges where the HBT-TIA noise is larger than the MTJ noise (normalized value ≤ 1). The HBT is biased such that $I_C = 10 \mu\text{A}$ and the transimpedance gain is $100 \text{ k}\Omega$. This model only accounts for frequency independent noise.

tion to measure MTJ noise, but the current HBT amplifier circuit could benefit from being optimized for this specific application. HBTs provide a significant gain without introducing a significant amount of their own noise. The largest drawback is the limited bandwidth of the HBT-TIA system. A high frequency roll-off starting around 400 kHz leaves only a very limited range over which the MTJ noise dominates over the low-frequency noise, which limits the type of emergent phenomena the MTJ sensors could detect to those that fall within this limited frequency range.

2.2.2 Other Transistors

The bandwidth limitations of the HBT preamplifier prompted the tests of other transistors that would operate over a wider bandwidth. Two different types of transistors were tested, pseudomorphic high-electron-mobility transistors (pHEMT) and complementary metal-oxide-semiconductor (CMOS) transistors. The amplifier circuits using these transistors were optimized by collaborators for high-gain and low-noise input over a wide frequency range. Both amplifier models experienced difficulty operating throughout the entire temperature range of interest. Some versions worked

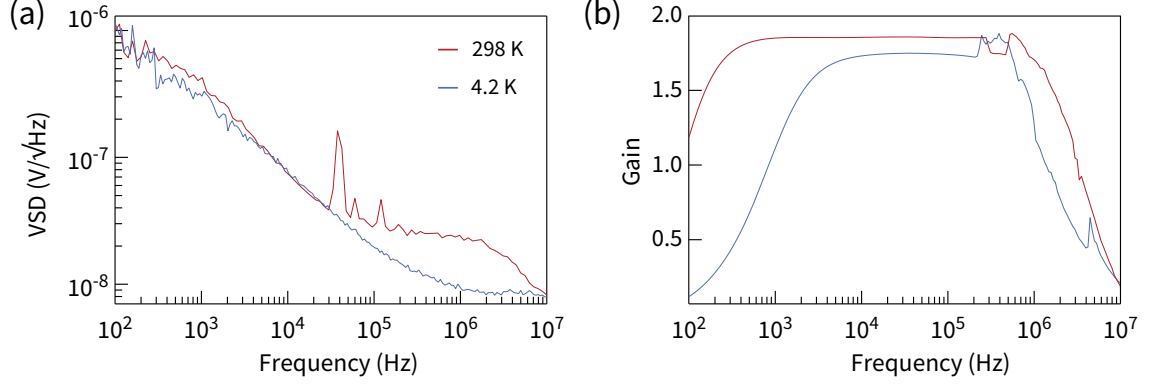


FIGURE 2.7: (a) Johnson noise voltage spectral density (VSD) and (b) gain of a pseudomorphic high-electron-mobility transistor (pHEMT)-based amplifier at room temperature (289 K) and 4.2 K.

well at 77 K and room temperature, but failed at 4.2 K and others worked poorly at room temperature and exactly as intended at 4.2 K. Many different factors were at play as the different behaviors of the various components of the amplifier circuit at cryogenic temperatures needed to be accounted for and were rarely predictable.

The testing of these amplifiers was done using the same dip stick that we designed for the MTJ measurements. Once the amplifier was mounted, most often with a dummy resistor in place of the MTJ, the dip stick was cooled in liquid nitrogen (77 K) and liquid helium (4.2 K) to test its operation at cryogenic temperatures. As the amplifier cooled, the current was monitored using the Keithley source meters. This gave some initial indication as to the functionality of the amplifier at cryogenic temperatures. Once thermally equilibrated at the target temperature, assuming that the amplifier remained operational, an oscilloscope was used to investigate the quality of the signal over the frequency range of interest. If the signal was satisfactory, then noise measurements were taken using the lock-in amplifier to ensure that the noise floor was sufficiently low to not dominate over the MTJ signal.

Figure 2.7 shows an example of noise and gain measurements taken on a pHEMT-based low-temperature amplifier. The noise is clearly not ideal as it changes a lot over the frequency range of interest, introducing a significant amount of low-frequency

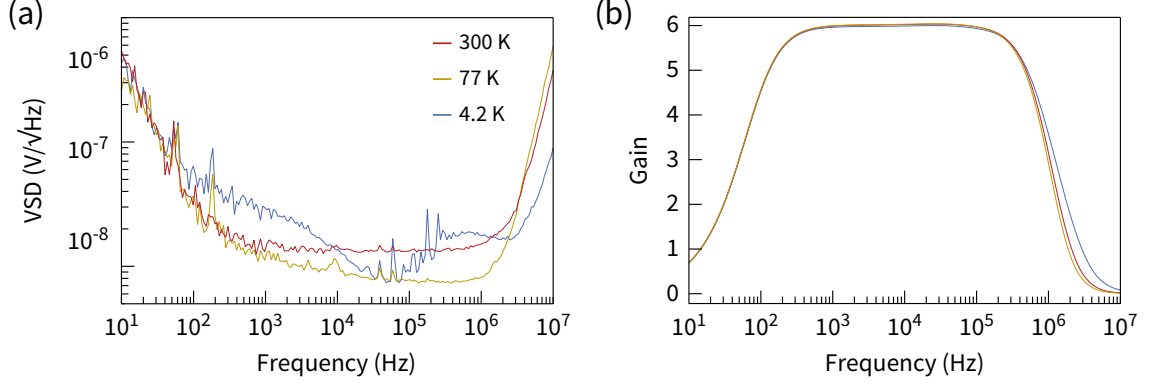


FIGURE 2.8: (a) Johnson noise voltage spectral density (VSD) and (b) gain of a complementary metal-oxide-semiconductor (CMOS) field effect transistor-based amplifier at room temperature (289 K), 77 K, and 4.2 K.

noise. The gain also only operates over a relatively small frequency range at 4.2 K which introduces significant limits on its applicability. The features in the high-frequency gain are expected to be due to the breakdown of the amplifier as its frequency bandwidth is reached.

Figure 2.8 shows an example of noise and gain measurements taken with a CMOS-based low-temperature amplifier. The noise is fairly low over a wider frequency range at room temperature and 77 K, but some breakdown is evident at 4.2 K. The gain also remains constant over consistent frequency ranges for all three temperatures measured, and the accessible frequency range is the same range of interest for the MTJ noise measurements to date, although future measurements would ideally reach a higher frequency range. Gain measurements for both amplifier models were taken with the lock-in amplifier, measuring the signal amplitude as the demodulator and input signal frequency are swept.

In the scope of this work, no low temperature amplifier was found that met all of the requirements of the MTJ sensors. The HBT-based amplifiers are a good solution, especially if a wider bandwidth TIA was implemented but they still face the limitation of high noise levels at low frequencies. The CMOS-based amplifier also worked well and is a good option for the continued development of an amplifier circuit using CMOS

transistors. Developing an appropriate low-temperature amplifier is an important part of realizing MTJ-based sensors of quantum magnetism and is the subject of continued work by collaborators.

2.3 Probe

The desire to measure small signals with high precision and low signal loss over a wide frequency range and in cryogenic environments motivated the need to design a probing instrument to meet these specific needs. Many sophisticated probes have been designed for applications in nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) and noise measurements [59–62]. Specialized dipsticks for measuring the shot noise of atomic and molecular junctions have also been designed [61,63]. The limitations of these previous designs in either signal loss, bandwidth, or functionality at cryogenic temperatures motivate the design of the probe discussed here.

2.3.1 Build Information

The goal of this project was to build a low-loss probe capable of measuring signals over a wide frequency range, maintaining a steep thermal gradient, and operating in a high magnetic field. Having a low-loss probe is necessary for measuring small signals and it needs to operate over a wide frequency range since the frequency range over which spin fluctuations characteristic of emergent quantum phenomena can occur is very large [29]. Most quantum phenomena emerge at cryogenic temperatures, thus motivating the need for it to maintain a steep thermal gradient, and the desire for the probe to be broadly applicable to many types of measurement motivated its design to be non-magnetic.

The main design of the probe is shown in Figure 2.9 and the part numbers and manufacturers of all the components are listed in Table 2.1. The probe head is

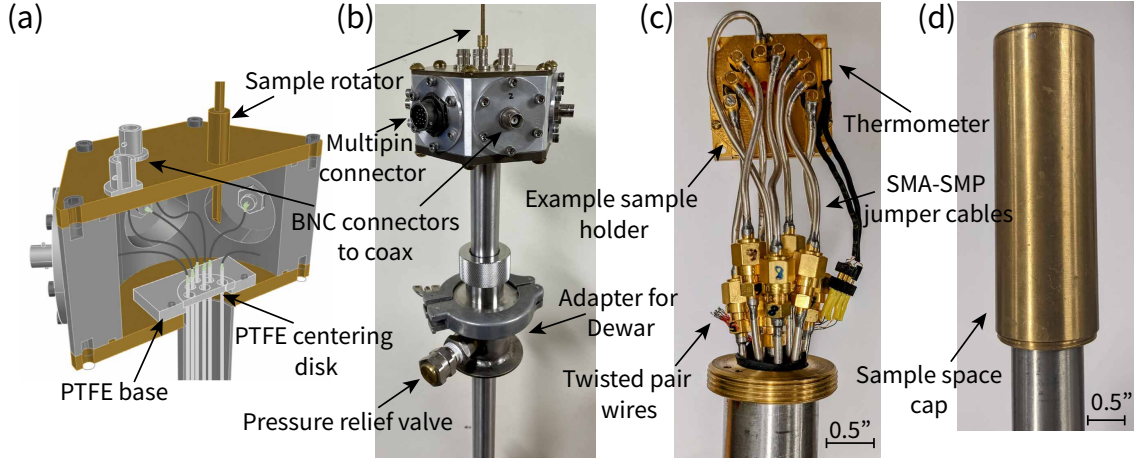


FIGURE 2.9: (a) Schematic cut-away showing the inside of the probe head, (b) photograph of the probe head, (c) of the foot of the probe with the MTJ sample holder, and (d) the foot of the probe with the sample space cap in place.

constructed from aluminum and measures 2.5 inches in height. The top and bottom plates are made of brass, just thick enough for the o-ring groove in order to minimize weight. A cross-sectional view of the probe head shown in Figure 2.1(a) shows the flexible coax cables that connect the BNC connectors to the semi-rigid coax that run the length of the probe. Care was taken to preserve the $50\ \Omega$ impedance of the lines at the solder joints by wrapping the inner conductor in polytetrafluoroethylene (PTFE) insulation and connecting the outer conductors of the coax with a conductive metal shielding over the insulator, which also serves to maintain a common ground. The semi-rigid coax lines that run the length of the probe are fed through PTFE centering rings spaced throughout the probe and suspended by a 304 stainless steel rod that provides vertical support. At the head of the probe, another centering disk sits in a PTFE base that allows the disk, and coaxial lines with it, to rotate freely throughout the length of the probe without putting strain on individual soldering joints at the head of the probe.

The probe is designed to be able to be inserted directly into a 60 L liquid helium Dewar for quick low temperature measurements. An external coupler, shown in Figure 2.9(b), slides over the body of the probe and makes a vacuum seal by means of

Item	Part Number	Manufacturer	Notes
Body of probe			
Semi-rigid coax	UT-085C-SP	Microstock	Silver-plated copper conductors, 0.45 dB/m insertion loss at 0.5 GHz
Quad-Twist wire	WQT-32-100	LakeShore	Two twisted pairs (4 leads), 32 AWG, phosphor-bronze
Head of probe			
BNC connector	031-4237	Amphenol RF	Hermetic, 50 Ω , rear mount, jack
Multi-pin connector	PT07A-12-14P	Amphenol RF	Hermetic, 14 pin, plug
Hand-formable coax	UT-047-FORM	Microstock	0.279 mm diameter, 0.95 dB/m insertion loss at 0.5 GHz
Multi-pin connector	7281-8PG-300	Conxall/Switchcraft	Hermetic, 8 pin, plug
Foot of probe			
SMP connector	18K201-271L5	Rosenberger	50 Ω , jack, in-line right angle
SMA connector	11.SMA-50-2-15	Microstock	CuBe alloy contacts, plug, in-line, UT-85 coax cable
SMA connector	21.SMA-50-2-15	Microstock	CuBe alloy contacts, jack, in-line, UT-85 coax cable
Thermometer	CX-1010-AA	Lakeshore	Cernox thin-film resistance thermometer
Dewar adapter			
Pressure relief valve	VALREL1/2-10	Cryofab, Inc.	10 PSIG, 1/2" NPT
Dewar gasket	GASKET2.5	Cryofab, Inc.	2 1/2" Buna o-ring for Dewar
Dewar cap	CAP2.5	Cryofab, Inc.	2 1/2" 304 SS cap to fit top of Dewar
Quick connect	NW50-Q100-VE	LDS Vacuum	NW50 quick connect for 1 inch tube
Blank SS cap	NW50-200-SB-OS	LDS Vacuum	NW50 blank

TABLE 2.1: Components used in the build of the probe.

the quick-connect so that the probe can slowly be lowered into a Dewar. Another external coupler, not pictured here, was made to allow for the probe to be inserted into the continuous flow Lakeshore cryostat so that finer temperature dependent measurements could be achieved. To allow for precise sample temperature monitoring, the probe has a Cernox thin film resistance thermometer placed in the sample space, shown in Figure 2.9(c), and connected by low-noise quad-twisted-pair wires (four leads) to a hermetic multi-pin connector in the probe head.

The foot of the probe is shown in Figure 2.9(c). The eight coaxial cables that run the length of the probe are terminated in SMA (sub miniature version A) connectors that attach to short SMA-SMP (sub miniature push-on) coax jumper cables to connect to the sample holder used for the MTJ measurements. These jumper cables can be easily switched out with other jumpers to facilitate connections to other sample holders for different applications, allowing the probe to be easily adapted to a range of applications. The foot of the probe also features an additional six twisted pair wires (12 leads) for DC connections. A brass cover to protect the sample space, shown in Figure 2.9(d), fits over the sample holder and threads into a connector at the bottom of the probe body.

The probe is designed to operate in both high and low magnetic field environments, so all of the components are made from non-magnetic materials. This makes it suitable for nuclear magnetic resonance measurements at several Tesla and for MTJ-based measurements at fields below a Gauss. For magnetic field sensing experiments with stringent low-field requirements, a sleeve of magnetic shielding material can be slipped into the sample sleeve cap to further reduce the local parasitic field.

2.3.2 Performance

Transmission and reflection

We used an Agilent E5061A vector network analyzer (VNA) to characterize the performance of the probe with S -parameter measurements over a wide temperature (295 - 4.2 K) and frequency (300 kHz - 1.5 GHz) range. S -parameter measurements provide a means of identifying the response of a system within a given frequency range. These measurements can be broken down into two main types: S_{11} which is a measure of the power reflected back to the same port from which it is transmitted, and S_{21} which is a measure of the power transferred from port 1 to port 2. S_{11} characterizes how well the impedance is matched in any given transmission line of the probe, and S_{21} characterizes how much of the signal is lost as it travels from one port to another.

S_{21} measurements were taken by connecting the VNA output to one transmission line on the probe and the input to another. The two coax lines were connected via a $50\ \Omega$ microstrip line wire bonded to the sample holder, which is connected to the probe by the jumper cables shown in Figure 2.9(c). These measurements were carried out with two microstrip lines, one straight and one bent, as shown in Figure 2.10(b), and then repeated with the sample holder replaced by an SMA-SMA coaxial jumper cable. Typical results of S_{21} measurements at 4.2 K, 77 K, and room temperature (295 K) are shown in Figure 2.10(a). The -3 dB point is the frequency at which half

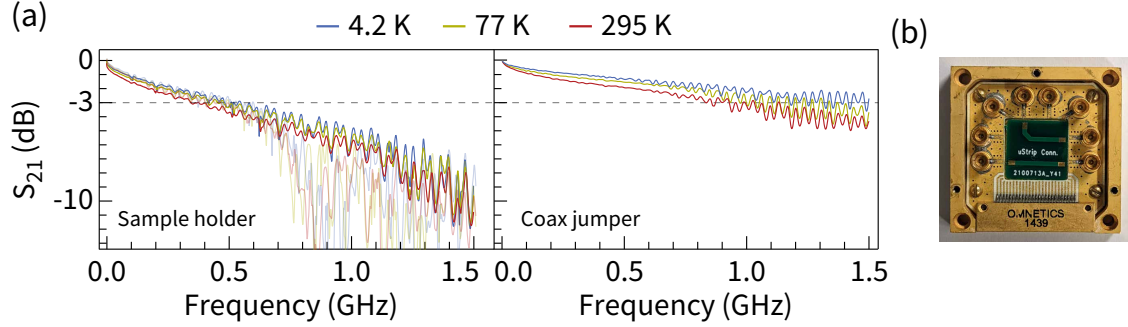


FIGURE 2.10: (a) (Left) S_{21} measurements at various temperatures for two coax going through a straight (opaque) and bent (faded) $50\ \Omega$ microstrip line wire-bonded to the sample holder, shown in the photo in (b). (Right) S_{21} when the sample holder is omitted and the two coaxial cables are connected by an SMA-SMA coaxial jumper cable. The light grey dashed line denotes the -3 dB point. (b) Sample holder used for MTJ and low temperature amplifier measurements with a wire-bonded $50\ \Omega$ microstrip.

of the signal power is dissipated and is marked on Figure 2.10(a) by a dashed line. The -3 dB point of the transmitted signal is lowest at room temperature at around 400 MHz and highest at 4.2 K where it increases to 550 MHz. The -3 dB point is about the same for the straight and bent microstrip line, but more signal is lost with the bent line at higher frequencies, as shown by the faded lines in the left panel of Figure 2.10(a).

The sample holder was found to be a significant contributor to signal loss. In the right panel of Figure 2.10(a), the S_{21} measurements without the sample holder show a -3 dB point above 1 GHz. For these measurements, the sample holder and microstrip were replaced with an SMA-SMA jumper cable made of the same coax and SMA connectors used in the rest of the probe to short the two coax lines. The increased signal loss with the sample holder is most likely due to the wire bonds connecting the contacts on the microstrip to those on the sample holder. Wire bonds are a necessary connection in mounting the MTJs in any sample holder, which means that the lower signal loss seen when the sample holder is omitted is likely unrealistic for these measurements but shows the possibilities for other measurements types, such as NMR, which do not require wire bonds to mount a sample. Furthermore, when

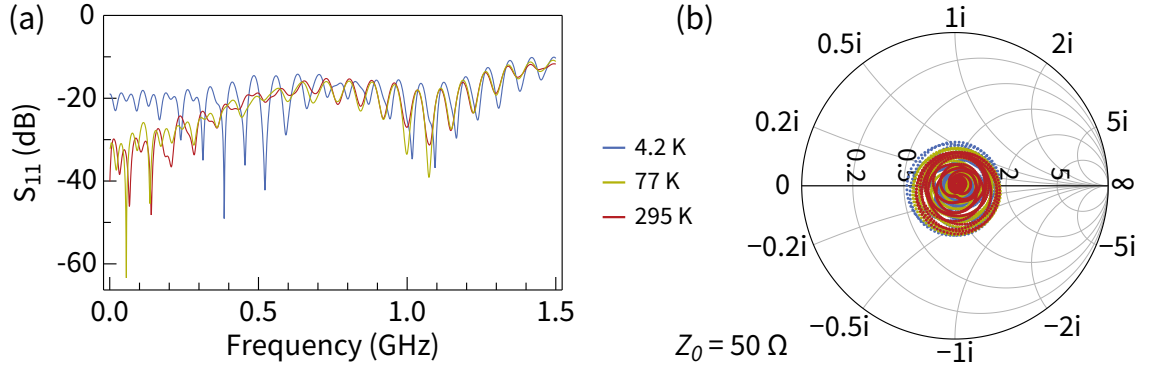


FIGURE 2.11: (a) S_{11} measurements of a representative coax at 4.2 K, 77 K, and room temperature (295 K) and (b) corresponding Smith chart measurement over the same frequency range. Each marker in (b) represents a measurement at a fixed frequency.

these measurements were repeated on the twisted pair wires, the -3 dB point fell to 10 MHz, highlighting the importance of using coaxial cable to achieve low levels of signal loss.

S_{11} measurements were taken by connecting the VNA to each coax line in turn at the head of the probe and terminating the foot of the probe with a 50Ω BNC terminator. A characteristic S_{11} measurement at room temperature (295 K), 77 K, and 4.2 K for a single coaxial line is shown in Figure 2.11(a). More signal is reflected back at 4.2 K than at room temperature or 77 K which is expected. Thermal contractions change the impedance of the coax, and since the probe is under a steep thermal gradient with one end of the probe at room temperature and the other at 4.2 K, it makes sense that the impedance would vary significantly along the length of the probe leading to an increase in the reflected power. Despite this increase at 4.2 K, the amount of reflected power is still minimal, demonstrating the degree to which the 50Ω impedance was matched throughout the probe.

The Smith plot in Figure 2.11(b) is a measure of transmittance and demonstrates the degree to which the characteristic impedance $Z_0 = 50 \Omega$ is matched at each temperature. Each point in the chart corresponds to a different frequency.

To understand these data, a brief explanation of impedance and Smith charts is

given. Impedance Z is a complex value that quantifies the opposition to alternating current (AC) in a circuit and is a combination of resistance R and reactance X : $Z = R + iX$. Reactance is the contribution to the impedance from the inductance L and the capacitance C of the circuit and depends on the frequency f of the signal: $X = X_L + X_C = 2\pi fL + (-1/2\pi fC)$. Parasitic contributions (unwanted capacitance in inductors, inductance in resistors, resistance in capacitors, etc.) dictate the frequency dependence of the total impedance, which produces the swirl shape of the data in Figure 2.11, with low frequencies sitting near the center of the Smith chart and high frequencies towards the edge [64, 65].

The Smith chart simultaneously represents both the normalized complex impedance $z = Z_L/Z_0$ for a line with characteristic impedance Z_0 terminated by a load with impedance Z_L , and the complex voltage reflection $\Gamma = (z - 1)/(z + 1)$. The horizontal axis of the Smith chart corresponds to a purely real normalized impedance, $\text{Re}(z)$. Along the circles that intersect the horizontal axis, $\text{Re}(z)$ is constant and $\text{Im}(z) > 0$ above the horizontal, $\text{Im}(z) < 0$ below, and $\text{Im}(z) = 0$ where the circles intersect the horizontal. Similarly, the arcs represent constant $\text{Im}(z)$ and varying $\text{Re}(z)$ (the real component always remains positive). A value of $\text{Im}(z) > 0$ corresponds to an inductive impedance and $\text{Im}(z) < 0$ to a capacitive impedance. At the center of the circle, where $z = 1$ and $\Gamma = 0$, the impedance is perfectly matched. At the far left end of the horizontal axis, $z = 0$ and $\Gamma = -1$ which is a short circuit. At the far right end, $z = \infty$ and $\Gamma = 1$ which is an open circuit [64].

Returning to the data in Figure 2.11(b), the Smith chart shows that the actual impedance is very close to the characteristic impedance in the measured frequency range. The impedance is best matched at room temperature, but only deteriorates slightly at 4.2 K. Additional parasitic effects are expected to arise at cryogenic temperatures because most electrical components are designed with room-temperature applications in mind. The majority of the points at all three measured temperatures

are tightly grouped around the center of the circle, indicating that for the majority of the frequency range measured ($0 - 1.5$ GHz), the impedance is very well matched and the contributions from parasitics are minimal.

Performance at Cryogenic Temperatures

The probe was designed to operate at cryogenic temperatures, so special consideration was taken to minimize heat loss along the length of the probe as the probe head always remains at room temperature. Our probe was fairly successful in mitigating helium consumption with a boil-off of less than 5 L a day when inserted into a 60 L Dewar of liquid helium, in the absence of large heat loads. Additional heat sinking could be achieved by breaking the coax at multiple points along the probe or by wrapping the coax around thermally conductive bobbins at various points along the probe. For our application, helium boil-off is not a strong consideration as we recover all of the boil-off and a consumption rate of about 5 L per day is not so high as to seriously constrict the time available to measure.

2.3.3 Possible Improvements

There are some possible improvements that could be made to the probe to improve its performance. One improvement is that the SMA connectors at the foot of the probe could be replaced by SMP connectors, which would greatly increase the ease of connecting the jumper cables and allow for more flexibility of the position of the coax at the foot of the probe. SMA connectors were originally used because in-line SMP connectors only exist as jacks—all the plug connectors are surface mount, which does not serve the purpose needed for this application. If such connectors were made available, it would be a great improvement to the current build of the probe.

Additionally, better support for the coax throughout the length of the probe would help to reduce some of the strain put on the solder connections in the head of the

probe. As currently built, the entire weight of the lines that run the length of the probe is put on the solder joints at the BNC connectors, which often leads to bends and breaks in the flexible coax jumpers in the head of the probe (shown in Figure 2.9(a)). To remedy this, rod connectors could be used to shift some of the weight onto the spacers placed along the length of the probe. Once the SMA connectors at the end of the probe are replaced by SMP connectors, this would be relatively easy to achieve, as the coaxial lines would fit more easily through the body of the probe, making any repairs more achievable.

Finally, if the probe were to be completely rebuilt following a similar design, it would be beneficial to redesign the shape of the probe head to make the connections inside the head more easily accessible to facilitate repairs.

2.4 Mitigating External Noise

With the goal of measuring the MTJ noise as an unobtrusive means of detecting magnetic fluctuations in materials, it is important that the measurement system introduces as little additional noise to the measurements as possible. Although all instruments were intentionally chosen to be low noise, any electronic device will inevitably introduce some level of electronic noise. The strategies already discussed in this chapter, such as the implementation of low-temperature amplifiers and the care taken in the design of the measurement probe, are the primary contributors to being able to accurately measure MTJ noise, however, some smaller steps were also taken to mitigate the introduction of external noise as much as possible.

2.4.1 Considerations in Measurement Set-Up

Source meters have many practical applications in these types of measurements, since they can simultaneously supply a specific voltage or current and measure the resulting current draw or voltage drop. This is helpful for determining the exact

resistance of a MTJ with a bias voltage applied and for achieving a high level of precision on the voltage (or current) applied to the system. However, we found that the Keithley 2400 and 2401 source meters introduced a significant amount of noise to the system when used to bias the MTJs. In attempts to mitigate this noise, a low-pass filter was placed at the output of the source meter with a cutoff frequency near 0 Hz to limit the output signal to just the desired DC voltage. This helped mitigate the high-frequency noise and most notably the 60 Hz noise, which was significant.

Even with the low-pass filter on the DC output of the Keithley, the measurements taken with the Keithley biasing the MTJ were found to be much less precise than when the MTJ was biased with a battery. The issue was narrowed down to a likely ground loop being introduced by the instrument's addition to the measurement circuit. To attempt to remove the ground loop, all the instruments were plugged into a single power strip and mounted on the same rack to which their chassis were grounded. This did not resolve the issue, so batteries were used to bias the MTJs during measurement.

An isolation transformer was used to mitigate the noise introduced into our measurement system from the grid. This noise is predominately 60 Hz noise which appears as peaks at the harmonics of the AC current frequency of the grid (60 Hz).

2.4.2 Noise Reduction Through Cross-Correlation

Cross-correlation is a signal processing technique that returns only the correlated components of two signals. To achieve this, a time average over the product of two signals is taken—noise that is uncorrelated between the two signals averages to zero, and what remains are only the correlated aspects of the two signals. This can be used in noise reduction by passing the same signal through two amplifiers placed as close to the signal source as possible. The idea is that all of the noise introduced by the amplifier and by the signal traveling from the source to the measurement instrument will be completely random, so when the two signals are averaged together, all of that

additional noise will average to zero and what remains will only be the noise from the device under test. Cross-correlation has been shown to be a very effective way to filter out uncorrelated noise [66, 67] and is likely to greatly increase the sensitivity of our measurements. Without multiple functioning low-temperature amplifiers, we were not able to successfully put this to the test; however, we have developed a technique to implement cross-correlation measurements using the Zurich Instruments lock-in amplifier.

In its general form, cross-correlation can be described by considering two signals coming from independent amplifiers measured simultaneously:

$$\begin{aligned} V_1(t) &= V_s(t) + V_{n1}(t), \\ V_2(t) &= V_s(t) + V_{n2}(t), \end{aligned} \tag{2.12}$$

where $V_s(t)$ is the desired signal and $V_{n1}(t)$ and $V_{n2}(t)$ are the uncorrelated noise of each measured signal. Therefore, the time average of the product of these two signals takes the form:

$$y = \lim_{t' \rightarrow \infty} \frac{1}{t'} \int_{t=0}^{t'} [V_s(t) + V_{n1}(t)] [V_s(t) + V_{n2}(t)] dt. \tag{2.13}$$

In the limit where $t' \rightarrow \infty$, the uncorrelated terms vanish and $y = \overline{V_s(t)^2}$.

In the context of measuring noise as a function of frequency, $V_s(t)$ is the desired signal within the frequency bandwidth at each demodulator frequency in the sweep. The demodulator time constant, which is inversely proportional to the demodulator frequency bandwidth, is varied with frequency to optimize between the signal-to-noise ratio and the sweep time. The noise amplitude sweep is measured in units of $V/\sqrt{\text{Hz}}$, so Eq. 2.13 must be normalized by the frequency bandwidth Δf in which it is measured. Additionally, since each frequency is measured over a time step Δt , also determined by the frequency specific time constant, the cross-correlated noise

amplitude becomes:

$$S_V = \sqrt{\frac{1}{\Delta f \Delta t} \int_{t_0}^{t_0 + \Delta t} V_1(f, t) V_2(f, t) dt}. \quad (2.14)$$

This equation outlines the lock-in parameters needed in order to obtain the cross-correlation of two noise measurements: the raw voltage signal from both channels $V_1(f, t)$ and $V_2(f, t)$, the time over which those signals are measured Δt , and the demodulator frequency bandwidth at each frequency step Δf . Unfortunately, the “Noise Amplitude Measurement” procedure in the “Sweeper Tab” of the Zurich Instruments lock-in interface does not record all of the necessary values, so the “Plotter Tab”, which can plot all streamed data (bandwidth, input voltage, etc.), is run synchronously to compensate.

In the “Plotter Tab”, the demodulator frequency and raw voltage should be recorded for the entire duration of the sweep carried out by the “Sweeper Tab”. The full “Noise Amplitude Sweep” data contains the frequency steps at which the noise is measured, as well as the demodulator bandwidth at each frequency. Since the “Plotter Tab” records data as a function of time, the duration of each frequency step Δt can be determined from the frequency data recorded by the “Plotter Tab” as a function of time. The bandwidth Δf at each frequency is recorded by the “Sweeper Tab”, which also records the associated frequency, so that the bandwidth and time step can be matched correctly for each frequency. The “Plotter Tab” also records the input voltage signal as a function of time, so the voltage signal at each frequency step can be extracted from the data over the whole time range with the time steps determined by the frequency data.

There is some settling time that must be taken into account each time the demodulator frequency changes. This settling time depends on the time constant τ_c and the filter order as outlined in Table 1 of the Zurich Instruments White Papers on the

Principles of Lock-in Detection [51]. The signal measured before the settling time has been achieved at each frequency step should not be included in the cross-correlated noise calculations.

Once the overall voltage signal is broken up for each demodulator frequency in the sweep, the initial points measured before the settling time are removed, and the bandwidth and time constant at each frequency are determined for both input signals; the cross-correlated noise can be calculated using Eq. (2.14) at each frequency step. The result will give a single noise value at each demodulator frequency which can be plotted as a function of the demodulator frequency to obtain the cross-correlated noise amplitude spectral density. If this procedure is carried out using Python or a similar programming language, some smoothing of the signal may be necessary to obtain accurate results. This process executes the same procedure as the “noise amplitude measurement” feature in the Sweeper Tab, but with the added step of performing cross-correlation of two signals before calculating the noise spectral density.

In the Arithmetic Unit Tab, a new variable created by multiplying two voltage signals together can be created. Previously, the equivalent of this existed within the Sweeper Tab but only multiplied the two noise signals together, not the voltage signals before calculating the noise, which prompted the need for the above procedure. It now appears that this new feature of the LabOne Software enables the voltage signals to be multiplied and the standard deviation of that multiplied signal to be calculated at each frequency step, just as with a “noise amplitude sweep” of a single input signal. If this is the case, the outlined procedure would no longer be necessary and cross-correlation could be performed completely within the LabOne Software. Future work should include testing this new feature to ensure that the correct procedure for noise cross-correlation is, in fact, being carried out by sweeping the product of two input signals.

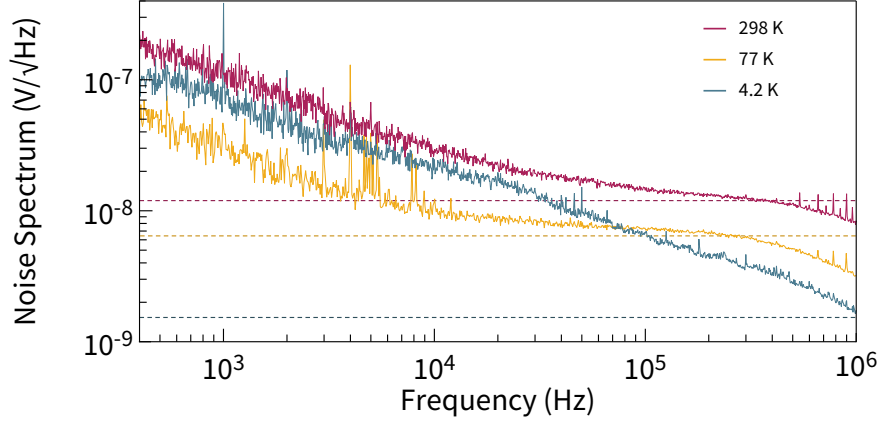


FIGURE 2.12: Thermal noise amplitude spectral density measured on an MTJ with resistance around 9 k Ω measured at 298 K, 77 K, and 4.2 K. Dashed lines represent the expected thermal noise calculated from Eq. (1.5).

2.5 Results

The majority of this project was focused on developing a measurement system capable of detecting the intrinsic electronic noise in MTJs, so the bulk of the results have already been presented in the description of the measurement system. However, in testing the efficacy of the system, we measured the shot noise and thermal noise of several MTJs. Some results of those measurements will be discussed below.

The thermal noise of an MTJ with resistance around 9 k Ω measured at 298 K, 77 K, and 4.2 K is displayed in Figure 2.12. These measurements were taken using the HBT low-temperature amplifier with around -2 V (-1.683 V at 298 K, -2.007 V at 77 K, and -2.088 V at 4.2 K) applied to the emitter to achieve a constant collector current of $I_C = 10$ μ A. The dashed lines in Figure 2.12 represent the expected thermal noise values calculated with Eq. (1.5). The measured values at 298 K and 77 K are higher than the expected value over the measured frequency range. The absence of any significant flat region, as is expected for a thermal noise measurement which is frequency independent, indicates that the thermal noise of the MTJ is likely concealed in the low-frequency noise.

Comparison of these measurements with those in Figure 2.2, where the thermal

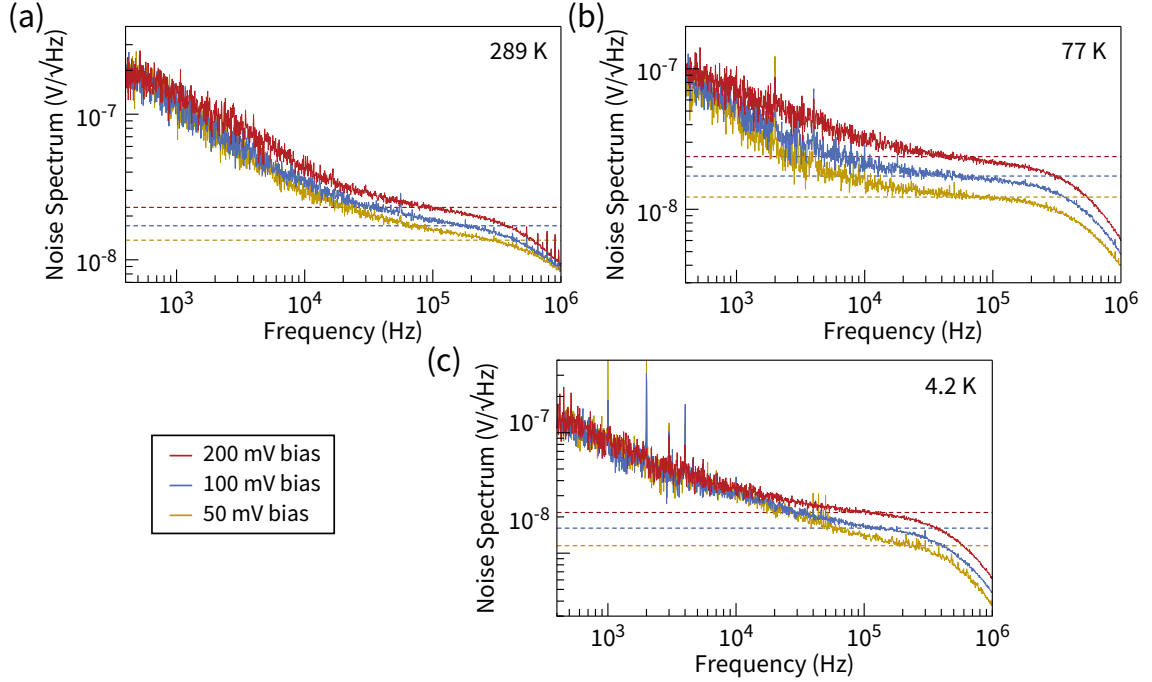


FIGURE 2.13: Shot noise amplitude spectral density measured on an MTJ with resistance around 9 k Ω and applied bias voltage of 200 mV, 100 mV, and 50 mV at (a) 298 K, (b) 77 K, and (c) 4.2 K. Dashed lines represent the expected shot noise calculated from Eq. (1.8).

noise measured without the use of the HBT low-T amplifier was in good agreement with the expected noise, suggests that the increased low-frequency noise is introduced into the signal by the HBT amplifier. This inability to accurately measure the MTJ thermal noise with the HBT amplifier was a strong motivation for exploring other options for low-temperature amplification. The thermal noise measurement at 4.2 K is dominated by low-frequency noise, making an accurate measure of the thermal noise at this temperature with an MTJ of such low resistance impossible. A higher resistance MTJ may increase the thermal noise above the other noise present in the system.

The shot noise of the same MTJ measured with three bias voltages (200 mV, 100 mV, 50 mV) at the same three temperatures is shown in Figure 2.13. Again, low-frequency noise dominates measurements at all three temperatures, but most significantly at 298 K and 4.2 K. At 77 K, shown in Figure 2.13(b), there is a small

Temperature	MTJ Bias	MTJ Resistance
298 K	200 mV	8.18 k Ω
	100 mV	8.68 k Ω
	50 mV	8.68 k Ω
77 K	200 mV	9.2 k Ω
	100 mV	9.68 k Ω
	50 mV	9.72 k Ω
4.2 K	200 mV	10.09 k Ω
	100 mV	9.34 k Ω
	50 mV	9.529 k Ω

TABLE 2.2: Resistance of a single MTJ at different temperatures and voltage biasing conditions.

region over which the shot noise is almost constant, the expected behavior for shot noise, as it is not frequency dependent. Most clear in the 77 K measurement, but also evident in the 298 K and 4.2 K measurements, is that the spacing between the measurements at different bias voltages is consistent with the expected spacing, calculated from Eq. (1.8), which indicates that we are actually measuring the shot noise, but that the actual signal is simply buried in the noise introduced by the HBT amplifier. This indicates that the measurement set-up and methods are effective in measuring MTJ shot noise but that a low-temperature amplifier with less low-frequency noise is necessary for obtaining an accurate measure of the shot noise over an extended frequency range. Extending the operating frequency range of the entire system to higher frequencies will also facilitate measuring MTJ shot noise with a high level of accuracy.

The resistance of MTJ depends on the temperature of the MTJ and the bias voltage applied to it. All measurements presented in this section were taken on the same MTJ and the MTJ resistance was measured for each bias voltage at each temperature and is listed in Table 2.2. The MTJ resistance increases overall as the temperature decreases, but there appears to be no predictable trend in the MTJ resistance as a function of bias voltage, which highlights the importance of obtaining

accurate measurements of the MTJ resistance before each measurement.

2.6 Next Steps

Overall, this work was successful in establishing the first steps toward the use of MTJs as sensors of quantum magnetism. A measurement system was designed and implemented, techniques were established to obtain accurate noise and MTJ resistance measurements, and multiple low-temperature amplifiers were tested with varying levels of success. We were able to accurately measure the MTJ thermal noise; however, some work could be done to increase the precision of the measurement to increase the sensitivity of the thermal noise as a means of detecting a change in the resistance. We were also able to measure the MTJ shot noise; however, an accurate value for the shot was not attainable with the current set-up.

Future work should focus on developing a low-temperature amplifier that operates over a wide frequency range without introducing substantial noise to the signal. With a low-temperature amplifier optimized for this application, it should be possible to measure the MTJ noise with a higher level of precision and accuracy, as well as measure the noise of lower resistance MTJs, which would help to increase the RC roll-off frequency of the system. In the design of a new low-temperature amplifier, it would be beneficial to consider a set-up that allows multiple low-temperature amplifiers to be in operation at once so that cross-correlation of a single MTJ signal between two amplifiers could be implemented. Future work could also include implementing some of the improvements to the probe outlined in Section 2.3.3. Once an optimized low-temperature amplifier is implemented, the MTJs could be tested as sensors, possibly by measuring one of the 2D antiferromagnetic van der Waals samples that will be discussed in the subsequent chapters.

CHAPTER 3

Nuclear Magnetic Resonance and Measure of Spin Interaction Strength in Solids

Nuclear magnetic resonance (NMR) is a powerful local probe of matter that uses nuclear spins to probe the surrounding environment of the nuclear site. It is sensitive to the spin, charge, lattice, and orbital degrees of freedom in solid state materials, making it an incredibly effective tool in the study of strongly correlated systems. This chapter will outline the basic principles of nuclear magnetic resonance in solid-state materials as well as an expansion on basic NMR techniques that enables a measurement of the strength of spin-spin interactions.

3.1 General Principles of Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a sensitive spectroscopic technique that uses nuclear spins polarized by a strong static external field as a probe of the local

environment of the nuclei by measuring the response of the nuclear spins to the application of a weaker oscillating field. The oscillating field $\mathbf{H}_1$ is applied perpendicular to the static field $\mathbf{H}_0$ at a frequency ω_0 proportional to the energy splitting induced by the interaction of the nuclear magnetic moment $\boldsymbol{\mu}$ with $\mathbf{H}_0$, called the Zeeman effect, to excite the spins from their ground state into an excited state. After the spin is excited, it will relax back to equilibrium over a period of time specific to its surroundings and release a quanta of energy equal to that which excited it. The behavior of the spins after excitation and the process of returning to equilibrium provide detailed insight into the local environment of the nuclear probe and is the basis of NMR.

3.1.1 NMR Measurements

As previously stated, NMR uses nuclear spins as probes of their local environment by exciting spins from their ground state to an adjacent Zeeman energy level. The quanta of energy needed to excite the spins is proportional to the static applied field $\mathbf{H}_0$ and the nuclear isotope specific gyromagnetic ratio. It is applied to the sample via an oscillating magnetic field $\mathbf{H}_1$ generated by a radio-frequency pulse sent through a resonant LC-circuit where the inductor is a coil of wire wrapped around the sample. The coil serves as both the transmitter and detector: the response of the system to the excitation occurs with the same resonant frequency as the transmitted signal, so the same LC circuit can be used. The current induced in the coil from the system response to excitation is measured as the NMR signal. The procedure for obtaining an NMR signal and the behavior of the nuclear spins after excitation are discussed in the following sections.

Free Induction Decay and Spin Echo

The most basic NMR signal that can be obtained is called a free induction decay or FID for short. In an FID measurement, a single pulse is applied to the system to rotate the spins from their relaxed state along the z -axis, parallel to $\mathbf{H}_0 = H_0\hat{z}$, into

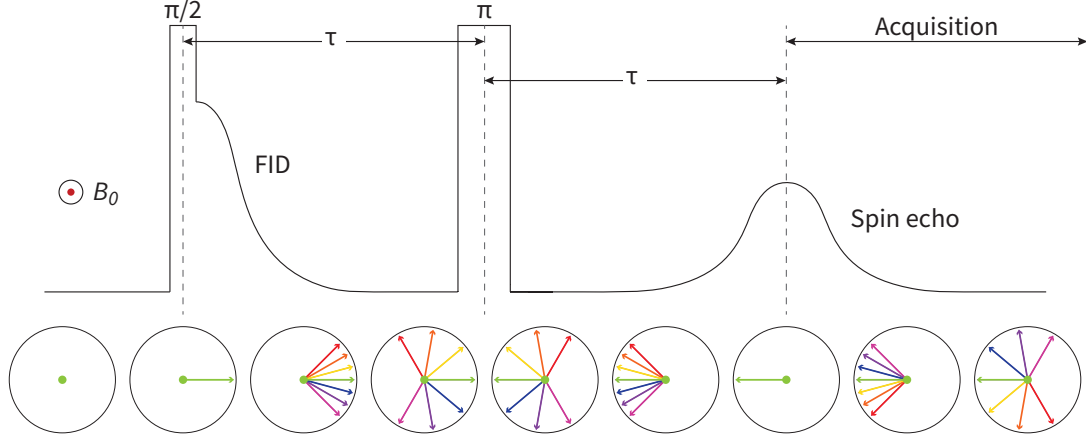


FIGURE 3.1: Diagram of a spin echo measurement.

the xy -plane. Because this pulse applies a 90° rotation to the spins, it is commonly called a π -half pulse. Once in the xy -plane, the spins begin to precess at the resonant frequency ω_0 , also called the Larmor precession frequency. Their precession creates an oscillating magnetic field at frequency ω_0 that induces a signal in the coil at that same frequency.

As shown in the first part of Figure 3.1, the FID signal decays after the pulse. This decay is due to the decoherence of the precessing spins. Decoherence occurs because the nuclear spin sites across the sample feel slightly different local fields and thus precess at slightly different rates. Directly after the application of the pulse, the spins are at their most coherent and the signal is strongest. As time progresses, the difference in the precession rate of the spins becomes more and more significant, and the spins across the sample end up precessing in an increasingly decoherent manner and the signal dies out.

Another common NMR pulse sequence is the spin echo, also called the Hahn echo. In a spin echo experiment, a second pulse twice the length of the first pulse is applied a time τ after the first pulse. Most often, the first pulse is a $\pi/2$ pulse, so the second pulse is a π pulse and rotates the spins by 180° . This rotation can be applied along the x - or y -axis—a π rotation about the y -axis is shown in Figure 3.1. The π pulse

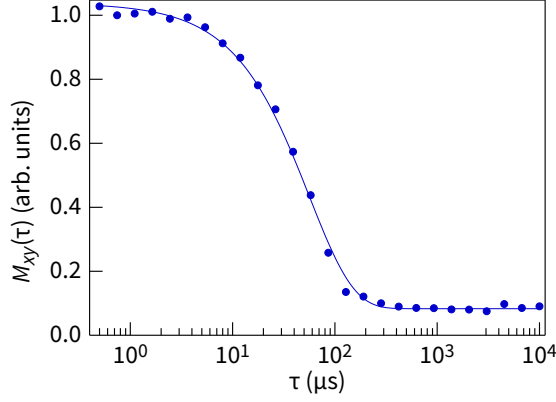


FIGURE 3.2: Example of a characteristic spin-spin decoherence measurement.

reverses the time evolution of the spins, so instead of continuing to decohere, they instead refocus back to the coherent state they started in directly following the first pulse. As the spins refocus, the signal begins to grow again, reaching a maximum when they return to their initial state at time τ after the second pulse and then decaying again in a symmetric fashion as they continue to precess and decohere again.

Spin-Spin Decoherence

In the preceding discussion of the FID and spin echo, we discussed the concept of spin decoherence due to slight variations of the local field at the nuclear sites across the sample, but did not touch on the characterization of this decoherence. The spin-spin decoherence rate is characterized by T_2^{-1} and is obtained by measuring the amplitude of the NMR signal as a function of the decoherence time τ . A characteristic spin-spin decoherence curve is shown in Figure 3.2. The signal is strongest at small τ and decays as τ increases.

The characteristic of the system that is being measured in a spin-spin decoherence measurement is the transverse, or in-plane, magnetization. Directly after the pulse, the spins are all precessing mostly coherently and the in-plane magnetization is high. As they dephase, the in-plane magnetization decays, and when the spins are precessing in a completely decoherent manner, the transverse magnetization is zero because the

spins are randomly oriented. The decay in transverse magnetization as a function of decoherence time τ can be described by the following equation,

$$M_{xy}(2\tau) = M_0 e^{-2\tau/T_2}, \quad (3.1)$$

where M_0 is the transverse magnetization directly after the pulse and $1/T_2$ is the spin-spin decoherence rate.

Spin-Lattice Relaxation

On a time scale that is generally longer than the decoherence time T_2 is the spin-lattice relaxation time, which describes the time period over which the spins relax back to their equilibrium state, or in other words, the rate at which the longitudinal (out-of-plane) magnetization recovers. This rate is characterized by T_1^{-1} and in its simplest form, can be described by the following equation,

$$M_z(t) = M_\infty(1 - e^{-t/T_1}), \quad (3.2)$$

where M_∞ describes the equilibrium longitudinal magnetization. For a complete picture of the spin-lattice relaxation, the initial state of the spins must be considered in the derivation of the spin-lattice relaxation equation. The initial state depends on the spin I of the nuclear isotope being probed and the initialization pulse sequence, the details of which are discussed in Appendix A for the case of $I = 9/2$.

The rate at which the spins relax back to equilibrium is dictated by the surrounding environment, as the process of relaxation involves emitting energy into the lattice. In a highly ordered state, it takes a long time for the spins to relax back to equilibrium because it is difficult to dissipate the energy absorbed from the excitation pulse, so T_1^{-1} is small. In contrast, when a system is highly disordered, for example near a magnetic transition when a significant amount of fluctuations are occurring as the

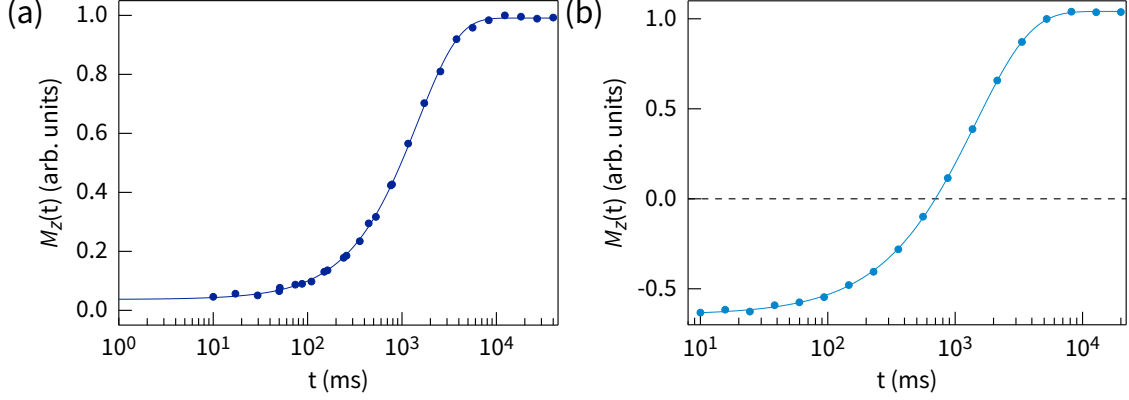


FIGURE 3.3: Example of a characteristic spin-lattice decoherence measurement using the (a) saturation recovery and (b) inversion recovery methods.

magnetic order begins to develop, the spins relax back to equilibrium quickly because the fluctuating surroundings can easily accept the emitted energy, thus T_1^{-1} is large.

The standard way in which T_1^{-1} is measured is using the saturation recovery method, a characteristic example of which is shown in Figure 3.3(a). In a saturation recovery T_1 measurement, the spins are tipped into the xy -plane by a $\pi/2$ pulse, after which a time t is waited, and then a spin echo is performed. This process is repeated for various times t until t is long enough for the spins to fully relax back to equilibrium before the spin echo. At a very short time t , the spins will still be in the xy -plane when the spin echo is applied, so the $\pi/2$ pulse of the spin echo will rotate the spins to be along the $-z$ -axis and the proceeding π pulse will rotate the spins back to their equilibrium position, which means no precession occurs and the signal will be zero. At intermediate t , the spins will be at some angle between the z -axis and the xy -plane after the π pulse, so there will be some precession which will result in a small signal.

Similar to the saturation recovery method is the inversion recovery method, shown in Figure 3.3(b). Instead of applying a $\pi/2$ pulse to initialize the spins, a π pulse is applied, tipping the spins along the $-z$ -axis, so instead of zero longitudinal magnetization at short t , the magnetization is negative. In a perfect system, the curve will be perfectly symmetric about zero, *i.e.* $M(0) = -M(\infty)$. Asymmetry about zero indicates some inhomogeneity in the oscillating field H_1 .

3.1.2 The Nuclear Interaction Hamiltonian

In solid state materials, the nuclei sit in a crystal lattice and interact with their surroundings. These interactions can be described by the complete nuclear interaction Hamiltonian,

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{hf} + \mathcal{H}_Q + \mathcal{H}_D, \quad (3.3)$$

where $\mathcal{H}_Z$ is the Zeeman Hamiltonian, $\mathcal{H}_{hf}$ describes the effects of hyperfine interaction, $\mathcal{H}_Q$ describes the quadrupolar interaction, and $\mathcal{H}_D$ denotes the dipolar interaction between nuclei. The details of each of these contributions and their effect on the NMR spectrum are described in the subsequent sections.

Zeeman Interaction

An isolated nuclear spin in a static external field $\mathbf{H}_0$ is subject to the Zeeman interaction,

$$\mathcal{H}_Z = -\boldsymbol{\mu} \cdot \mathbf{H}_0, \quad (3.4)$$

where the nuclear magnetic moment $\boldsymbol{\mu} = \gamma\hbar\mathbf{I}$ and γ is gyromagnetic ratio of the nuclear isotope with spin $\mathbf{I}$ that is being probed. Assuming the static field is applied along the z -axis, $\mathbf{H}_0 = H_0\hat{z}$, the Zeeman interaction lifts the $(2I + 1)$ -fold degeneracy of the nuclear spin's ground state and creates $(2I + 1)$ non-degenerate states with energy

$$E_m = \langle I, m | \mathcal{H}_Z | I, m \rangle = -m\hbar\gamma H_0, \quad (3.5)$$

where the nuclear quantum number $m = -I, -(I - 1), \dots, I - 1, I$. The energy difference between adjacent levels is

$$\Delta E = \hbar\gamma H_0 = \hbar\omega_0, \quad (3.6)$$

where ω_0 is the resonant frequency of the nuclear isotope. When $\mathbf{H}_0$ is the only field felt by the nucleus, NMR resonance occurs when energy $\hbar\omega_0$ is transmitted to the nucleus, inducing a transition to an adjacent energy level. When considering nuclei that are not isolated, for example in a solid-state crystal material, local fields from the surrounding environment will also contribute to the splitting between adjacent energy levels, varying the resonant frequency from ω_0 .

Hyperfine Interaction

One contribution from the environment to the local field at the nucleus comes from the interaction between the nucleus and the spin and orbital degrees of freedom of the surrounding electrons, called the hyperfine interaction. The hyperfine interaction can be described by the following Hamiltonian,

$$\mathcal{H}_{hf} = \frac{\mu_0}{4\pi} g_e \mu_B \sum_i \left[\frac{\boldsymbol{\mu} \cdot \mathbf{L}_i}{r_i^3} - \frac{\boldsymbol{\mu} \cdot \mathbf{S}_i}{r_i^3} + \frac{3(\boldsymbol{\mu} \cdot \mathbf{r}_i)(\mathbf{S}_i \cdot \mathbf{r}_i)}{r_i^5} + \frac{8\pi}{3} \mathbf{S}_i \delta(\mathbf{r}_i) \right] \quad (3.7)$$

where μ_0 is the permeability of free space, g_e is the electronic g-factor, μ_B is the Bohr magneton, and $\mathbf{L}_i$ and $\mathbf{S}_i$ are the orbital and spin angular momentum, respectively, of the i^{th} electron a distance $\mathbf{r}_i$ from the nucleus with magnetic moment $\boldsymbol{\mu}$ centered at the origin.

The first term of Eq. (3.7) describes the interaction between the nucleus and the orbital degrees of freedom of the electron. Most often, this term vanishes for solid-state materials because the ground state $|0\rangle$ is non-degenerate, which means that it must have a real eigenfunction. Since the angular momentum operator $\hat{\mathbf{L}}$ is imaginary, acting it on any real eigenfunction would produce a purely imaginary result, so $\langle 0 | \hat{\mathbf{L}} | 0 \rangle$ must be purely imaginary. However, since $\hat{\mathbf{L}}$ is Hermitian, its diagonal matrix elements must be real, forcing $\langle 0 | \hat{\mathbf{L}} | 0 \rangle$ to be purely real. Therefore, $\langle 0 | \hat{\mathbf{L}} | 0 \rangle = 0$ is the only viable solution, and all components of the angular momentum are quenched for a non-degenerate ground state [68, 69].

In cases where the orbital angular momentum is not completely quenched, the spin-orbit coupling can be introduced as a perturbation. This results in a quenched ground state, but with a slight change in g_e from its expected value of 2 due to the non-zero angular momentum states and occasionally an anisotropic g -factor that depends on the direction of the applied magnetic field with respect to the crystal axes [68,69]. The second and third terms of Eq. (3.7) describe the dipolar hyperfine interaction between the nuclear magnetic moment $\boldsymbol{\mu}$ and electron spin $\mathbf{S}_i$. The fourth term is the contact hyperfine interaction which is only non-zero for s -orbital electrons as they have a non-vanishing wavefunction at the origin.

The local internal field due to the hyperfine interaction is expressed in terms of the hyperfine coupling tensor $\mathbb{K}$:

$$\mathbf{H}_{loc} = \mathbb{K} \cdot (\mathbf{g}\mu_B\mathbf{S}) = (\mathbb{A} + \mathbb{D}) \cdot (\mathbf{g}\mu_B\mathbf{S}), \quad (3.8)$$

where $\mathbb{D}$ is the dipolar interaction tensor and $\mathbb{A}$ is the contact hyperfine tensor. The contact hyperfine tensor is itself the sum of two parts, the transferred and the on-site hyperfine interaction tensors. The transferred hyperfine interaction tensor originates from the interaction of the electron wavefunction of one atom with the nucleus of another, mediated by intermediate ions with overlapping wavefunctions, whereas the on-site hyperfine interaction tensor arises from a direct overlap of the s -orbital electron wavefunction with the nucleus of the same atom. The shift in the resonant frequency ω_{res} from the Larmor frequency ω_0 due to the local field is

$$\Delta\omega = \omega_{res} - \omega_0 = \gamma H_{loc} \hat{h}, \quad (3.9)$$

where $\hat{h}$ is a unit vector in the direction of the static field $\mathbf{H}_0$. The shift in resonant frequency due to a local field is called the Knight shift which is expressed as the

unit-less ratio,

$$K = \frac{\mathbf{H}_{loc} \cdot \hat{h}}{H_0}. \quad (3.10)$$

The dipolar interaction tensor $\mathbb{D}$ is simple to calculate as only the relative positions of the interacting electron and nucleus need to be known. The components of $\mathbb{D}$ for a pair of interacting electronic and nuclear spins separated by a distance r are:

$$\mathbb{D}_{i,j} = \frac{\mu_0}{4\pi r^3} [\delta_{ij} - 3(r_i \cdot r_j)], \quad (3.11)$$

where i, j represent the (x, y, z) axes.

The contact hyperfine interaction is difficult to calculate because the exact wave function of the electron must be known. Instead, it is determined from experimental results. One way of determining the value of $\mathbb{A}$ is by determining the local field along each of the principal crystal axes from the measured Knight shift along each crystal axis. Then, if $\mathbb{D}$ is calculated from Eq. (3.11), the components of $\mathbb{A}$ can be determined from Eq. (3.8), noting that $\mathbf{S} = \langle \mathbf{S}_{\parallel} \rangle$ is the expectation value of the spins parallel to $\mathbf{H}_0$ [70].

Another way of determining the diagonal elements of $\mathbb{A}$ is from the relationship between the Knight shift and magnetic susceptibility at temperature T since,

$$g_i A_{ii} = \frac{K_i(T) - K_i^0}{\chi_i(T) - \chi_i^0}, \quad (3.12)$$

where $K_i(T)$ is the Knight shift and $\chi_i(T)$ the susceptibility along principal crystal axis i at temperature T , and χ_i^0 and K_i^0 are the temperature independent components of the susceptibility and Knight shift, respectively. The slope of a so-called Clogston-Jaccarino plot, where the Knight shift at temperature T is plotted as a function of the susceptibility at T , gives $g_i A_{ii}$ [71].

Quadrupolar Interaction

Nuclei with spin $I > 1/2$ have a non-spherical charge distribution, and thus quadrupolar moment eQ , which couples to the electronic field gradient at the nuclear site produced by the surrounding electrons. If the surrounding electric field gradient (EFG) is symmetric, as is the case in a cubic environment, no quadrupolar interaction will occur, regardless of how large the EFG is. For quadrupolar interactions to produce finite effects, $I > 1/2$, and the electronic charge distribution must be asymmetric [72].

The electronic field gradient is described by a second-rank tensor with principal axis components defined by:

$$V_{\alpha\beta} = \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}, \quad (3.13)$$

for principal axes $\alpha = x, y, z$, where V is the electrostatic potential. By convention, $V_{zz} \equiv eq$, where q is the field gradient, is defined as the principal component of the EFG and $|V_{xx}| < |V_{yy}| < |V_{zz}|$.

In the coordinate system defined by the principal axes of the EFG, the quadrupolar interaction contribution to the Hamiltonian is

$$\mathcal{H}_Q = \frac{e^2 Q q}{4I(2I-1)} [(3I_z^2 - I^2) + \eta(I_x^2 - I_y^2)], \quad (3.14)$$

where $\eta \equiv |V_{xx} - V_{yy}|/V_{zz}$ is the asymmetry parameter [69].

The electronic field gradient lifts the degeneracy in the nuclear energy levels, shifting the energy levels by $\pm\delta_q = 3e^2 q Q / 4hI(2I-1)$ which produces $2I$ quadrupolar satellite peaks symmetrically about the central peak ($2I + 1$ total peaks). In the presence of a strong static field, the quadrupolar interaction can be treated as a perturbation to the Zeeman Hamiltonian and the separation between NMR lines is

given by:

$$\delta_q = \frac{\nu_q}{2} (3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi), \quad (3.15)$$

where θ is the angle between the static field and V_{zz} , ϕ is the standard azimuthal angle between the static field and V_{xx} , and $\nu_q \equiv 3e^2qQ/2hI(2I - 1)$. To first order, the correction to the central peak ($m = -1/2 \rightarrow m = 1/2$ transition) due to the quadrupolar perturbation is zero, so the central line remains unaffected by the quadrupolar interaction.

Dipolar Interaction

The final contribution to the NMR signal that we will discuss is from the dipolar interaction of nuclear spins. Nuclear spins have a magnetic moment $\boldsymbol{\mu} = \gamma\hbar\mathbf{I}$ which interacts with the dipolar field produced by the magnetic moments of the neighboring nuclear spins. The dipolar interaction of magnetic moment $\boldsymbol{\mu}$ with neighboring nuclear magnetic moments $\boldsymbol{\mu}_i$ a distance $\mathbf{r}_i$ from $\boldsymbol{\mu}$ is

$$\mathcal{H}_D = \frac{\mu_0}{4\pi} \sum_i \left[\frac{\boldsymbol{\mu} \cdot \boldsymbol{\mu}_i}{r_i^3} - \frac{3(\boldsymbol{\mu} \cdot \mathbf{r}_i)(\boldsymbol{\mu}_i \cdot \mathbf{r}_i)}{r_i^5} \right], \quad (3.16)$$

where μ_0 is the vacuum permeability.

The dipolar interaction Hamiltonian can equivalently be written as a 4×4 matrix of six operators,

$$\mathcal{H}_D = \frac{\gamma_1\gamma_2\hbar^2}{r^3} (A + B + C + D + E + F) = \frac{\gamma_1\gamma_2\hbar^2}{r^3} \begin{pmatrix} A & C & C & E \\ D & A & B & C \\ D & B & A & C \\ F & D & D & A \end{pmatrix}, \quad (3.17)$$

where

$$\begin{aligned}
A &= I_{1z}I_{2z}(1 - 3\cos^2\theta) \\
B &= -\frac{1}{4}(I_1^+I_2^- + I_1^-I_2^+)(1 - 3\cos^2\theta) \\
C &= -\frac{3}{2}(I_1^+I_{2z} + I_{1z}I_2^+)\sin\theta\cos\theta e^{-i\phi} \\
D &= -\frac{3}{2}(I_1^-I_{2z} + I_{1z}I_2^-)\sin\theta\cos\theta e^{i\phi} \\
E &= -\frac{3}{4}I_1^+I_2^+\sin^2\theta e^{-2i\phi} \\
F &= -\frac{3}{4}I_1^-I_2^-\sin^2\theta e^{2i\phi}
\end{aligned} \tag{3.18}$$

for raising operator $I^+ = I_x + iI_y$ and lowering operator $I^- = I_x - iI_y$, where I_x , I_y , and I_z are the standard nuclear spin matrices [73]. Writing the dipolar Hamiltonian in this form separates the qualitatively different actions of the dipolar interaction on the unperturbed Hamiltonian into separate terms. The affect of each term on the unperturbed state is illustrated in Figure 3.4 for two identical moments with nuclear spin 1/2. The A term is completely diagonal and describes the effect of the static external field, H_0 . The B term simultaneously flips two spins in opposite directions and describes the effect of the oscillating field H_1 . The C and D terms flip just one spin and E and F both flip both spins up or both spins down. The C , D , E , and F terms are off-diagonal and have the effect of creating a slight admixture of states. The results of this very small admixture of states is to allow previously forbidden transitions from the $|++\rangle$ to $|--\rangle$ which produces very weak absorption at 0 and $2\omega_0$. Since these peaks are very weak and also the primary effect of the C , D , E , and F , it is a very good approximation to drop the terms from the Hamiltonian [69,73]. The remaining homonuclear dipolar Hamiltonian takes the form:

$$\mathcal{H}_D = \frac{\gamma^2\hbar^2}{2r^3}(1 - 3\cos^2\theta)(3I_{1z}I_{2z} - \mathbf{I}_1 \cdot \mathbf{I}_2). \tag{3.19}$$

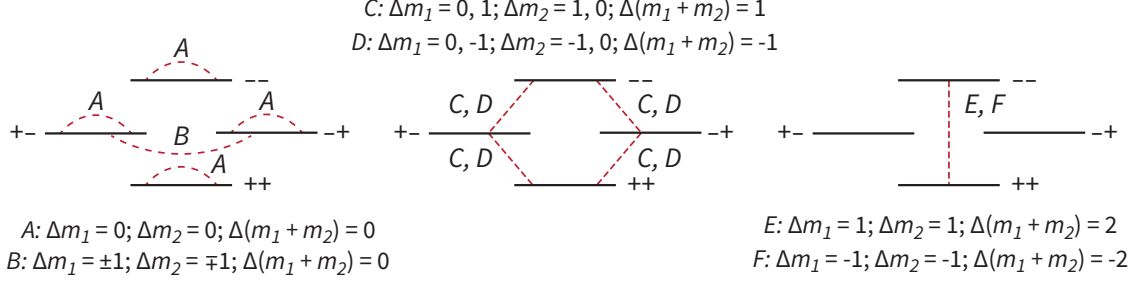


FIGURE 3.4: Energy states of two identical moments with nuclear spin $1/2$ joined by the matrix elements in Eq. (3.18). The $m_i = 1/2$ state is denoted by $+$ and $m_i = -1/2$ by $-$. Adapted from figures in Ref. [69].

The projection of $\boldsymbol{\mu}$ along the static field $\mathbf{B}_0$ slightly alters the local field felt by the nuclear spin which results in a broadening of the NMR line in solid state materials. This small change in the local field slightly shifts the resonant frequency, producing a distribution in the local field felt at the nuclear sites across the material. Without this contribution, the NMR line would resemble a Dirac delta function at the resonant frequency.

3.2 NMR Experimental Set-Up and Techniques

Now that we have a solid understanding of the theoretical aspects of nuclear magnetic resonance, we can discuss how NMR measurements are actually implemented. A brief outline of the experimental set-up is given, and more details can be found in the PhD and master theses of previous group members, as well as in the MagRes2000 spectrometer user manual [74]. Some experimental techniques that are not covered in these other sources will also be discussed in this section.

3.2.1 Experimental Set-Up

A basic description of the experimental set-up for an NMR experiment is described in Figure 3.5. The sample under investigation is mounted in a wire coil that is in turn mounted on a laboratory-built NMR probe as the inductor in the NMR resonant circuit, described in the bottom right corner of Figure 3.5. The probe is inserted into

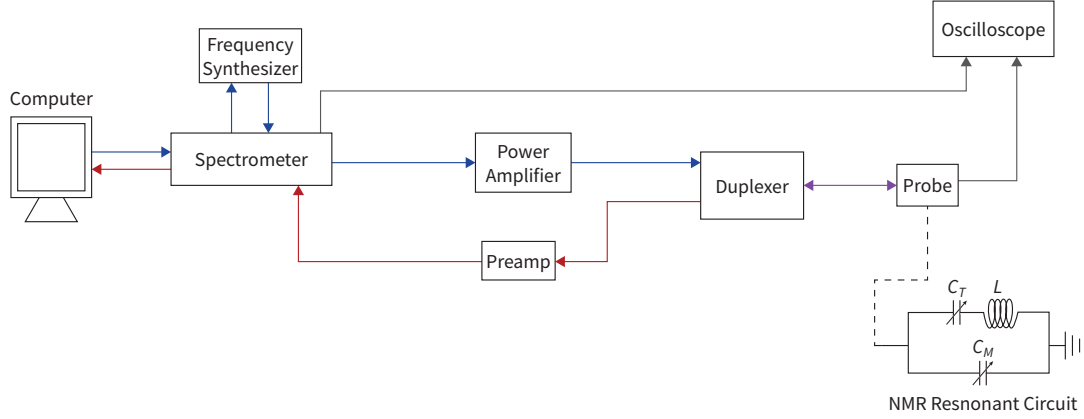


FIGURE 3.5: A basic diagram showing the experimental set-up for NMR measurements. The transmission path is shown by blue arrows and the receiver path is shown by red arrows. Purple denotes a shared path between the transmission and reception and gray lines denote passive components to monitor the pulse. The NMR resonant circuit (series-tuned) is displayed at the bottom where C_M denotes the impedance matching capacitor, C_T is the tuning capacitor, and L is the inductor (coil). It is connected to the probe by a dashed line to indicate that it is a part of the probe.

a cryostat for cryogenic temperature control which sits in a superconducting magnet that provides the static field $\mathbf{B}_0$ for the experiment.

The pulse sequence is programmed on a computer that communicates directly with a lab-built spectrometer. The spectrometer communicates with a frequency synthesizer which produces a continuous radio-frequency signal at the desired frequency. The output from the frequency synthesizer is sent back to the spectrometer which applies the pulse program and outputs pulses in accordance with the pulse diagram set by the user. The pulses are then sent to a power amplifier that amplifies the signal before being sent to the probe. Since the same inductive coil is used to apply the pulses and to read out the NMR signal, a duplexer is placed between the probe and the instrumentation. The duplexer is the rf traffic controller; it uses diodes and constructive/destructive interference to route the transmitted signal from the transmitter to the probe and the receiver signal from the probe to the receiver.

After the NMR signal from the sample passes through the receiver branch of the duplexer, it is amplified by a preamplifier and transmitted to the probe input of the

spectrometer. Once in the spectrometer, quadrature detection is implemented, and the two resulting channels of the signal are sent to the computer and digitized for analysis.

To monitor what is happening at the foot of the probe, the bare inner conductor of a coaxial cable placed near the coil is used as an antenna to pick up the pulse in the coil. The antenna signal is displayed on an oscilloscope. This provides an image of the pulse that is being applied to the coil to ensure that the power is reaching the coil and that there is no arching of voltage between any points of the NMR circuit. To ensure that the scope remains triggered on the pulse, the spectrometer provides a binary signal with $V \neq 0$ during the pulse and $V = 0$ at all other times for the scope to trigger on. A vector network analyzer (VNA) can be connected to the probe input to tune the frequency and match the impedance of the resonant circuit.

3.2.2 Quadrature Detection

Most NMR spectrometers utilize quadrature detection so that signals shifted above and below the resonant frequency can be distinguished from each other. The basics of quadrature detection are described in Section 2.1.1. As described in Eq. (2.5), quadrature detection returns a signal with real and imaginary components. In the context of NMR, the in-phase (real) component of the signal corresponds to the in-plane magnetization component along the axis along which the spins were initially tipped and the out-of-phase (imaginary) component corresponds to the in-plane magnetization along the orthogonal in-plane axis. In the frequency domain, the real part of the signal is the absorption spectrum, and the imaginary part is the dispersion spectrum.

An example of the real and imaginary components and the magnitude of the NMR signal in the time and frequency domains are shown in Figure 3.6. This signal is well-phased—the absorption spectrum is purely negative and the dispersion spectrum is

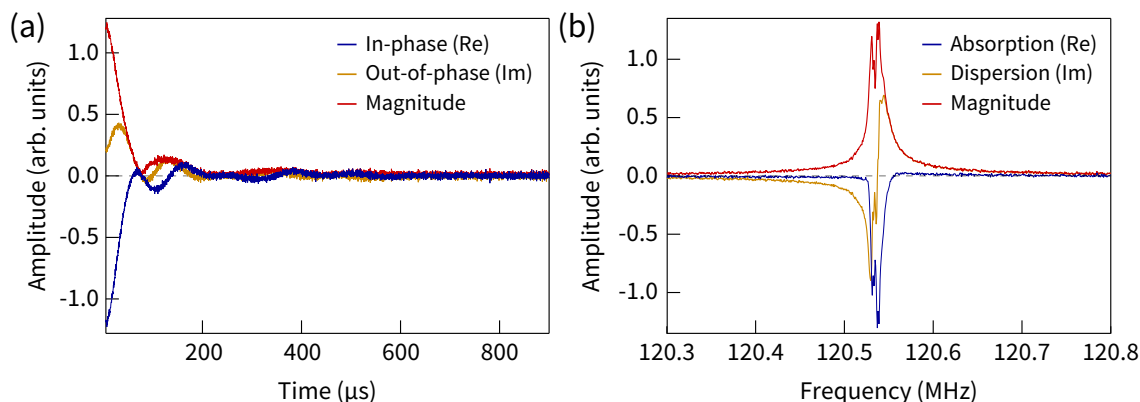


FIGURE 3.6: Representative example of the (a) time and (b) frequency domain of an NMR spin echo.

mostly symmetric about zero. In this case, the difference in symmetry about zero comes from the split peak in the signal. In the time domain, a well-phased signal has an imaginary component equal to zero at $t = 0$ and a peak in the real component at $t = 0$. This would correspond to the spins being tipped exactly along the intended axis without any phase shift. In Figure 3.6(a), the imaginary component isn't exactly zero because we are only acquiring half of the spin echo and are essentially missing the signal $t = 0$. In an FID, $t = 0$ occurs during the pulse and will never be acquired.

If the spins are tipped in-plane slightly off-axis, the in-plane magnetization at $t = 0$ will contain components along the x and y axes and the absorption and dispersion components will both be asymmetric about zero. This can be corrected by applying a phase shift to the signal in the signal processing stage. There are also experimental techniques that can be used to reduce errors in the phase during an experiment, which will be described in the next section.

3.2.3 Phase Cycling and Anti-Ringing

The radio-frequency signal output by the spectrometer to excite the spins can be assigned a phase that corresponds to the direction in the rotating frame along which the excitation pulse rotates the spins. In older spectrometers, like the MagRes system, the phase of the signal is produced electronically using quadrature hybrids which

divide an input signal and produce two 90° phase-shifted output signals. Since the phase is achieved electronically, instead of numerically like in newer spectrometers, the relative phase of the output signals is not exactly 90° . This slight inaccuracy in the relative phase between pulses creates spurious effects which can be eliminated through phase cycling. To implement phase cycling, the phase of the initial pulse is set along $+x$, $+y$, $-x$, $-y$ with the inversion pulse and reception phases correspondingly changing to produce physically identical copies of the same signal taken along each of the four directions. When averaged together, the slight errors in the phase produced by the spectrometer are averaged to zero. If the phase of the signal is exact, this technique will produce four completely identical measurements, making phase cycling useless.

The phase can also be cycled in a way that eliminates contributions to the signal from the system and from experimental effects. For example, the phase can be manipulated to select signals from nuclear spins that are J -coupled and suppress the signal from those that are not [75]. The applications of this type of phase cycling that will be discussed here focus on eliminating spurious signals introduced by experimental effects, namely the ring-down effect. The ring-down effect is an acoustic standing wave created by the applied rf pulse that can be picked up by the coil, obscuring the NMR signal [76]. Because the ring-down effect is created by the pulse, it cannot be attenuated by averaging, nor can it be distinguished from the NMR signal by changing the phase of the pulse. Ringing can occur in the body of the probe or in the coil itself and is most common for high-power pulses at low frequency and in high magnetic field. Techniques for minimizing ringing can be addressed in the design of the probe, but some ringing will persist because of the nature of discharging a large amount of rf power into a system.

To eliminate these effects, an anti-ringing phase sequence is implemented. Anti-ringing sequences share surface-level similarities with phase cycling, but in actuality

$\pi/2$ -pulse phase	π -pulse phase	acquisition phase
$+x$	$+y$	$+$
$-x$	$+y$	$-$
$-x$	$+x$	$+$
$+x$	$+x$	$-$

TABLE 3.1: “Double-anti-ringing” NMR phase sequence.

produce quite different effects on the NMR signal. Phase cycling sequences correct for imperfections in the phase without changing anything about the nature of the NMR signal measured, whereas anti-ringing sequences remove spurious effects in the signal by adding or subtracting FIDs depending on the phase of the pulse. Ringing occurs directly after the pulse, so for systems with a long decoherence time, the ringing after the first pulse does not impact the signal and a simple anti-ringing sequence can be implemented to eliminate the ringing after the second pulse so that the signal can be measured as soon after the second pulse as possible without interference from ringing. The ringing after the second pulse can be eliminated by repeating the same pulse but changing the sign of the acquisition. That means adding a measurement where the first pulse is applied along the $+x$ -direction and the second pulse along the $+y$ -direction, and subtracting a measurement where the first pulse is applied along the $-x$ -direction and the second pulse along the $+y$ -direction. When the decoherence time is much shorter, the ringing after the first pulse should also be canceled out, resulting in the slightly more complex “double-anti-ringing” phase sequence described in Table 3.1. Here, each pulse in the sequence is added at one point and subtracted at another. For example, looking at the first column, $+x$ is added in row 1 and subtracted in row 4 and $-x$ is added in row 3 and subtracted in row 2. Maintaining the relative phase between the first ($\pi/2$) and second (π) pulses in Table 3.1 while cycling through all four possible directions results in the 16-fold phase cycling and anti-ringing phase tables used in MagRes NMR measurements.

3.2.4 Calibrating Excitation Pulse

Properly calibrating the excitation pulse is an important part of obtaining a reliable NMR measurement. An ideal excitation pulse will tip the spins by $\theta_1 = 90^\circ$ so they lie fully in the xy -plane, assuming the external static field polarizes the spins along the z -axis. If $\theta_1 \neq 90^\circ$, then the spins will have some component along the z -direction which can introduce spurious effects into the NMR signal and attenuate its magnitude. There are two knobs to tune when calibrating the excitation pulse: the applied rf power and the pulse length. Increasing the attenuation (decreasing the power of the rf pulse) and decreasing the pulse length both act to reduce the amount of energy applied to the system by the pulse.

When calibrating the pulse, it is often more effective to start by maximizing the power. This is because short pulse lengths are generally favorable as they are more likely to irradiate the entire spectral linewidth, and most analytic models of NMR systems assume the pulse is instantaneous since the spins begin to decohere during a finite pulse. To maximize power, the transmitter attenuation is decreased while the pulse shape picked up by the probe antenna is monitored on the oscilloscope. The power is too high when the shape of the pulse is distorted by the arching of power from the incoming rf pulse to some other point at the foot of the probe. When arching begins to occur, two or three decibels of attenuation should be added, and then the pulse length can be calibrated.

There are two common ways to determine the correct pulse length to tip the spins by $\theta_1 = 90^\circ$. The first is to measure the NMR signal with a range of applied pulse lengths and integrate the signal to determine the pulse length that produces the strongest signal (largest integrated value). The strongest signal will correspond to the pulse length that tips the spins closest to $\theta_1 = 90^\circ$. A more precise method involves using a spin-lattice relaxation (T_1) pulse sequence ($\pi/2 - t_d - \pi/2 - \tau - \pi - \tau$

- *acquisition*), where $t_d \ll T_1$ so that the spins do not have time to relax back before the second $\pi/2$ pulse is applied. When a perfect $\pi/2$ pulse is applied, the initial pulse tips the spins into the xy -plane and then the spin echo sequence rotates the spins back to their initial relaxed position. Therefore, the ideal pulse length does not produce a signal when the above sequence is applied. Even a small deviation from the ideal $\pi/2$ pulse length on the initial pulse will introduce some z component after the first pulse, which will be amplified by the spin echo sequence and result in a visible NMR signal, making this a very precise way to determine the ideal rf pulse length.

The homogeneity of the oscillating field B_1 induced by the rf pulse through the coil across the sample can be checked by performing a standard inversion recovery spin-lattice relaxation measurement. If the field is completely homogeneous across the sample, all of the spins will be tipped 180° by the initialization pulse, so the magnetization for $t_d \ll T_1$ will have the same magnitude but opposite sign as when the spins are fully relaxed, *i.e.* $M(0) = -M(\infty)$. If there is a distribution in the B_1 field, some spins will be tipped by an angle not equal to 180° , which will decrease the magnitude of the total magnetization for $t_d \ll T_1$ and the T_1 relaxation curve will not be symmetric about zero. This distribution is averaged out when the initialization pulse tips the spins by 90° and can only be seen by the inversion recovery curve. If the entire sample is completely enclosed by a very homogeneous coil and significant asymmetry is seen in the inversion recovery curve, this could instead indicate that the π -pulse is not well calibrated. In quantum mechanical systems, it is possible that doubling the time of the $\pi/2$ -pulse will not produce a perfect π -pulse.

3.3 Measure of Spin Interaction Strength

Developing a complete and accurate understanding of the microscopic nature of emergent quantum phenomena is the cornerstone of condensed matter research. As such, many highly effective probes of matter have been developed to provide exper-

imental evidence to support and guide theoretical models. In the study of a single material, multiple different probes are often needed in order to gain a thorough understanding of the properties of the material. The reason is that the available experimental probes face limitations in the energy scales accessible to them, so by applying multiple probes that operate across different energy scales, a more complete picture of the emergent phenomena under investigation, which may occur across a broad energy scale, can be obtained. This workaround isn't without its own limitations, however. It is not uncommon for probes of different energy scales to yield conflicting results or for the complete nature of the dynamics of the system to lie outside the range of accessible time scales, as is most notably the case with glassy phase transitions [77, 78]. To provide a means of obtaining an accurate experimental description of such systems, we implement a measure of spin interaction strength (MSIS) that directly probes the ground state of a material by examining the properties of spins under rotation [79].

Unlike standard experimental probes, the MSIS does not measure a response function or the development of an order parameter and is insensitive to the thermodynamics of the system. Instead, it measures the relative phase incurred through the time evolution of spins and thus is not subject to the time- or energy-scale limitations of standard probes. This puts the MSIS in the unique position to provide a great deal of additional insight into the development of emergent quantum phenomena by detecting previously inaccessible changes in the quantum mechanical ground state of systems undergoing a phase transition. Additionally, the MSIS is sensitive not only to the magnitude of the spin interaction strength but also to its distribution, which essentially expands the resolution of the MSIS to every individual site in the system under investigation. The MSIS expands on standard nuclear magnetic resonance (NMR) techniques, so the dynamics captured by NMR measurements are also accessible by application of the MSIS.

3.3.1 Overview

The MSIS manipulates the time evolution of the nuclear spins being probed to independently refocus the effects from contributions to the microscopic Hamiltonian with different symmetry under inversion [79]. In a standard NMR spin echo pulse sequence, shown in Figure 3.7(a), the nuclear spins are excited by an applied rf pulse and then allowed to evolve (precess) over some time τ before a second pulse is applied which inverts the direction of time evolution, refocusing the spins back to their original position after the initial pulse. As the time evolution operator carries the Hamiltonian, the evolution of the spins over time τ depends on their environment and interactions with their surroundings. As an example, we will consider two spin-1/2 nuclei interacting via a dipole-dipole interaction placed in a static external field B_0 . This produces an interaction Hamiltonian of the form [80]:

$$\mathcal{H}_{int} = \omega_0 I_z + \omega_D I^2 (3 \cos^2 \phi - 1), \quad (3.20)$$

where ω_D is the strength of the dipole-dipole interaction, ϕ is the angle between the bond of the two spin-1/2 nuclei and the static field B_0 , and $\omega_0 = \gamma B_0$ is the Larmor precession frequency of the nuclei being probed with gyromagnetic ratio γ . The first term in Eq. (3.20) is the Zeeman term which accounts for the effect of the static field and admits an inversion asymmetric (I_i^n , n odd) term. The second term is the dipolar interaction term which admits an inversion symmetric (n even) term. Neglecting the spin-singlet state of the coupled spin-1/2 system is valid as the spin singlet does not couple to the external field nor does it mix with the triplet states to which it is orthogonal. The difference in inversion symmetry between these two terms becomes very important when considering the pulse sequence described above, in which the nuclear spin evolution is inverted in time by the π -pulse.

Because these terms in the Hamiltonian behave differently under inversion, they

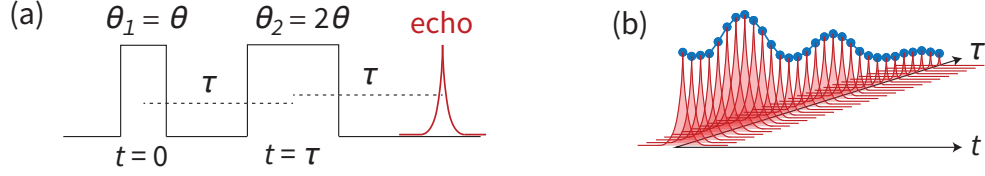


FIGURE 3.7: (a) Pulse sequence used to measure the spin interaction strength and (b) modulation of the NMR signal as a function of spin evolution time τ and experiment time t .

can be probed independently by studying the way they interfere with each other under different time evolutions. What results is a modulation of the NMR signal due to interference of these components with different symmetries upon inversion which creates a τ dependence to the amplitude of the spectral lines, as is shown in Figure 3.7(b). The frequency of the modulation is proportional to the strength of the dipole-dipole interaction.

3.3.2 Comparison to Other Measurement Techniques

At first glance, it may appear that everything the MSIS measures can be obtained through the application of other measurement techniques. An experimental probe that may seem especially similar to MSIS is muon spin spectroscopy (μ SR), a technique that characterizes the magnetic ordering of a material by detecting positrons emitted from excitations caused by embedding muons in the sample. μ SR is very sensitive to small magnetic fields and provides a good measure of the volume fraction of different local fields in a material, making it useful for studying materials with very weak magnetic ordering, zero net magnetization, or with short ranged or not fully formed magnetic ordering [68,81]. The MSIS is also sensitive to small local fields, any form of magnetic ordering, and to the presence of a distribution of local fields within the material.

The MSIS goes beyond the capabilities of μ SR in two main respects. First, μ SR does not provide spatial information, as the site of the embedded muon is unknown. The MSIS expands on standard NMR techniques, and so the location of the probe

is always known to be at the site of the nucleus whose spins are being excited. This provides a greater level of certainty to the MSIS as the interpretation of μ SR results requires assumptions to be made about the muon site and the nature of the coupling. Secondly, μ SR can only detect dynamics that occur on time scales accessible during the finite lifetime of the embedded muon which makes it unable to detect slow relaxation processes. This makes standard NMR a useful complementary probe as it has no problem detecting slow relaxation processes, but is not sensitive to the very short relaxation times that μ SR can measure [81]. In contrast to both standard NMR and μ SR, the MSIS technique directly probes the ground state, foregoing any timescale considerations, and can therefore provide the precise moment at which a material magnetically orders regardless of the energy scale of the dynamics involved with its onset, effectively achieving in a single measurement what would otherwise require the application of multiple probes at different energy scales to achieve. In addition, while MSIS is not measuring dynamics, it is still sensitive to variations in the local field at the nuclear site throughout the sample caused by effects such as short- or long-ranged correlations.

Neutron scattering is another measurement technique that provides information similar to that of the MSIS. In neutron scattering, spectral peaks occur when the scattering vector is equal to a reciprocal lattice vector, making this a great tool for determining the crystal structure of a material. Similarly to the MSIS, it can also be used to determine the magnetic ordering of a material. The magnetic moment of the neutrons makes them sensitive to the net moment of the atoms they're scattering off, so additional spectral peaks corresponding to the magnetic unit cell will appear with the onset of magnetic order [82, 83]. Inelastic neutron scattering can measure the nature of exchange interactions in a material, which provides information about orbital overlap similar to the MSIS. While neutron scattering provides direct access to the full magnetization-magnetization density correlation function, it remains constrained

by a limited accessible energy scale and cannot provide a measure of the distribution in the spin-spin interaction strength that the MSIS is sensitive to. Additionally, since MSIS is an expansion of standard NMR techniques, it utilizes the same simple and cost-effective setup, making it a much more accessible technique than μ SR or neutron scattering.

3.3.3 Derivation of Theoretical Model for a Dipolar System

To understand mathematically how the MSIS technique works, we will go through the derivation of the theoretical model for a dipolar system which is the type of system we will examine with this technique in Chapter 4. We will start by writing a Hamiltonian to describe two interacting nuclei with nuclear spin $I = 1/2$ which will help to define what the interaction strength we are measuring physically corresponds to. Then we will apply rotation operators to the Hamiltonian to describe the effects of a pulse and time evolution operators to describe the evolution of the spins over time τ between pulses. By applying the pulse sequence used to measure the decay of in-plane magnetization as a function of τ (T_2) to the interaction Hamiltonian, we will obtain the magnetization decay equation for a dipolar system.

Spin-Spin Interaction Hamiltonian

To obtain a theoretical description of the modulation of the NMR signal as a function of τ , shown in Figure 3.7(a), we must first obtain an accurate quantum mechanical description of the system. The dimer formed by two closely coupled spin- $1/2$ nuclei discussed in Section 3.3.1, which create a spin singlet and a spin triplet state, acts as our experimental probe. The spin singlet state does not couple to the external field—it is insensitive to NMR and remains in the same eigenstate when the excitation pulse is applied—and is orthogonal to the spin triplet state, meaning it

cannot mix with them. Therefore, it is only the spin triplet state that determines the time propagation of the observable magnetization, and the singlet state can be disregarded. Consequently, we can treat this two spin-1/2 system as an effective spin-1 system.

To prove that this is valid, we start by writing a Hamiltonian for two $I = 1/2$ nuclei coupled by a general interaction term sitting in an external field:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{int} = -\hbar\gamma \mathbf{B}_0 \cdot (\mathbf{I}_1 + \mathbf{I}_2) - J_{12} \mathbf{I}_1 \cdot \mathbf{I}_2, \quad (3.21)$$

where $\mathcal{H}_Z$ is the Zeeman term and $\mathcal{H}_{int}$ is the interaction term, γ is the nuclear gyromagnetic ratio, J_{12} is the exchange interaction term between two spins, and $\mathbf{I}_{i=1,2}$ is the conventional spin operator for spin 1 and spin 2. If we define the static field $\mathbf{B}_0 = B_0 \hat{z} = B_z$ which gives:

$$\mathcal{H} = \hbar\gamma (I_1^z + I_2^z) B_z + J^\parallel I_1^z I_2^z + J^\perp (I_1^x I_2^x + I_1^y I_2^y), \quad (3.22)$$

where $J^\parallel$ describes component of the exchange interaction parallel to the external field (z -axis) and $J^\perp$ describes the perpendicular (xy -plane) component. Two spin-1/2 particles form a single state

$$|s\rangle = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} \quad (3.23)$$

and triplet states

$$\begin{aligned} |t_+\rangle &= |\uparrow\uparrow\rangle, \\ |t_-\rangle &= |\downarrow\downarrow\rangle, \\ |t_0\rangle &= \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}. \end{aligned} \quad (3.24)$$

Acting just the interaction portion of Eq. (3.22) on the states in Eq. 3.23 and 3.24 produces the following eigenenergies:

$$\begin{aligned} E(s) &= \left(\frac{J^{\parallel}}{4} + \frac{J^{\perp}}{2} \right), \\ E(t_0) &= \left(\frac{J^{\parallel}}{4} - \frac{J^{\perp}}{2} \right), \\ E(t_{\pm}) &= -\frac{J^{\parallel}}{4}. \end{aligned} \tag{3.25}$$

Ignoring the singlet state, these eigenstates give the following effective spin-1 Hamiltonian,

$$\mathcal{H}_{\text{eff}} = [E(t_{\pm}) - E(t_0)] I_z^2 = \left(-\frac{J^{\parallel}}{4} - \frac{J^{\parallel}}{4} + \frac{J^{\perp}}{2} \right) I_z^2 = \frac{J^{\perp} - J^{\parallel}}{2} I_z^2 \tag{3.26}$$

from which it is straightforward to see that that this equation is equivalent to the interaction term in Eq. (3.21) and therefore, that two closely coupled spin-1/2 particles can effectively be modeled as a single spin-1 particle.

To understand how this interaction term compares to the dipolar interaction, we can repeat the procedure above with the dipolar Hamiltonian,

$$\hbar \mathcal{H}_{\text{dip}} = \sum_{j < k} \frac{\mu_0 \hbar^2 \gamma_i \gamma_j}{4\pi r_{jk}^3} \left[\mathbf{I}_j \cdot \mathbf{I}_k - 3 \frac{(\mathbf{I}_j \cdot \mathbf{r}_{jk})(\mathbf{I}_k \cdot \mathbf{r}_{jk})}{r_{jk}^2} \right] \tag{3.27}$$

where the vector $\mathbf{r}_{jk}$ describes the relative position of the spins. For just two homonuclear spins, we can rewrite this as

$$\mathcal{H}_{\text{dip}} = \omega_D \left[\mathbf{I}_1 \cdot \mathbf{I}_2 - 3 \frac{(\mathbf{I}_1 \cdot \mathbf{r}_{12})(\mathbf{I}_2 \cdot \mathbf{r}_{12})}{r_{12}^2} \right] \tag{3.28}$$

where $\omega_D = \mu_0 \hbar \gamma^2 / 4\pi r_{12}^3$. Orienting the bond between the coupled spin-1/2 nuclei to

be parallel to the external field $B_0\hat{z}$, we can rewrite the dipolar Hamiltonian as:

$$\mathcal{H}_{\text{dip}} = \omega_D [\mathbf{I}_1 \cdot \mathbf{I}_2 - 3I_1^z I_2^z] = -\omega_D [2I_1^z I_2^z - I_1^y I_2^y - I_1^x I_2^x]. \quad (3.29)$$

Acting $\mathcal{H}_{\text{dip}}$ on the states in Eq. (3.23) and Eq. (3.24) results in the following eigenstates:

$$\begin{aligned} E(s) &= 0 \\ E(t_0) &= \omega_D \\ E(t_{\pm}) &= -\omega_D/2 \end{aligned} \quad (3.30)$$

which gives the following dipolar Hamiltonian:

$$\mathcal{H}_{\text{eff}} = [E(t_{\pm}) - E_0] I_z^2 = \left(-\frac{\omega_D}{2} - \omega_D \right) I_z^2 = -\frac{3}{2} \omega_D I_z^2. \quad (3.31)$$

Comparing this to the general interaction equation in (3.26), we see that

$$\begin{aligned} J^{\parallel} &= 2\omega_D \\ J^{\perp} &= -\omega_D \end{aligned} \quad (3.32)$$

which is expected for a dipolar interaction.

Magnetization Decay Equation

Now that we have a good description for a system of two closely coupled spin-1/2 nuclei, we can move on to understanding how the system evolves with the application of the NMR pulse sequence described in 3.7(a). The NMR spin echo pulse sequence consists of an initial excitation pulse that tips the spins, typically by $\theta_1 = 90^\circ$, followed by some time τ over which the spins are allowed to evolve in time, *i.e.* precess, before a second pulse $\theta_2 = 2\theta_1$ is applied to invert the spins. The spins are then allowed to

precess for another time τ before the signal is acquired. To model the evolution of our system with the application of the described pulse sequence, we will follow the derivation in Ref. [84] for an analogous system with quadrupolar interactions.

The spin echo pulse sequence can be written as quantum mechanical operators acting on an initial state in which the spins are in thermal equilibrium aligned along the z -axis by the static field $\mathbf{B}_0 = B_0 \hat{z}$. I_x , I_y , and I_z will denote the standard spin operators for spin-1 particles. The first pulse rotates the spins by θ_1 along the y -axis. Neglecting all relaxation mechanisms and assuming the pulses are instantaneous and therefore that no decoherence occurs during the pulse, the rotation operator for a rotation about the y -axis can be written as:

$$U_y = e^{-iI_y\theta} = \begin{pmatrix} A & -C & D \\ C & B & -C \\ D & C & A \end{pmatrix}, \quad (3.33)$$

where θ is the spin tip-angle ($\theta_1 = \theta$ for the excitation pulse and $\theta_2 = 2\theta$ for the inversion pulse) and

$$\begin{aligned} A &= \frac{1}{2}(\cos \theta + 1), \\ B &= \cos \theta, \\ C &= \frac{1}{\sqrt{2}} \sin \theta, \\ D &= \frac{1}{2}(1 - \cos \theta). \end{aligned} \quad (3.34)$$

If the spins are instead rotated about the x -axis,

$$U_x = e^{-iI_x\theta} = \begin{pmatrix} A & -iC & -D \\ -iC & B & -iC \\ -D & -iC & A \end{pmatrix}. \quad (3.35)$$

The inverse of U_x and U_y maintain the same form, but with a sign change on C . When the spins are evolving over time τ , the interaction Hamiltonian takes the form:

$$\mathcal{H}_{int} = \omega_{int} I_z^2, \quad (3.36)$$

where $\omega_{int} = -3\omega_D/2$ from Eq. 3.31. The time propagation operator then takes the standard form:

$$U_t = e^{-i\mathcal{H}\tau} = \begin{pmatrix} e^{-i\omega\tau} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\omega\tau} \end{pmatrix}. \quad (3.37)$$

The initial pulse acts on a density matrix which describes the motion of the spin system in the rotating frame given in its equilibrium state by a thermal distribution along the z -direction,

$$\rho(0) = U_y I_z U_y^{-1} = \cos \theta_1 I_z + \sin \theta_1 I_x. \quad (3.38)$$

The amplitude of the signal, which is proportional to the voltage induced in the coil by the precessing magnetization, as a function of τ is:

$$\langle I(\tau) \rangle = \text{Tr}(\rho(2\tau) I_+), \quad (3.39)$$

for $I_+ = I_x + iI_y$. Applying the time evolution and second rotation to $\rho(0)$, we get

$$\langle I(\tau) \rangle = I_x U_t U_i U_t \rho(0) U_t^{-1} U_i^{-1} U_t^{-1}, \quad (3.40)$$

where $i = x, y$ depending on whether the inversion pulse acts along the x - or y -axis. If the inversion pulse acts along the y -axis,

$$\langle I(\tau) \rangle \propto 2 [\cos(2\omega_{int}\tau) \cos \theta_2 \sin \theta_1 + \cos(\omega_{int}\tau) \cos \theta_1 \sin \theta_2]. \quad (3.41)$$

If the inversion pulse acts instead along the x -axis,

$$\langle I(\tau) \rangle \propto 2 \sin \theta_1 [\cos(2\omega_{int}\tau) \cos^2 \theta_2 + \sin^2 \theta_2]. \quad (3.42)$$

Finally, in order to get an accurate description of the process that the spins undergo in the experiment, we must consider the anti-ringing sequence applied which is commonly used to cancel out spurious effects introduced into the signal by ringing in the circuit from the applied rf pulse. The anti-ringing sequence used for the measurements that will be discussed in the next chapter is: $\theta_1 = [+y, -y, -y, +y]$ and $\theta_2 = [+x, +x, +y, +y]$ with an acquisition sign $[+, -, +, -]$. While the MagRes sequence is 16-fold instead of 4-fold, there are only four unique combinations, which are equivalent to this sequence. MagRes cycles through the four unique combinations to simultaneously apply a phase-cycling scheme, in addition to the anti-ringing, to remove any effects from slight imperfections in the phasing of the signal.

Applying the anti-ringing phase sequence to our calculations results in a cancellation of the $\cos \omega \tau$ term, leaving only the $\cos 2\omega \tau$ term which results in the following equation:

$$\langle I_x(2\tau) \rangle \propto 4 \sin \theta_1 \cos \theta_2 [\cos \theta_2 - 1] \cos(2\omega_{int}\tau) + \sin^2 \theta_2 \sin \theta_1. \quad (3.43)$$

Further assuming that $\theta_2 = 2\theta_1 \equiv \theta$,

$$\langle I_x(2\tau) \rangle \propto -8 \sin^3 \theta \cos 2\theta \cos(2\omega_{int}\tau) + 16 \sin^3 \theta \cos^2 \theta. \quad (3.44)$$

The above equation describes the amplitude of the spin echo using the described pulse sequence and anti-ringing in the presence of the spin-spin interaction described in Eq. (3.26).

To get a full expression for the decay in magnetization in the presence of spin-spin

decoherence, Eq. (3.44) is multiplied by an exponential decay, $\exp[-(2\tau/T_2)^\alpha]$, where $1/T_2$ is the spin-spin decoherence rate and $\alpha = 1$ gives a Lorentzian decay and $\alpha = 2$ a Gaussian decay. The distribution in the ^{31}P - ^{31}P interaction strength would cause a decay in the oscillations at a rate different from the overall decay in the signal due to spin-spin decoherence, as will be described more fully later on. To account for this in Eq. (3.44), a second exponential decay of the form $\exp[-(2\tau\Gamma_{int})]$, where Γ_{int} is the distribution in ω_{int} , acts only on the $\cos 2\omega_{int}\tau$ term. Adding these two decay terms, one obtains the following equation for the magnetization as a function of τ :

$$M(\tau) = [-8 \sin^3 \theta \cos 2\theta \cos(2\omega_{int}\tau) e^{-(2\tau\Gamma_{int})} + 16 \sin^3 \theta \cos^2 \theta] e^{-(2\tau/T_2)^\alpha}. \quad (3.45)$$

To further simplify Eq. (3.45) and make the spin tip-angle θ dependence more explicit, we can represent the trigonometric factors as follows:

$$A(\theta) = F(4 \sin \theta - 3 \sin 3\theta + \sin 5\theta), \quad (3.46)$$

$$B(\theta) = F(2 \sin \theta + \sin 3\theta - \sin 5\theta). \quad (3.47)$$

which gives the final equation:

$$M(\tau) = [A(\theta) \cos(2\omega_{int}\tau + \varphi) e^{-2\tau\Gamma_{int}} + B(\theta)] e^{-(2\tau/T_2)^2}, \quad (3.48)$$

where φ is introduced as a phase correction to account for the fact that is impossible to measure at $\tau = 0$ since it occurs during the pulse. $A(\theta)$ and $B(\theta)$ describe the way $M(\tau)$ changes with spin tip-angle θ , and fitting them to experimental data acts as a check that the system and model are in good agreement. It should also be noted that with ideal pulsing conditions ($\theta_1 = 90^\circ$ and $\theta_2 = 180^\circ$) $B(\theta = 90^\circ) = 0$ which makes it impossible to distinguish between the Γ_{int} decay and the T_2 decay. Therefore, to obtain an accurate measure of T_2 and Γ_{int} , the spins must be tipped at an angle

off-90° so that $B(\theta) \neq 0$.

CHAPTER 4

Measure of Spin Interaction Strength in van der Waals Antiferromagnet NiPS_3

Our NMR study of NiPS_3 was originally motivated by the need to characterize the material prior to measuring with MTJ sensors. As it is a van der Waals antiferromagnetic material, it was a strong candidate for applying the MTJ sensor to the study of layer dependence in low-dimensional magnetic systems. However, the NMR results ended up being interesting in their own right, showing very clear oscillations in signal amplitude as a function of the decoherence time τ . Further investigation of these oscillations revealed a striking change in their frequency with magnetic ordering and subsequent theoretical work revealed a connection between the oscillation frequency and the interaction strength of the coupled ^{31}P nuclei being probed. This chapter covers the details of these measurements and results.

4.1 Crystal and Magnetic Structure of NiPS₃

The transition metal phosphorus trichalcogenide family MPX_3 ($M = \text{Mn, Fe, Co, Ni}$; $X = \text{S and Se}$) is a particularly interesting group of magnetic van der Waals materials. In this family of materials, the transition metals M are arranged in a hexagonal structure. Two phosphorus atoms sit symmetrically across the plane of the transition metal atoms in the center of the hexagon, and X ligands bond the phosphorus atoms to the M atoms and the M atoms to each other. The crystal structure of NiPS₃ is shown in Figure 4.1(a).

The magnetic properties of this family of materials are strongly influenced by the choice of transition metal and chalcogenide ligand, likely due to a change in the dominant exchange interaction with transition metal substitution and tuning of the magnetic anisotropy with chalcogenide substitution [14, 85–89]. In bulk, all compounds in this family exhibit some form of antiferromagnetic (AFM) order below their respective Néel temperatures T_N , but display different magnetic behaviors in the monolayer [90, 91]. NiPS₃ displays zigzag AFM ordering of the nickel spins in bulk which disappears in the monolayer [90, 92].

NiPS₃ is a self-doped negative charge-transfer insulator, so its electronic and spin structures are closely related [86, 93]. The filled t_{2g} d -orbitals of Ni²⁺ mean that there is no direct exchange between nickel atoms, so all interactions between nickel atoms occur instead through a superexchange process mediated by the sulfur ligands. The third nearest neighbor (3nn) spin coupling J_3 is negative and about four times as large as the first nearest neighbor (1nn) spin coupling J_1 , indicative of a strong AFM superexchange interaction whereas J_1 is positive, and thus ferromagnetic in nature. The second nearest neighbor (2nn) nickel atoms do not share a common sulfur atom, so J_2 is very small as electron exchange occurs only through direct orbital overlap. Interactions between 3nn nickel atoms are mediated by the p -orbital of a single sulfur

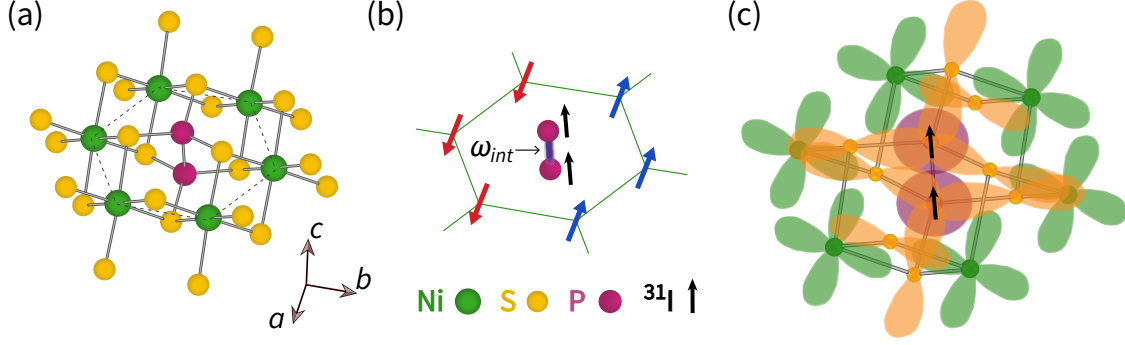


FIGURE 4.1: (a) Local environment of the ^{31}P dimer [97] created using VESTA software package [98] and (b) an illustration showing the orientation of the nickel atoms' spins in the $z\text{AFM}$ ordered state in red and blue and the direction of the static applied field H_0 , and thus nuclear spin orientation, in black. ω_{int} denotes the strength of the interaction between the coupled ^{31}P atoms. (c) An approximate sketch of the overlap in electronic orbitals in NiPS_3 .

atom that serves both nickel. The covalent bonding of the phosphorus and sulfur atoms creates a strong hybridization of their p -orbitals and, by extension, interaction between the phosphorus and nickel atoms [86, 88, 94–96]. A sketch of the orbital overlap is given in Figure 4.1(c). This allows the MSIS technique, which probes the ^{31}P nuclei, to effectively probe the electronic behavior of the nickel atoms as well.

4.2 Motivation for Studying NiPS_3

NiPS_3 is a system well suited to the application of the MSIS technique for multiple reasons. For one, the structure of this material lends itself well to the application of this probe. The two phosphorus atoms that sit symmetrically above and below the ab -plane (see Figure 4.1) are in close enough proximity to each other to form a dimer with dipole-dipole interaction [80]. The resulting intra-dimer interaction creates an effective nuclear spin-1 from the two ^{31}P spin-1/2 nuclei, creating a spin singlet and spin triplet state which. The interaction of the phosphorus atoms with the nickel atoms through the sulfur ligand makes this interaction more complicated than a simple interaction between two magnetic dipoles. This added complexity in the interaction makes this probe so effective in studying NiPS_3 and also allows the

^{31}P nuclei to be an effective probe of nickel spins.

NiPS_3 is also a fairly well-understood and well-studied material. Its magnetic ordering has been well characterized—it is paramagnetic (PM) above its Néel temperature $T_N = 155$ K [16,85,86,88,90,99] and displays zigzag antiferromagnetic order below T_N , with spins aligned mostly in the ab -plane with a slight cant towards the c -axis [15,88,100,101], as illustrated in Figure 4.1(b), and disappearing magnetic order in the monolayer [90,92]. The nature of its exchange interactions, as well as how they change through evolution from NiPS_3 to MPX ($M = \text{Fe}, \text{Mn}$; $X = \text{Se}$), has also been thoroughly studied revealing the presence of a strong third-nearest-neighbor interaction between nickel atoms that involves the phosphorus atoms [14,85–89,91,94]. This provides a strong base on which to rely in the application of the MSIS to this sample.

Although much about NiPS_3 is well understood, there remain open questions and disagreements between the results obtained by different measurement techniques. For example, previous NMR experiments found the presence of quasi-2D correlations at $T > T_N$ [16,17], behavior typical for 2D magnetic materials [102], but that were conspicuously absent in ESR measurements that found that the strong interlayer coupling in NiPS_3 produced more 3D-like spin dynamics than 2D-like, explaining the absence of 2D correlations [14,15]. Since the MSIS directly probes the electronic orbital interaction between the two ^{31}P nuclear spins, which includes overlap with the orbitals of the magnetic nickel atoms that would participate in such correlations through the sulfur atoms, sketched in Figure 4.1(c), and because we can obtain a measure of the distribution of this interaction as well as its strength, we can essentially get a snapshot of what is occurring at every nickel site across the sample and conclusively say that there are no 2D correlations present in the paramagnetic state.

The final reason for applying the MSIS measurement technique to this material is that standard NMR techniques yield little useful information. As will be discussed

in the next section, the spin-lattice relaxation rate as a function of temperature does not produce the standard features characteristic of a magnetic transition and measurements of the peak splitting below the magnetic transition yield wildly inaccurate results due to spectral broadening with the development of the order parameter. Furthermore, specific heat measurements, presented in Section 4.6, did not reveal conclusive results on the nature of the phase transition. The inconclusive nature of these results highlights the need for further study of this sample using new measurement techniques, such as the MSIS technique.

Finally, we chose to study NiPS₃ with this unique probe for the simple reason that quasi-2D magnetic van der Waals materials hold great potential for applications to technological advancements such as in spin and valleytronics [1–3], magnetic tunneling junctions [36, 103, 104], photodetectors [6, 7], and transistors [4, 5], to name a few. They also provide an environment in which to explore magnetic phenomena such as topological spin phases, the quantum spin Hall effect, and quantum spin liquids [105–108] and in which to investigate the nature of 2D magnetic ordering [90–92, 109] as they are easily exfoliatable down to a monolayer. The application of the MSIS has already provided additional insight into open questions about this material in bulk and its application to the study of monolayer NiPS₃ and other quasi-2D magnetic materials is expected to be similarly illuminating.

4.3 Experimental Methods

All of the ³¹P NMR measurements presented here were performed on a single bulk crystal of NiPS₃, 6.6 x 3.25 x 0.2 mm, shown in Figure 4.2(a), grown by the same procedure as in Ref. [92]. A different crystal, grown by the same sample growers, was measured for the specific heat measurements.

The measurements presented in this paper were taken at two different facilities. All data taken at 7 T were measured at Brown University, and those taken at 7.2 T

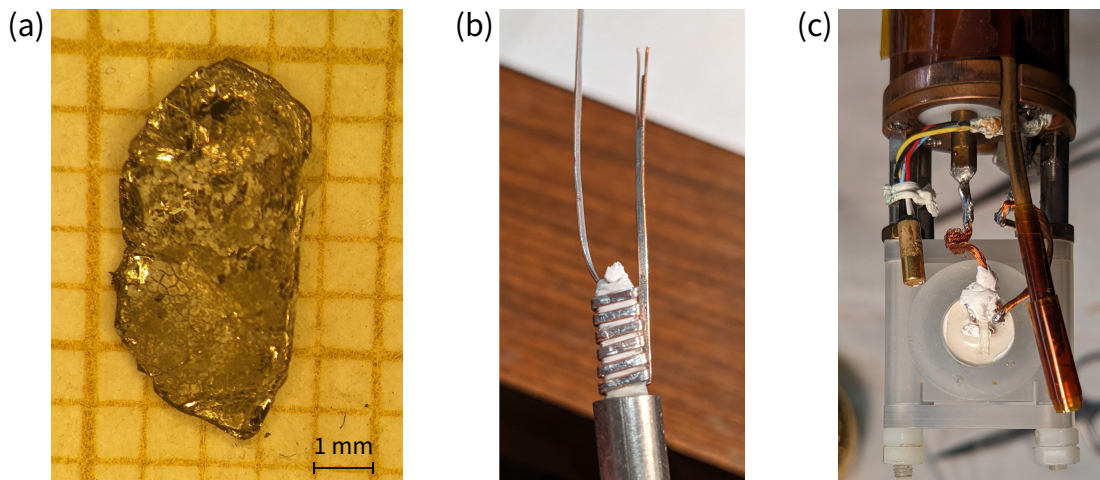


FIGURE 4.2: (a) Photo of the NiPS₃ crystal measured in these experiments on a 1 mm² grid. Photo shows the *ab*-plane looking along the *c**-axis. (b) Coil made for measurements taken at the LNCMI. Three copper wires are soldered together in order to make the coil long enough to cover the full sample while maintaining proper inductance for the NMR circuit to resonate in the desired frequency range. (c) Photo of the sample mounted in the goniometer on the probe used for measurements taken at the LNCMI.

and 14 T were taken at the Laboratoire National des Champs Magnétiques Intenses (LNCMI) in Grenoble, France. The magnets at both facilities are high homogeneity superconducting magnets and, in both cases, state-of-the-art laboratory-made NMR spectrometers were used. Different NMR coils were used for the two different sets of measurements. The NMR coil used for the measurements taken at the LNCMI is shown in Figure 4.2(b). In both cases, the sample was mounted in the coil without the use of glue or other fixing agent and inserted into a single-axis goniometer for sample rotation on a lab-built probe. The sample in the goniometer on the LNCMI probe is shown in Figure 4.2(c). Measurements were taken with the crystallographic *c**-axis (out-of-plane direction) aligned to be parallel to the static field B_0 within a margin of error no greater than $\pm 2^\circ$. For the measurements taken at Brown, the sample was rotated relative to the static field B_0 using the single-axis goniometer from the $B_0 \parallel c^*$ -axis orientation to the $B_0 \perp c^*$ -axis orientation.

For the 7 T measurements taken at Brown University, temperature control was

achieved using a closed cycle ^4He cryostat. At the LNCMI (7.2 T and 14 T measurements), a variable temperature insert (VTI) was used, which made finer tuning of the temperature possible and increased the temperature stability. In both set-ups, the temperature was measured using a calibrated Lakeshore Cernox thermometer mounted on the probe near the sample. The distance between the sample and the thermometer in both cases was comparable.

A standard spin echo pulse sequence ($\pi/2 - \tau - \pi - \tau$) was used for spectral and relaxation measurements. The ideal pulse length to achieve a $\theta = 90^\circ$ spin tip angle was calibrated using a T_1 relaxation process, since the spectral amplitude displays a non-standard dependence on the pulse length, making nutation measurements unsuitable for pulse calibration in this context. For pulse-length-dependent measurements, the pulse length is varied to change the spin tip angle θ and the second pulse in the spin echo (rephasing pulse) is always equal to twice the length of the first pulse (excitation pulse). The spin-spin relaxation (T_2) measurements were obtained by varying the time τ between pulses in the spin echo, and each point of the T_2 relaxation curve is the integrated spectrum for each value of τ .

Spin-lattice relaxation (T_1) was measured using a standard T_1 pulse sequence ($\pi/2$ (x10) - t - $\pi/2$ - τ - π - τ) with varying t and $\tau = 10 \mu\text{s}$. The spin-lattice relaxation rate T_1^{-1} was extracted using a simple exponential of the form:

$$M(t) = (M_\infty - M_0)(1 - e^{-t/T_1}) + M_0, \quad (4.1)$$

where M_∞ is the thermal equilibrium value of the longitudinal magnetization and M_0 is its value at $t = 0$.

4.4 Results

Application of the MSIS to NiPS_3 revealed a change in the ^{31}P - ^{31}P interaction strength at the magnetic phase transition which indicates some change in the hybridization of the orbitals participating the nickel superexchange pathways. A change in the electronic shielding of the ^{31}P nuclei concurrent with the change in interaction strength confirms the electronic origin of the ^{31}P - ^{31}P interaction. Furthermore, interactions at equivalent lattice sites are found to be uniform across the sample in the paramagnetic state because no distribution in the ^{31}P - ^{31}P interaction strength was found above the transition. The results of standard ^{31}P NMR measurements of NiPS_3 will also be presented.

4.4.1 ^{31}P - ^{31}P Interaction Strength from MSIS

The ^{31}P - ^{31}P interaction causes a sinusoidal modulation of the spin echo amplitude as a function of the time τ between pulses in a standard spin echo, which causes oscillations in the characteristic decay of the NMR signal, shown in Figure 4.3(a). Tracing the temperature dependence of ω_{int} , shown in Figure 4.3(b), reveals a strikingly clear drop in ω_{int} from one constant value in the PM phase (ω_{int}^{PM}) to another constant value in the AFM phase ($\omega_{int}^{\text{AFM}}$) with some region between where a mixture of the two frequencies causes beats in the T_2 decay. The onset of the change occurs around 156.5 K and reaches a stable value again at around 152.5 K, which plainly defines the region over which the magnetic phase transition occurs. The onset of the PM-AFM transition is consistent with the reported value of T_N determined by electron spin resonance [14,15], SQUID magnetometry [110], and neutron diffraction [100] and the most cited value of $T_N = 155$ K [16,85,86,88,90,99] is precisely the temperature at which ω_{int}^{PM} and $\omega_{int}^{\text{AFM}}$ contribute equally to the signal. The continuous nature of the system evolution from being dominated by ω_{int}^{PM} to being dominated by $\omega_{int}^{\text{AFM}}$

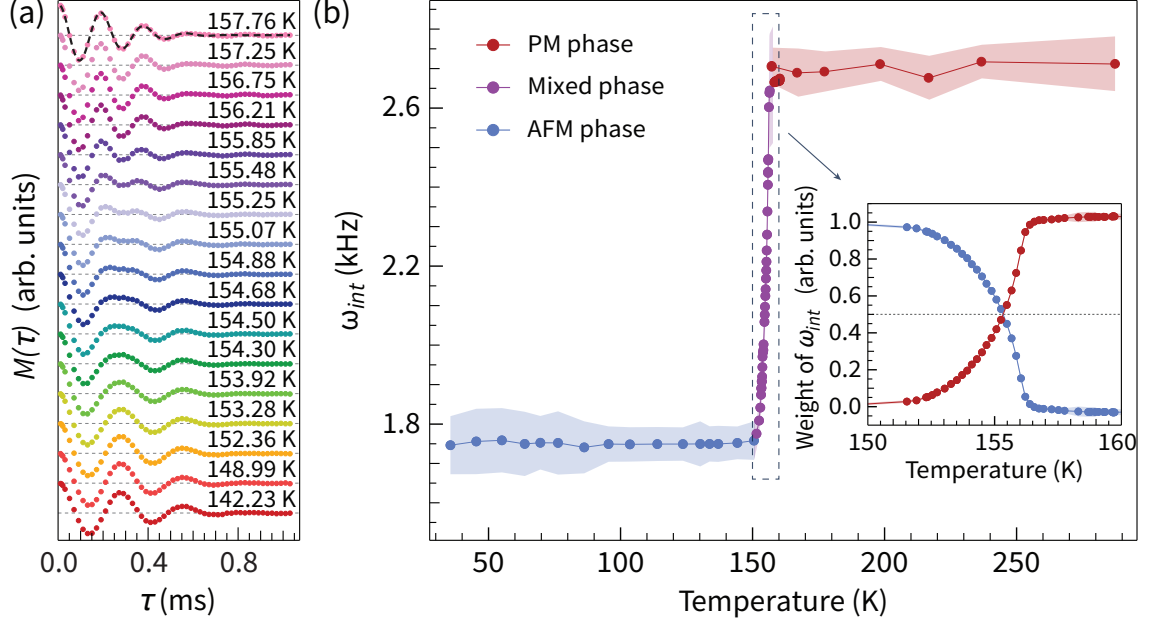


FIGURE 4.3: (a) Oscillations in the integrated signal as a function of the spin-spin decoherence time τ measured at $B_0 = 7.2$ T. The dashed black line overlaid on the 157.76 K curve represents a characteristic fit of Eq. (3.48) to the data. (b) The ^{31}P - ^{31}P interaction strength ω_{int} extracted from fitting Eq. (3.48) to the T_2 relaxation curves $M(\tau)$ for measurements at all three fields measured. The 7 T data is included to show that ω_{int} remains constant in the PM state. As it was taken using an entirely different system, the y -data is offset by -0.16 kHz and the x -data by -2.7 K to show it aligned with the 7.2 T and 14 T data.

is shown in the beginning of Figure 4.3 (b) where the weight of $\omega_{int}^{\text{PM(AFM)}}$ (*i.e.* 1 = fully PM (AFM) and 0 = fully AFM (PM)) is plotted through the transition. This change in the relative weight of $\omega_{int}^{\text{AFM}}$ over ω_{int}^{PM} in the overall signal is also visually apparent in the magnetization recovery curves in Figure 4.3(a). There is a clear region over which beats from the interference of these two frequencies develop, reach a maximum, and then decrease again, revealing a mixed phase state characteristic of a weakly first-order phase transition, consistent with previous findings [18].

This drop in ω_{int} across the transition indicates some change in the ^{31}P - ^{31}P interaction strength between the PM and AFM states. Without any influence from the surroundings of the ^{31}P dimer, the only contributions to ω_{int} are the value of the ^{31}P nuclear gyromagnetic ratio and the distance between the two ^{31}P nuclei. However,

the reduction in ω_{int} in the vicinity of T_N is too large to be solely due to a change in the distance between the two phosphorus atoms. To account for the observed change in ω_{int} , the separation would need to increase by about a third of an angstrom, around 14% of the distance between the P atoms. No such changes in the lattice parameters have been detected with magnetic ordering [95, 100].

Since the ^{31}P dimer does interact with its surroundings and since the change in ω_{int} at T_N cannot be accounted for purely by a change in the distance between the ^{31}P nuclei in the dimer, there must be some interaction between the phosphorus atoms and the nickel atoms that develops in the PM-AFM transition resulting in a change in ω_{int} with the magnetic ordering of the nickel atoms. This conclusion is strongly supported by previous studies of the exchange interactions in NiPS_3 , and other members of its family of materials, which found that the choice of metal and ligand tunes the relative strengths of the parameters in the magnetic Hamiltonian [14, 85–89]. In the case of NiPS_3 , there is no direct exchange between the metal ions since the t_{2g} orbitals are filled for Ni^{2+} , so magnetic couplings occur only through superexchange interactions mediated by sulfur ligands [86, 88, 94]. The covalent bonding of sulfur and phosphorus creates a strong hybridization of their $3p$ -orbitals [16, 86, 94] which makes ^{31}P sensitive to the nickel ions and the interactions between them. The drop in ω_{int} at T_N detected by the MSIS can then most likely be explained by a change in orbital hybridization with magnetic ordering, resulting in a change in the strength of the ^{31}P - ^{31}P interaction. Although theoretical work has been done to model the nature of orbital hybridization in NiPS_3 [94, 111, 112], the MSIS provides a quantitative measure of these interactions and how they change at T_N , which supports existing theoretical models and will be a useful tool in the development of future models.

To compare the measured results with the expected value of the pure ^{31}P - ^{31}P dipole-dipole interaction strength, which remains unchanged throughout the magnetic transition, we calculated the dipolar interaction matrix of a single dimer using lattice

parameters retrieved from Ref. [97]. We obtain the following dipolar interaction tensor with values given in units of kHz:

$$\mathbb{A}_{dip} = \begin{bmatrix} 1.890 & 0.0 & 0.0 \\ 0.0 & 1.890 & -0.019 \\ 0.0 & -0.019 & -3.781 \end{bmatrix}. \quad (4.2)$$

The non-zero off-diagonal terms indicate a small xy axial asymmetry that is caused by a 0.2° tilt of the ^{31}P - ^{31}P dimer along the y -axis. This tiny axial asymmetry is neglected in the theoretical description of this system, the details of which can be found in Section 3.3. Indeed, the diagonalization of the matrix in Eq. (4.2) results in negligibly small changes in the values of $\mathbb{A}_{dip}$, which validates the assumption of an axially symmetric dipolar interaction. To investigate the effect of inter-dimer interactions, we summed the dipolar interaction of a single ^{31}P site with all other ^{31}P sites within a radius of 500 Å. This produced a reduction of the principal component of the interaction by -5% and introduced a small xy asymmetry as a 4% difference between the A_{xx} and A_{yy} components (diagonal of $\mathbb{A}_{dip} = [A_{xx}, A_{yy}, A_{zz}]$).

As described in Section 3.3, the measured value ω_{int} relates to the dipole-dipole interaction strength by the relation $\omega_{int} = (3/2)\omega_D$, where $\omega_D = A_{xx} = A_{yy} = A_{zz}/2$. Applying this relationship returns $\omega_{int}^{\text{calc}} = 2.84$ kHz, which is in very good agreement with the average value of ω_{int} measured in the PM phase, $\omega_{int}^{\text{PM}} = 2.67 \pm 0.11$ kHz. Further applying a -5% correction to the calculated value to account for inter-dimer interactions reduces the dipolar interaction strength to $\omega_D = 1.80$ kHz and thus returns $\omega_{int}^{\text{calc}} = 2.70$ kHz which lies within the error bar of the measured value of ω_{int}^{PM} . This indicates that the value of ω_{int} that is measured in the PM state is achieved purely by the dipole-dipole interaction. The reduction to $\omega_{int}^{\text{AFM}} = 1.75 \pm 0.06$ kHz measured in the AFM phase indicates that some contribution to the ^{31}P - ^{31}P interaction strength changes with magnetic ordering.

4.4.2 Distribution of ^{31}P - ^{31}P Interaction Strength

The distribution in the ^{31}P - ^{31}P interaction strength is determined by Γ_{int} , the decay rate of the oscillations separate from the characteristic decay of the NMR signal T_2^{-1} . Since in Eq. (3.48) $B(\theta = 90^\circ) = 0$, the spin tip angle of the excitation pulse θ must not be equal to 90° in order for Γ_{int} to be distinguishable from the overall decay of the signal caused by the spin-spin decoherence. Despite the $\theta = 90^\circ$ condition yielding no insight into the value Γ_{int} through application of the mathematical model, a visual analysis of the oscillations at long τ provides some insight into its nature. In the case where equivalent ^{31}P sites across the sample feel different ^{31}P - ^{31}P interaction strengths, the modulation of the spin echo amplitude as a function of τ should become less distinct at long τ as even small differences in ω_{int} would become significant, creating interference between the different values of ω_{int} and attenuating the oscillations. In Figure 4.3(a), we see that the oscillations persist to the longest values of τ when $T > T_N$ and disappear slightly before the longest values of τ are reached when $T < T_N$.

Although a visual analysis provides some insight, extracting Γ_{int} using the mathematical model allows a much more reliable and precise understanding of the nature of the distribution. Therefore, in order to verify that $\Gamma_{int} = 0$ for $T > T_N$ and $\Gamma_{int} \neq 0$ for $T < T_N$, the ^{31}P spins were probed with an excitation pulse that tipped the spins at an angle closer to $\theta = 55^\circ$ than the ideal $\theta = 90^\circ$. Since these pulsing conditions produce a non-zero value for $B(\theta)$, Γ_{int} becomes distinguishable from T_2^{-1} in Eq. (3.48) and a value for both decay rates can be extracted simultaneously. Figure 4.4 shows that $\Gamma_{int} = 0.0 \pm 0.13$ kHz in the PM phase and $\Gamma_{int} = 1.00 \pm 0.42$ kHz in the AFM phase.

In fact, Γ_{int} increases to about half of the value of ω_{int} in the AFM state, indicating a significant distribution in the ^{31}P - ^{31}P interaction strength across the sample in the

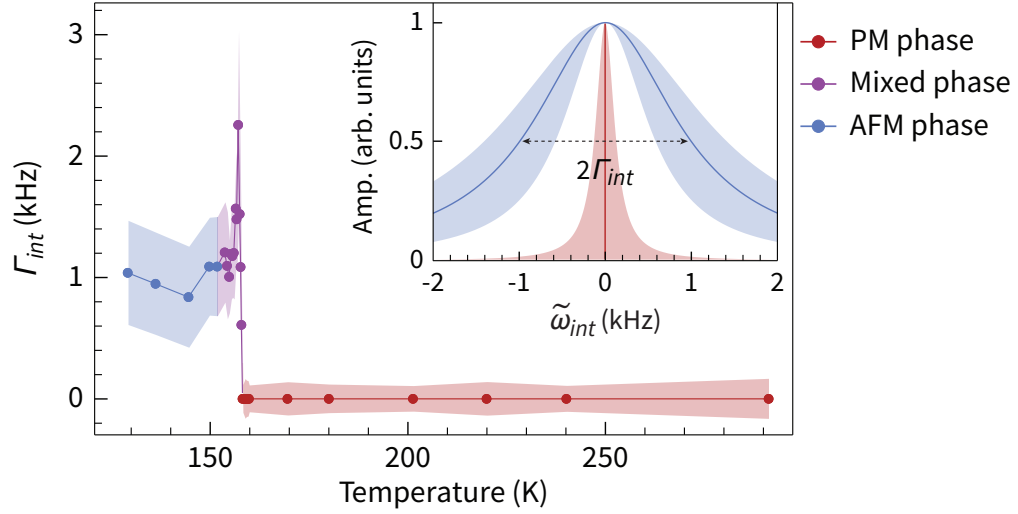


FIGURE 4.4: The distribution in the ^{31}P - ^{31}P interaction Γ_{int} extracted from fitting Eq. (3.48) to the T_2 relaxation curves $M(\tau)$ taken at 7 T. The shading around the curves represents the error associated with each value extracted from the fit. The inset shows the distribution model of the interaction strength, a Lorentzian distribution with full width at half max equal to $2\Gamma_{int}$ in the AFM phase (blue) and PM phase (red), where $\tilde{\omega}_{int}$ is the interaction strength shifted by the respective value in the AFM or PM phase such that both curves are centered about zero. The shading around the curve represents the error in Γ_{int} .

magnetic state. The distribution in ω_{int} can be modeled by a Lorentzian distribution function centered about ω_{int} and with full width at half max (FWHM) of $2\Gamma_{int}$ of the form,

$$f(\omega_{int}) = \frac{1}{\pi} \left(\frac{\Gamma_{int}}{(\omega_{int} - \omega'_{int})^2 + \Gamma_{int}^2} \right), \quad (4.3)$$

where ω'_{int} is the average value of ω_{int} in the PM or AFM phase. This distribution is plotted in the inset of Figure 4.4. The shading around the distribution of Γ_{int} represents the distributions calculated with $\Gamma_{int} = \Gamma_{int} \pm \sigma$, where σ is the uncertainty associated with the average value of Γ_{int} . To more easily compare the distribution in the PM and AFM phases, the distribution is plotted as a function of $\tilde{\omega}_{int} = \omega_{int} - \omega'_{int}$ such that both curves are centered about zero. The significant increase in Γ_{int} between the AFM and PM phases is evident in this graph, highlighting the spread of values of ω_{int} across the sample introduced with magnetic ordering.

A non-existent distribution of the ^{31}P - ^{31}P interaction strength for $T > T_N$ reveals that the only interactions in this material are ones that develop at every equivalent site across the sample, precluding the presence of short-range 2D correlations in this region. The increase in Γ_{int} in the transition region is consistent with the gradual development of the change in ω_{int} . The non-zero distribution in the magnetic phase points to either a continual development of the order parameter below the transition or to the presence of some other emergent phenomena. These possibilities will be discussed more in subsequent sections.

4.4.3 Evolution of Spin Tip Angle Dependent Parameters

As confirmation that the MSIS measures what we expect, the excitation pulse length was varied to tip the spins at angles away from $\theta = 90^\circ$, the results of which are shown in Figure 4.5(a). The evolution of these curves with the change in spin tip angle is reflected in Figure 4.5(b), where the fitting parameters $A(\theta)$ and $B(\theta)$ are plotted as a function of the spin tip angle in the PM (164.4 K) and AFM (152.54 K) phase. In the PM phase, the data follow Eq. (3.46) and (3.47) confirms that the model proposed by the MSIS is in accordance with the experimental results.

There is a change in the degree to which $A(\theta)$ agrees with the predicted behavior in the AFM phase, shown in the deviation of the data from the theoretical prediction in Figure 4.5(b). $A(\theta)$ describes the amplitude of the signal and $B(\theta)$ describes its offset. A non-zero value of $B(\theta)$ indicates a deviation from the ideal pulsing conditions ($\theta = 90^\circ$). Since $B(\theta)$ agrees with the predicted behavior in both phases, it is accurate to say that the pulse is well calibrated throughout the measurements, which is expected as we recalibrated the pulsing conditions as we changed the temperature to account for normal changes in the system due to thermal contraction or expansion. The deviation of $A(\theta)$ in the AFM phase from the predicted behavior as described by Eq. (3.46) indicates that there is some contribution to the signal that develops with

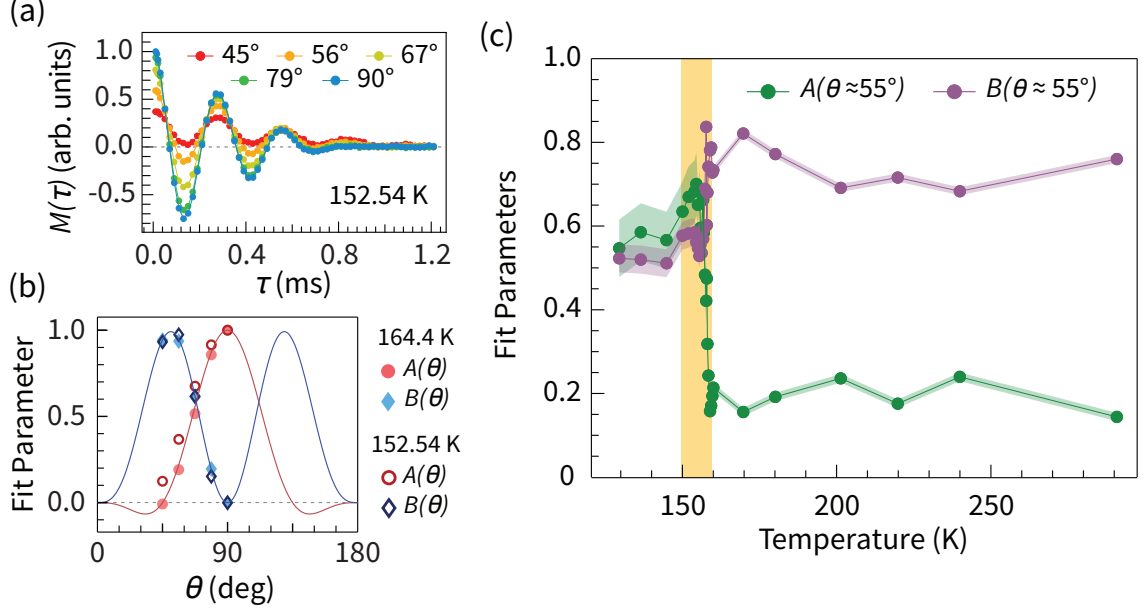


FIGURE 4.5: (a) The transverse magnetization recovery curve $M(\tau)$ measured at $B_0 = 7.2$ T and $T = 152.54$ K at different spin tip angles as labeled on the plot. (b) Fitting parameters $A(\theta)$ and $B(\theta)$ extracted from (a) and a synonymous measurement at 164.4 K as a function of θ compared to the expected behavior predicted by Eq. (3.46) and (3.47) shown by the solid lines. (c) Fitting parameters $A(\theta \approx 55^\circ)$ and $B(\theta \approx 55^\circ)$ extracted from Eq. (3.48) fit to data taken at 7 T. The orange box in the inset corresponds to the temperature range over which the magnetic transition occurs determined by the range over which ω_{int} changes. The shading corresponds to the associated error.

magnetic ordering that is not well described by the model. Further modeling of the magnetic system, especially ones including the phosphorus atoms, will help unravel the contributions to the NMR signal and origin of the changes detected with the MSIS.

At the magnetic transition, with a fixed spin tip angle $\theta \approx 55^\circ$, Figure 4.5(c) shows a clear change in both $A(\theta \approx 55^\circ)$ and $B(\theta \approx 55^\circ)$ at the magnetic transition. For these measurements, the pulse conditions were fixed for all the temperatures measured. Although we may expect some change in pulsing conditions with temperature due to experimental effects (change in capacitance of the capacitors in the resonant circuit, change in impedance of the coax, thermal contraction of the coil, ...), the fact that the change in $B(\theta \approx 55^\circ)$ occurs synchronously with the magnetic transition

indicates that this change is somehow related to the magnetic order.

The change in $A(\theta \approx 55^\circ)$ at T_N indicates that there is also a change in the signal amplitude with magnetic ordering. These results indicate that there is probably some electronic screening of the ^{31}P nuclei by the surrounding electrons developing with magnetic ordering. As the screening is caused by induction effects from the motion of the surrounding electrons, it is not surprising that a change in hybridization at T_N would also result in a change in the amount of electromagnetic screening at the ^{31}P site. When the pulse conditions were recalibrated with temperature, it was found that the power needed to tip the spins by $\theta = 90^\circ$ increased from 49.1 dBm in the PM phase to 50.9 dBm at 143 K (AFM) to 52.2 dBm at 35 K. An increase in the power required to tip the spins by $\theta = 90^\circ$ is consistent with increased electronic screening of the ^{31}P nuclei. This confirms the electronic nature of the changes that occur with the magnetic transition.

4.4.4 Standard Spin-Spin and Spin-Lattice Relaxation

To investigate the dynamics of the system, transverse and longitudinal magnetization recoveries, also known as T_2 or spin-spin decoherence and T_1 or spin-lattice relaxation, respectively, were measured. The spin-lattice relaxation (T_1) was measured using a standard T_1 pulse sequence ($\pi/2$ (x10) - t - $\pi/2$ - τ - π - τ) with varying t and $\tau = 10 \mu\text{s}$. The spin-lattice relaxation rate T_1^{-1} was extracted from Eq. 4.1, and plotted as a function of temperature in Figure 4.6.

In most materials undergoing a magnetic transition, measuring the spin-lattice relaxation rate T_1^{-1} as a function of temperature yields a peak at the magnetic transition due to the increase in spin fluctuations with the onset of magnetic order. No such peak in $T_1^{-1}(T)$ occurs in this system, as is apparently clear in Figure 4.6. The absence of a peak in $T_1^{-1}(T)$ at T_N suggests that this standard NMR measurement does not probe the right magnetic wavevector to be a good probe of the magnetic ordering

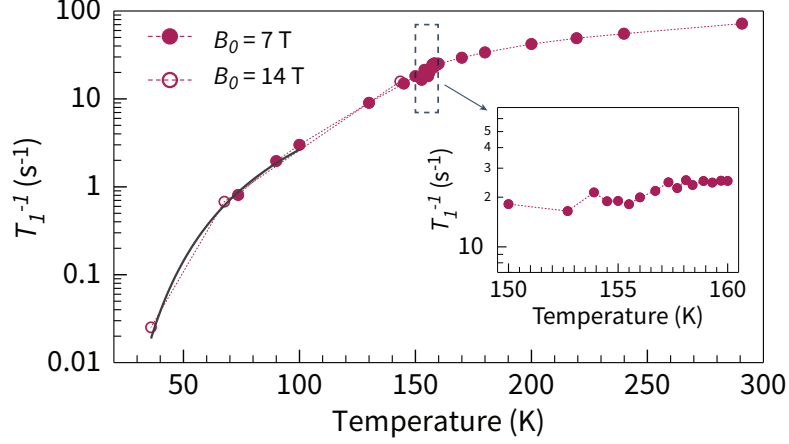


FIGURE 4.6: Spin-lattice relaxation rate T_1^{-1} as a function of temperature extracted from Eq. (4.1). The solid black lines shows the fit of Eq. (4.4) to the low temperature data. The inset shows the region around T_N . Error bars are smaller than the point size.

in this material. That being said, it does provides insight into the dimensionality of the interactions [113]. The low temperature region of the curve in Figure 4.6 can be fit to the following power law relation:

$$T_1^{-1}(T) \propto T^\beta e^{-\Delta/T}, \quad (4.4)$$

where $\beta = d - 1$ for a d -dimensional system and Δ gives a measure of the energy gap [114]. The fit is shown by the black line in Figure 4.6 and yields a gap of $\Delta = 213.64 \pm 9.81$ K and $\beta = 1.12 \pm 0.15$, confirming the two-dimensional nature of the system in this low temperature region.

The spin-spin relaxation rate T_2^{-1} as a function of temperature with spin tip angle $\theta \approx 55^\circ$ and $\theta = 90^\circ$ is shown in Figure 4.7. For both spin tip angles, there is a change in T_2^{-1} at the magnetic transition. In Figure 4.7(a), where the decoherence rate is extracted from measurements taken with the spin tip angle $\theta \approx 55^\circ$, T_2^{-1} increases slightly with magnetic ordering. This change is relatively small, especially when compared with the much larger change in the distribution of the ^{31}P - ^{31}P interaction strength Γ_{int} that occurs over the same temperature range. In Figure 4.7(b), the

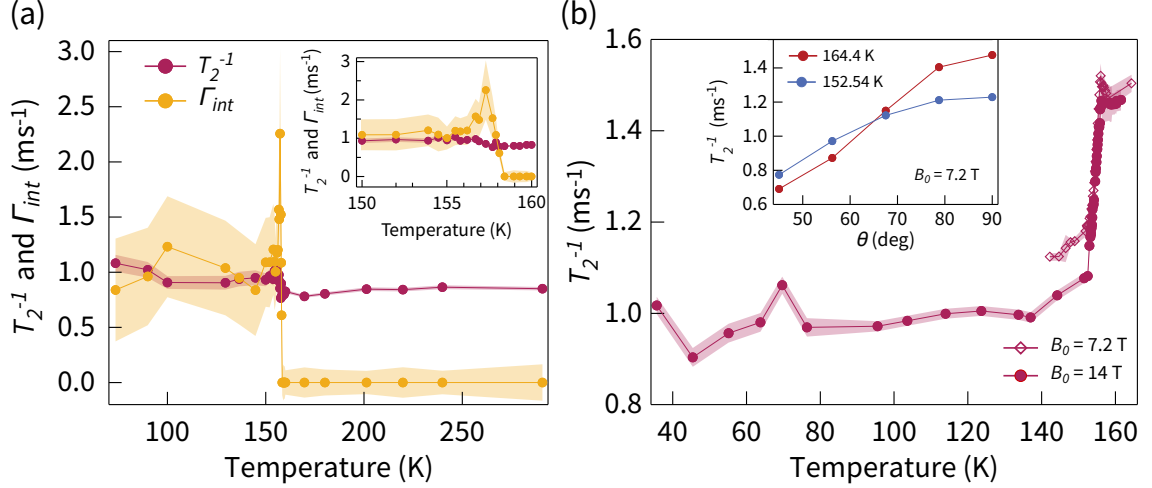


FIGURE 4.7: (a) Spin-spin decoherence rate T_2^{-1} and Γ_{int} , the distribution in ω_{int} , extracted from fitting Eq. (3.48) to the T_2 relaxation curves $M(\tau)$ for measurements taken at 7 T and with spin tip angle $\theta \approx 55^\circ$. The inset shows the region around T_N . (b) The spin-spin relaxation rate T_2^{-1} measured at 14 T and 7.2 T with $\theta = 90^\circ$. The inset shows T_2^{-1} as a function of spin tip angle in the PM (red) and AFM (blue) phase. The shading around the curves represents the error associated with each value extracted from the fit. Where the shading is not visible, the error bars are smaller than the point size.

decoherence rate is extracted from measurements where the spin tip angle is $\theta = 90^\circ$ and instead of increasing below the magnetic transition, T_2^{-1} decreases. This trend is explained in the inset of Figure 4.7(b) where the spin-spin decoherence rate in the PM and AFM phase is plotted as a function of spin tip angle θ . This plot shows that the change in T_2^{-1} as the spin tip angle moves away from the ideal $\pi/2$ condition is smaller in the AFM phase than in the PM phase, resulting in T_2^{-1} increasing with magnetic ordering for $\theta < \sim 70^\circ$ and decreasing for $\theta > \sim 70^\circ$. This means that if the spin tip angle is poorly calibrated or chosen to be around 70° , there would be no apparent change in T_2^{-1} at the magnetic transition and therefore, similarly to T_1^{-1} , would not be a good parameter to determine the onset of magnetic ordering.

4.4.5 Spectral Broadening in AFM Phase

To confirm that the order parameter continues to develop below the transition, the full linewidth at half the maximum of the spectra (FWHM) was extracted to

track the broadening of the linewidth as the temperature decreases, the results of which are plotted in Figure 4.8. At around 145 K, the spectral width becomes larger than the spectral window, artificially decreasing the width of the spectrum, which is why lower temperature data are not available for $B_0 = 7.2$ T. Full spectrum sweeps were taken at some low temperature values with $B_0 = 14$ T, which confirms that the linewidth continues to increase with decreasing temperature.

The data was fit to the following power law relation:

$$FWHM(T) = A(T_N - T)^\beta + FWHM(T > T_N) \quad (4.5)$$

where T_N is the Néel temperature, β is the critical exponent describing the development of the order parameter with temperature, $FWHM(T > T_N)$ is the FWHM in the paramagnetic state, and A is simply a scaling factor. The transition temperature extracted from the fits to the data in both fields was consistent with the accepted values of T_N ; $T_N = 153.73 \pm 0.03$ K with $B_0 = 7.2$ T and $T_N = 154.61 \pm 0.02$ K with $B_0 = 14$ T.

The fits of Eq. (4.5) to the data return very different values for β depending on the temperature range over which the fit is performed, as is reflected by the drastically different shapes of the line fits to the high versus low temperature data in Figure 4.8. The different values of β are listed in Table 4.1. The low temperature data, giving $\beta = 0.26 \pm 1.5\text{e-}5$, was taken at 14 T and the high temperature data, where $\beta = 0.43 \pm 0.06$, was taken at 7.2 T, but it is unlikely that this change in β is due to the difference in B_0 for a couple of reasons. For one, while the spectral width is expected to be overall smaller with an increased field, this difference should not change the way it evolves with temperature and thus is unlikely to result in such a significant change in β . Secondly, the single higher temperature point at 14 T, near 153 K, falls close to the values found at 7.2 T and does not fall along the curve

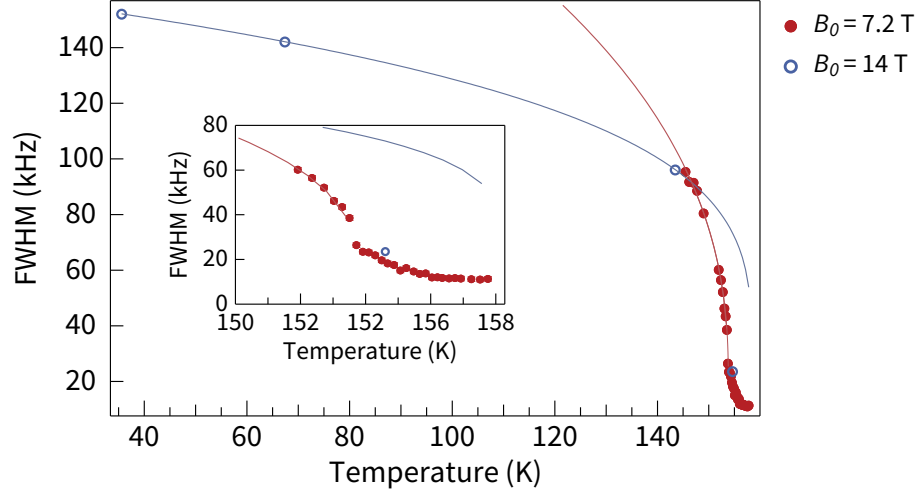


FIGURE 4.8: Full width at half maximum (FWHM) of the spectra as a function of temperature. Data taken at $B_0 = 7.2$ T is plotted in red and at $B_0 = 14$ T in blue. Both fields are shown because of the data available; the linewidth is not expected to be the same for different values of B_0 . Solid lines depict the fit of Eq. (4.5) to the data. Error bars are smaller than the point size.

resulting from the fit to the lower temperature data at 14 T. Finally, since there was no appreciable difference between measurements taken at the two fields in any of the other parameters measured, it is unlikely that the characteristics of the system change enough between these two field values to create the large change in β observed here.

The results of other measurement techniques also support the conclusion that there is a crossover in β , and thus in the dimensionality of the interactions in NiPS_3 , between the high- and low-temperature range of the AFM phase. Neutron diffraction measurements also found that β in the high-temperature range of the magnetic state was different from that in the low-temperature range [100]. As shown in Table 4.1, the value of β found in Ref. [100] doubles as T approaches T_N . A similar crossover near T_N was found in MnPS_3 [115], another member of the transition metal phosphorus trichalcogenide family, and is consistent with a transition from 2D-like to 3D-like behavior [116, 117].

It is difficult to make any strong conclusions from our data as there are too few data points at low temperature to produce a very reliable fit. From the data available,

Measurement Method	T range	β	Source
NMR FWHM with $B_0 = 7.2$ T	> 145 K	0.43 ± 0.06	-
NMR FWHM with $B_0 = 14$ T	< 155 K	$0.26 \pm 1.5\text{e-}5$	-
Neutron single crystal monochromatic diffraction	> 143 K	0.3 ± 0.005	[100]
	< 143 K	0.15 ± 0.005	
NMR FWHM	< 155 K	0.28 ± 0.02	[16]

TABLE 4.1: Critical exponent β and Néel temperature T_N extracted from Eq. (4.5) (top two rows) compared to that obtained from other sources (bottom two rows).

it is likely that a crossover in β similar to what is observed in Ref. [100] occurs here as well, but additional data must be taken to confirm these results. However, we can point to the behavior of $T_1^{-1}(T)$ at low temperatures as an indication that the low-temperature region behaves more 2D-like than 3D-like as the dimensionality of the system extracted from fitting Eq. (4.4) to the low temperature data revealed that the interactions are 2D.

We also see that the values of β obtained here are different from those found in Ref. [100], further supporting the need for additional data. Other NMR measurements found a value of β closer to what was determined by [100], but only a single value was found for the entire temperature range measured, from T_N down to around 10 K [16]. Looking at the FWHM data as a function of temperature, presented in Figure 10 of Ref. [16], however, an argument could be made that additional data below $T \approx 145$ K might support a different value of β for this low-temperature range. In all, whether or not our data support XY-like behavior near T_N and neither XY nor Ising-like behavior at lower temperatures as proposed by Ref. [100] cannot be definitively stated without additional data in the low-temperature region.

However, our data do provide some insight into the nature of the phase transition. As the FWHM continues to grow as the temperature decreases below T_N , it is clear that the order parameter continues to develop below the transition, which is characteristic of a second-order phase transition. The region around T_N where the

spin-spin decoherence curves clearly show a mixed phase region, where oscillations at the PM and AFM frequencies are present, more closely support the transition being weakly first-order. These inconclusive results reflect the complex nature of the phase transition in this material.

4.4.6 Sample Rotation in Field

The measurements taken with $B_0 \parallel c^*$ -axis presented in the main text were repeated with the sample rotated by 90° relative to the static field B_0 about the ab -plane (out-of-plane rotation) such that $B_0 \perp c^*$ -axis. The spectra in the PM, mixed, and AFM phase with $B_0 \perp c^*$ are shown in Figure 4.9(a). In the PM phase, the spectrum remains largely the same between both orientations; the linewidth is small and the peak is split from the dipolar interaction, but there is a slight spectral shift between the two orientations and there is more overlap between the two peaks with the external field fully in-plane. As the AFM phase is approached from above, additional peaks begin to develop and the central peak, characteristic of the PM phase, begins to lose spectral weight before completely disappearing around 154 K. This coexistence of spectra with characteristics of both the PM and AFM phase spectra in the temperature region around T_N confirms the presence of a mixed phase region, consistent with findings presented in previous sections.

The splitting of the additional peaks in the AFM phase is on the scale of 100 kHz, well above what could be caused by the dipole interaction. Although only two pairs of resonant peaks are found compared to the three found in previous NMR measurements [16], the splitting between the peaks as the sample is rotated from the $B_0 \parallel c^*$ to the $B_0 \perp c^*$ orientation in the AFM phase is consistent with the evolution found in Ref. [16] and thus it is likely that the third pair of peaks is buried in noise. By simulating the spectra through an exact numerical diagonalization of the nuclear spin Hamiltonian, the authors of Ref. [16] found that these additional peaks were consis-

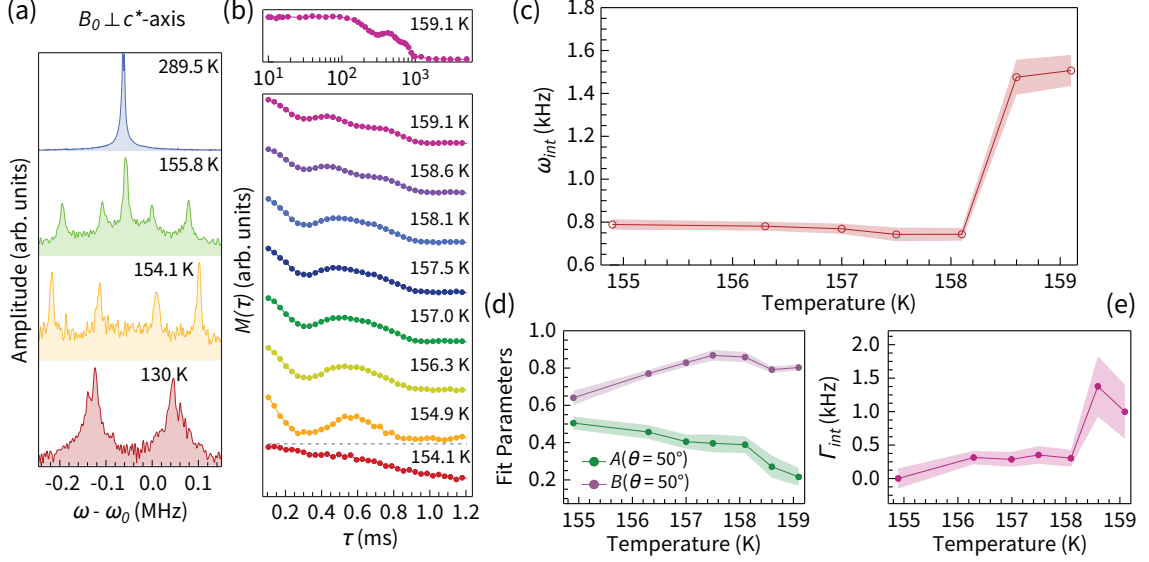


FIGURE 4.9: Data collected with the sample rotated 90° out-of-plane relative to the static field such that $B_0 = 7 \text{ T} \perp c^*$ -axis. (a) Spectra in the PM (blue), mixed (green), and AFM (orange and red) phase. (b) Oscillations in the T_2 relaxation curves over a range of temperatures. All of the curves in (b) are taken on the central peak of the AFM spectrum, except the curve below the dotted line ($T = 154.1 \text{ K}$), which was taken on the center left peak. (c) The ^{31}P - ^{31}P interaction strength ω_{int} , (d) fitting parameters $A(\theta = 50^\circ)$ and $B(\theta = 50^\circ)$, and (e) the distribution in the ^{31}P - ^{31}P interaction strength Γ_{int} , extracted from fitting Eq. 3.48 to the T_2 relaxation curves in (b). Shading behind the curves represents the error associated with each value.

tent with the presence of three sets of hyperfine field pairs offset with respect to each other by $\pm 60^\circ$ and 0° . The appearance of these additional peaks in the AFM phase further exemplifies the utility of the MSIS, as the presence of these additional hyperfine fields at the ^{31}P lattice site adds enough artifacts to the NMR spectrum that the ^{31}P - ^{31}P interaction strength can no longer be extracted from the peak splitting. In both sample orientations, the spectral linewidth remains constant in the PM phase and increases with decreasing temperature in the AFM phase. Additional peaks are expected to exist outside the frequency range measured at 130 K.

The oscillations in the T_2 relaxation curves with $B_0 \perp c^*$ are shown in Figure 4.9(b). Similar characteristics are seen here as are seen in the $B_0 \parallel c^*$ orientation. There is a clear difference in the oscillation frequency in the PM and AFM phases,

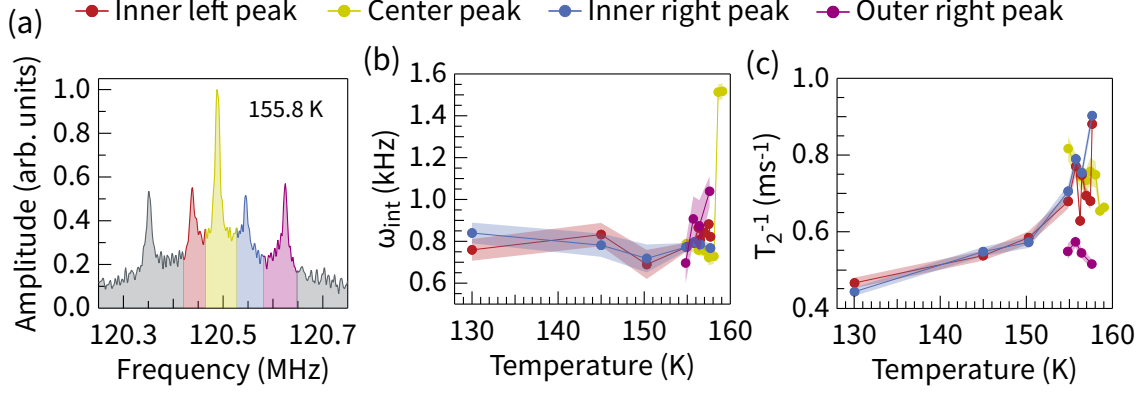


FIGURE 4.10: (a) Spectrum measured at 155.8 K for $B_0 \perp c^*$ -axis. (b) ^{31}P - ^{31}P interaction strength ω_{int} and (c) spin-spin relaxation rate T_2^{-1} extracted from fits of Eq. (3.48) to spin-spin decoherence measurements taken on different spectral peaks in the $B_0 \perp c^*$ orientation. Shading represents the associated error.

although the oscillations appear to be attenuated before zero magnetization in both the PM and AFM phase. The values extracted from fitting Eq. (3.48) to the curves in Figure 4.9(b) confirm these observations. As shown in Figure 4.9(c), there is a drop in the oscillation frequency across the magnetic transition. The value of ω_{int} is smaller in both phases in this orientation compared to the $B_0 \parallel c^*$ orientation. It is unsurprising that the ^{31}P - ^{31}P interaction strength should be different when the axis of the dimer (parallel to the c^* -axis) lies perpendicular to the field than when it is parallel to the field. The fitting parameters $A(\theta = 50^\circ)$ and $B(\theta = 50^\circ)$, shown in Figure 4.9(d), jump slightly synchronously with ω_{int} . As with $B_0 \parallel c^*$, $B(\theta = 50^\circ)$ decreases through the transition and $A(\theta = 50^\circ)$ increases. The main difference seen here is that Γ_{int} , plotted in Figure 4.9(e), appears to return rather quickly to zero after the expected increase at the magnetic transition. This could indicate that the origin of the distribution in ω_{int} is from in-plane interactions that cannot be measured when B_0 is parallel to the plane. More data would be necessary to make any conclusive remarks.

It should be noted that the oscillations in the $B_0 \perp c^*$ orientation are less well defined than in the $B_0 \parallel c^*$ orientation. This is most likely simply due to the fact that

with $B_0 \perp c^*$, the ^{31}P spins are precessing in the plane of the zAFM magnetization which adds magnetic anisotropy that is not felt for $B_0 \parallel c^*$. For this reason, the temperature dependence is more fully traced for the $B_0 \parallel c^*$ orientation.

The additional peak splitting in the AFM state raises the question as to whether the ^{31}P - ^{31}P interaction strength is the same for each peak. Applying the MSIS to the two central peaks of the four AFM peaks (red and blue), the outer high frequency peak (purple), and the central PM peak (yellow) show no appreciable difference in the fitting parameters extracted from the fits to the different peaks, as shown in Figure 4.10. This indicates that while there are inequivalent hyperfine fields at the ^{31}P sites leading to additional spectral splitting, the ^{31}P - ^{31}P interaction strength remains consistent across the ^{31}P sites.

4.4.7 ^{31}P - ^{31}P Interaction Determined by Standard NMR Techniques

Standard NMR techniques can provide a measure of the ^{31}P - ^{31}P interaction strength, but not as easily or effectively as what can be achieved by the MSIS. The splitting of the spectrum in the PM phase into two peaks is due to the ^{31}P - ^{31}P interaction [16, 80] and so the strength of the interaction ω_{int} can be determined by the magnitude of the splitting $\Delta f = 2\omega_{int}$. Characteristic spectra at a sampling of temperatures throughout the measured range are shown in Figure 4.11(a) and (b) normalized by the spectral peak and the area, respectively.

Spectral broadening with a decrease in temperature below the magnetic transition is apparent, indicating the presence of additional local magnetic fields, likely simply due to the development of the order parameter as discussed in Section 4.4.5. The magnitude of the peak splitting was extracted from the spectra measured at 7 T and is plotted as a function of temperature in Figure 4.11 (c) and (d). In the PM phase this yields $\omega_{int}^{PM} = 3.05 \pm 1.2$ kHz and in the AFM phase yields $\omega_{int}^{AFM} = 6.2 \pm 1.36$ kHz.

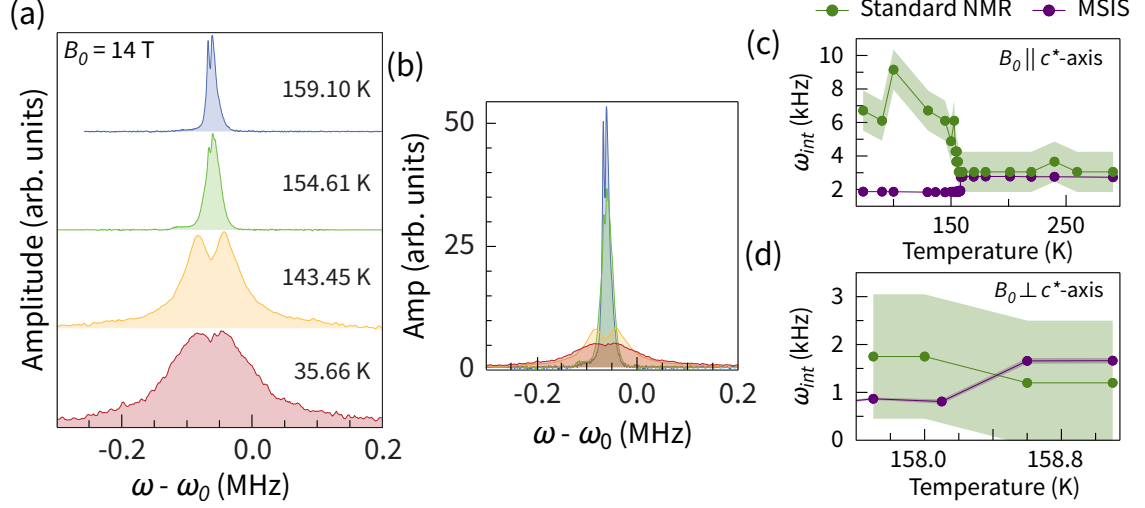


FIGURE 4.11: (a) A characteristic spectra with $B_0 \parallel c^*$ above (blue), below (orange and red), and near (green) $T_N = 155$ K normalized to their respective (a) peak and (b) area. Frequency splitting of the peaks (green) as a function of temperature compared to the values extracted using the MSIS (purple) with (c) $B_0 \parallel c^*$ and (d) $B_0 \perp c^*$. Shading behind the curve represents the associated error. Where shading is not visible, error is smaller than the point size.

The value found in the PM phase is close to what was determined by the MSIS technique, but with larger uncertainty. In the AFM phase, the interaction strength is much larger than that measured with the MSIS and increases at the magnetic transition. Unlike the MSIS, standard NMR techniques cannot distinguish between contributions to the NMR spectrum from the ^{31}P - ^{31}P interaction and contributions from other sources such as magnetic noise. So in the AFM phase, where magnetic noise and local fields due to the magnetic order introduce additional effects to the NMR signal, it becomes impossible to extract just the ^{31}P - ^{31}P interaction from all the other contributions to the NMR signal and this standard means of measuring the interaction strength fails. Despite the linewidth broadening to multiple hundreds of kHz in the AFM state, the MSIS can just as easily detect the ^{31}P - ^{31}P interaction strength, which is on the order of a single kHz, in the AFM phase as it can in the PM phase, where the linewidth and interaction strength are of a similar order of magnitude.

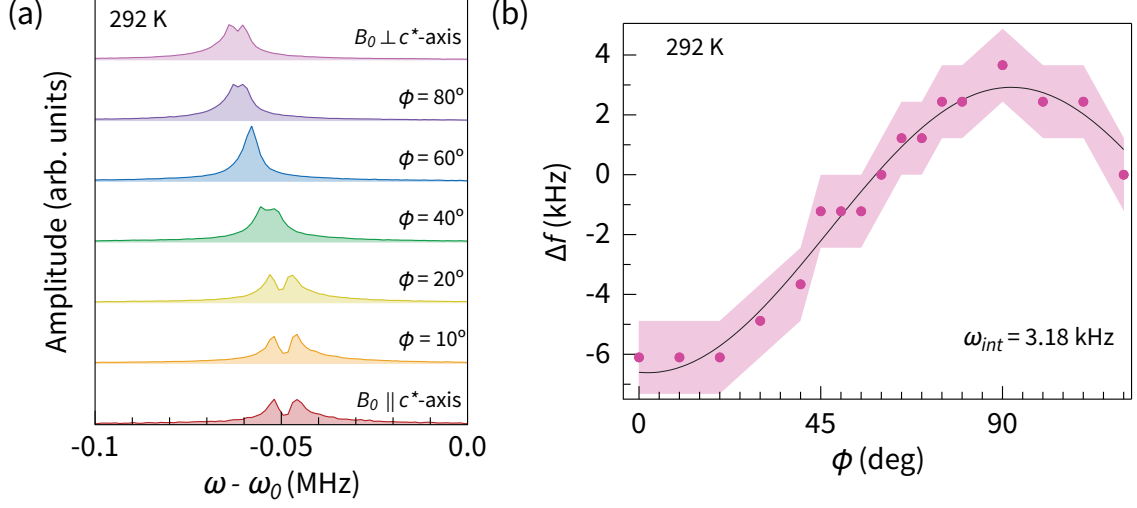


FIGURE 4.12: (a) Room temperature spectra with $B_0 = 7$ T as the sample is rotated about the ab plane from the $B_0 \parallel c^*$ -axis to the $B_0 \perp c^*$ -axis orientation. (b) The peak splitting as a function of rotation angle ϕ extracted from (a). The shading around the curve represents the associated error and the solid line represents the fit of Eq. (4.6) to the data.

The error bars associated with these data, denoted by the shaded regions, are much larger than those for the same value determined by the MSIS. This is because of the narrowness of the linewidth in the PM phase which makes achieving a high resolution of points on the peak difficult. This can be improved by fitting the spectra to a convolution of Gaussian and Lorentzian functions, where the Gaussian component accounts for the peak splitting and the Lorentzian component for magnetic broadening. This works well enough for spectra in the PM phase, but it loses accuracy in the AFM phase, where there are additional contributions to the spectra because of the magnetic order.

Orienting the sample such that $B_0 \perp c^*$ -axis is even less effective in determining the ^{31}P - ^{31}P interaction strength. Again we see that the values obtained in the PM phase are close to what was obtained with the MSIS, but it becomes impossible to extract the peak splitting in the AFM phase as additional peaks develop with peak splitting orders of magnitude greater than what could be accounted for by the ^{31}P - ^{31}P interaction, as shown in Figure 4.9. These additional peaks make extracting

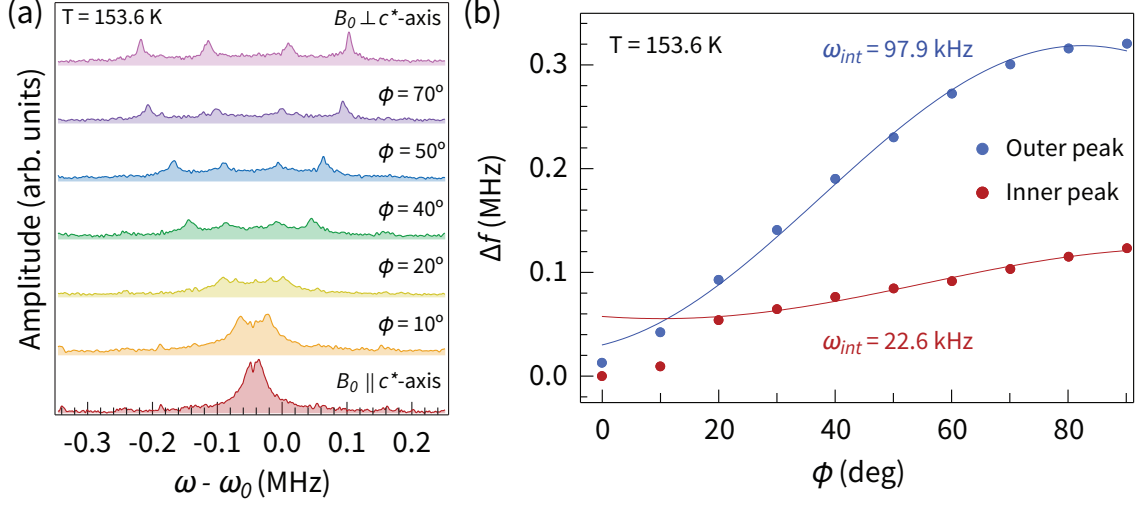


FIGURE 4.13: (a) Spectra at $T = 153.6$ K $< T_N$ with $B_0 = 7$ T as the sample is rotated about the ab -plane from the $B_0 \parallel c^*$ -axis to the $B_0 \perp c^*$ -axis orientation. (b) The peak splitting of the outer pair of peaks (blue) and inner pair of peaks (red) as a function of sample rotation angle ϕ . Solid lines represent fits of Eq. (4.6) to the data. Error associated with each value is smaller than the point size.

the ^{31}P - ^{31}P interaction from the peak splitting at a single angle relative to the external field impossible in the AFM phase.

The ^{31}P - ^{31}P interaction strength can also be extracted by analyzing the dependence of the spectral peak splitting on the angle ϕ between the ^{31}P - ^{31}P bond and the static field B_0 . The ^{31}P - ^{31}P interaction strength can be extracted from the magnitude of the peak splitting as the sample is rotated relative to the static field by the following relation [80]:

$$\Delta f(\phi) = \omega_{int} [1 - 3 \cos^2(\phi)] . \quad (4.6)$$

Fitting this equation to the room temperature data, shown in Figure 4.12(b), yields $\omega_{int}^{PM} = 3.18 \pm 0.14$ kHz, which is larger than the value measured by the MSIS, $\omega_{int}^{PM} = 2.67 \pm 0.11$ kHz.

The peak splitting of both pairs of peaks that develop in the AFM phase as a function of the rotation angle is shown in Figure 4.13(b). It is clear from Figure 4.13(a)

and (b) that ω_{int} extracted from this fit will be different between the peak pairs and much larger than the value determined by the MSIS. Sure enough, the outer pair of peaks yield $\omega_{int} = 97.9$ kHz and the inner pair of peaks yields $\omega_{int} = 22.6$ kHz. This confirms that an accurate measure of the ^{31}P - ^{31}P interaction strength in the AFM phase is not possible using this standard NMR technique. In addition to being applicable only in the PM phase, this method of extracting ω_{int} is also much less efficient than the MSIS as it requires multiple measurements to be taken for each temperature point compared to the one required for the MSIS, not to mention the need to rotate the sample, which can introduce additional error as accurate results depend on precise knowledge of the sample orientation in the field, which can be difficult to achieve.

4.5 Discussion

4.5.1 Absence of Short-Range 2D Correlations

Since the ^{31}P - ^{31}P interaction is mediated by the surrounding nickel atoms, the strength and distribution of this interaction can be used as an indirect probe of the nickel atoms. As seen in Figure 4.3, the only change in ω_{int} with temperature occurs at T_N which means that there is little change in the nickel atoms outside their magnetic ordering at the transition. Since 2D correlations would locally change the electron cloud of the nickel atoms and since we have already established that ω_{int} depends on the state of the nickel atoms, it is expected that their presence would also result in some change in ω_{int} , which is not seen in these measurements. This suggests a lack of the appearance of short-range 2D correlations for $T > T_N$.

However, by looking only at the average value of ω_{int} at each site across the entire sample, it is not possible to conclusively say that there are no short-range 2D correlations, as the number of sites participating in these correlations could be too

small to be detected over the other magnetic noise in the material, as was proposed by a previous NMR study [16]. If this were the case, even very few sites participating in the correlations would still result in some distribution in ω_{int} to which the MSIS is sensitive. Since $\Gamma_{int} = 0$ for $T > T_N$, we can conclusively say that there are no short-range 2D correlations occurring in the PM phase. This is consistent with the results found in recent electron spin resonance (ESR) studies of NiPS₃, which found no signatures of short-range 2D correlations in the PM phase [14, 15].

4.5.2 Change in Orbital Hybridization

The most striking result of the application of the MSIS to NiPS₃ is the change in the ^{31}P - ^{31}P interaction strength at the magnetic transition. This change in ω_{int} reflects a change in the hybridization of the orbitals involved in the exchange pathways. A change in orbital hybridization is not a standard characteristic of magnetic phase transitions and therefore prompts the question of why this change in hybridization occurs in NiPS₃. Some possible explanations are discussed below.

One possibility is that a slight change in the crystal structure due to magnetostriction from the magnetic ordering shifts the overlap of the sulfur and phosphorus orbitals enough to change the anisotropy of the ^{31}P - ^{31}P interaction. Magnetostriction develops with magnetic ordering which occurs gradually with temperature and would result in a distribution in ω_{int} (*i.e.* $\Gamma_{int} \neq 0$) near and below the transition, which is reflected in the data shown in Figure 4.4. However, it should be noted that recent DFT calculations found that the lattice parameters of NiPS₃ remain virtually unchanged with magnetic ordering [95], so other possible sources for the change in hybridization must also be considered.

We can rule out small exchange fields being the source, as these should strengthen as the order parameter develops and the data show no change in ω_{int} after the initial jump at T_N . One possibility is that there could be some change in the electronic spin

coupling J at the phase transition, reflecting a change in orbital hybridization. NiPS_3 is a self-doped negative charge-transfer insulator [86, 93], so J is not simply a function of the on-site Coulomb repulsion, but also has some complicated dependence on the charge-transfer energy [92, 96, 118], which could possibly result in a change in J with magnetic ordering.

Another possible explanation is that the change in hybridization is related to the breaking of local inversion symmetry at the nickel site with the onset of magnetic order. In the PM phase, the nickel atoms are disordered, and the sulfur ligands are indistinguishable. However, with the onset of the zigzag AFM order, sulfur ligands become distinguishable as bridging nickel atoms of the same spin or of opposite spin [18, 119–122]. Since the sulfur atoms are also coupled to the phosphorus atoms, this introduces additional anisotropy in the ^{31}P - ^{31}P interaction, seen in the change in ω_{int} at T_N .

Several studies of this material have observed an intrinsic exciton quasiparticle in the AFM phase [93, 119–123]. The exciton is understood to be strongly coupled to the magnetic order and forms from a triplet-singlet excitation that is characterized by a ground state that may be dominated by coupling between the localized d orbital of the nickel and p orbital of the neighboring sulfur ligand ($d^9\bar{L}$ dominant, where $\bar{L}$ denotes sulfur holes) [93] or simply by the singlet-triplet splitting of the d^8 nickel orbital (d^8 dominant) [120]. Both cases result in a change in the local electronic structure [18, 93, 120, 124], which could explain the distribution of the interaction strength.

4.5.3 Single-Ion Anisotropy

Equation (3.48), which describes the decay in magnetization due to spin-spin decoherence, assumes a dipolar interaction without any additional anisotropy. To consider the possibility of additional anisotropy in the ^{31}P - ^{31}P interaction, we can

introduce a transverse single-ion anisotropy into the interaction Hamiltonian [125],

$$\mathcal{H}_{int} = \omega_{int} \left[I_z^2 + \frac{\eta}{3} (I_x^2 - I_y^2) \right], \quad (4.7)$$

where $0 \leq \eta \leq 1$ is the anisotropy constant. Applying the same procedure as is outlined in Section 3.3.3, but using the above Hamiltonian, the magnetization as a function of procession time τ becomes:

$$M(\tau) = \left[A(\theta) \cos \left(2\omega_{int} \frac{\eta - 3}{3} \tau \right) e^{-2\tau\Gamma_{int}} + B(\theta) \right] e^{-(2\tau/T_2)^2}, \quad (4.8)$$

which shows that the presence of a single-ion anisotropy would decrease ω_{int} . Since the measured value of ω_{int} without considering the single-ion anisotropy is smaller in the AFM phase than in the PM phase, we can assume $\eta = 0$ in the PM phase and that ω_{int} remains constant at the value measured in the PM phase. Now we can let η be a fitting parameter for the data in the AFM phase to extract a value for the single-ion anisotropy. Applying this to data taken at $T = 142.23$ K finds $\eta = 1.003 \pm 0.003$ which indicates that the change in ω_{int} could be explained by a single-ion anisotropy with $\eta = 1$ developing in the AFM phase.

It should be noted that replacing the transverse anisotropy with a longitudinal anisotropy ($I_x^2 - I_y^2 \rightarrow I_z^2$) does not result in a change in Eq. (4.8). Additionally, including both longitudinal and transverse anisotropy, with anisotropy constants η_l and η_t , respectively, does change Eq. (4.8), but not in a way that allows η_l and η_t to be distinguished from each other ($\eta \rightarrow \eta_t + \eta_l$).

Several papers have presented magnetic models for NiPS₃ that include one or more single-ion anisotropies, both in-plane (generally aligned along the magnetic easy-axis) and out-of-plane, but these models only consider interactions between the transition metal [88,90,91,101]. Additional theoretical work that includes the phosphorus atoms

would be required to elucidate the nature of the anisotropy in the ^{31}P - ^{31}P interaction.

4.6 Specific Heat Measurements

Measuring the ^{31}P - ^{31}P interaction strength gives a fairly clear picture of the temperature range over which the magnetic transition occurs. In an effort to gain additional information about the nature of this transition, such as confirming whether the transition is first- or second-order and obtaining a measure of the magnetic entropy through the transition, the specific heat was measured. These measurements did not provide conclusive information on the nature of the transition, further emphasizing the utility of the MSIS measurements on NiPS_3 .

4.6.1 Method

The heat capacity option of the Quantum Design Physical Property Measurement System (PPMS) was used to measure the isobaric specific heat of the sample C_p . The PPMS uses a relaxation technique in which the sample temperature is monitored as heat is applied to the sample for a set amount of time, after which it is allowed to cool back to its initial temperature. To achieve this, the sample is mounted, with a very small amount of vacuum grease, on a sample platform that is suspended from the puck by thin, thermally conductive wires that serve as electrical connections to the sample heater and thermometer. The puck remains in thermal equilibrium with the environment and serves as a thermal bath for the sample holder. Before mounting the sample on the puck, an addenda measurement must be taken to establish a baseline for the system so that the sample heat capacity can be extracted from the total heat capacity (sample + system). In order to establish an accurate baseline, the vacuum grease used to mount the sample to the sample platform needs to be applied to the platform, and if any vacuum grease is added or removed during the sample mounting

process, the addenda must be retaken.

Each measurement is divided into two portions, the heating portion and the cooling portion. During the heating portion, a constant amount of power P is applied to the sample for a time t_h to heat it. After time t_h , the power is turned off ($P = 0$) and the cooling portion begins in which the sample returns to thermal equilibrium with the bath. The sample is allowed to cool for another fixed amount of time t_c . During the entire process, the sample temperature is measured in small, even intervals, producing raw data of dT/dt . Some time is then allowed for the sample to return to thermal equilibrium, and the measurement is repeated six times. The bath temperature is then changed, the sample is allowed to return to thermal equilibrium, and the measurement is repeated.

Once data are collected, the measurements at each temperature step are averaged together or thrown out if they were taken before the sample had reached thermal equilibrium with the bath, which can occur for the first couple of measurements after the bath temperature is changed. To ensure that such measurements were not included in the analysis, the first three measurements after the temperature was changed were thrown out, and only the second three were included in the average. The total specific heat is extracted using a simple model that assumes that the sample and sample platform are in thermal equilibrium for the duration of the measurement such that the temperature T over measurement time t obeys the following equation [126]:

$$C_P^{\text{total}} \frac{dT}{dt} = -K_w (T - T_b) + P(t) \quad (4.9)$$

where K_w is the thermal conductance of the wires supporting the sample platform, T_b is the temperature of the thermal bath, and $P(t)$ is the power applied by the heater which is constant during sample heating and zero during sample cooling.

To obtain the specific heat of the sample from C_P^{total} , calculated from the data using

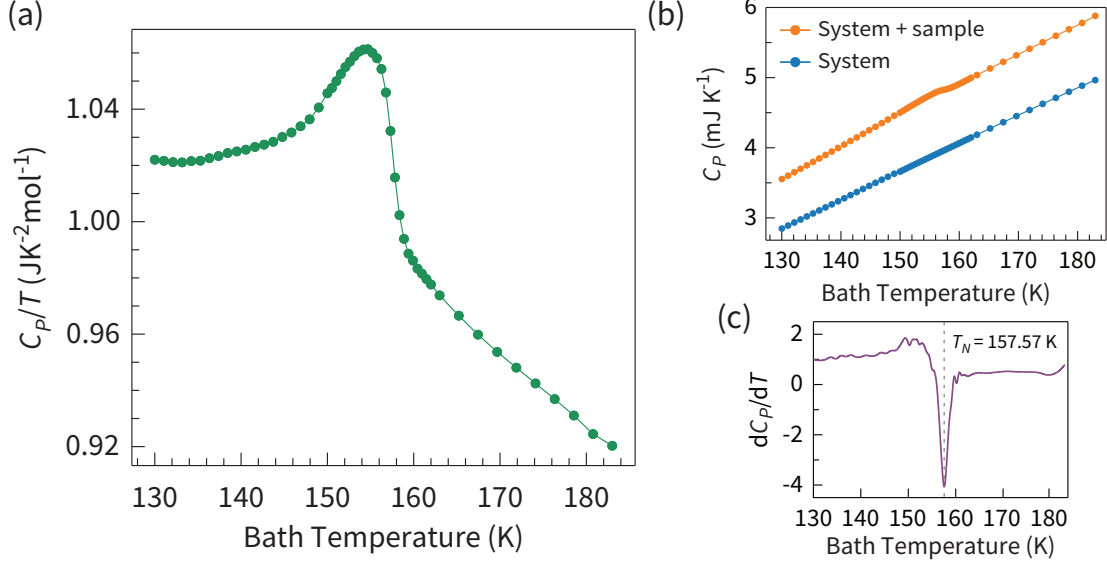


FIGURE 4.14: (a) Sample specific heat, including the phonon background, normalized by the bath temperature through the magnetic transition, (b) total specific heat (sample + system) measured compared to the large addenda (system) specific heat, and (c) the temperature derivative of the sample specific heat used to determine the Néel temperature $T_N = 157.57 \text{ K}$. Error bars for (a) and (b) are smaller than the point size.

Eq. (4.9), the addenda and the phonon background must be subtracted out. The addenda heat capacity can be subtracted from the total heat capacity by interpolating the addenda measurement to the temperature steps of the sample measurement. The data presented in Figure 4.14(a) are the specific heat of the sample plus the phonon background with the addenda subtracted.

The phonon background can be determined by fitting the data to the following equation [126]:

$$C_p^{\text{phonon}} = 9R \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (4.10)$$

where R is the ideal gas constant and T_D is the Debye temperature treated here as a fitting parameter. Once the phonon background and addenda are subtracted from C_p^{total} , what remains is the sample heat capacity from which information about the system can be obtained.

4.6.2 Results

The results of these measurements do not provide new information because the specific heat of the system is large compared to that of the sample—at 130 K, the system specific heat is 80% of the total specific heat measured, as shown in Figure 4.14(b). Because of this, the values of C_P may not be accurate, which makes it impossible to correctly determine the phonon background. Without accounting for the phonon background, it is impossible to extract the magnetic entropy, critical exponents, or make any conclusive statements about the nature of the phase transition.

However, we can extract a value for the Néel temperature. The magnetic phase transition occurs at the inflection point of the initial increase in C_p approaching T_N from above, so the transition temperature is given by the minimum in dC_p/dT , shown in Figure 4.14(c). The transition temperature is indicated by a dashed line and is found to be $T_N = 157.57$ K. This value falls within the transition range extracted from the temperature dependence of the ^{31}P - ^{31}P interaction strength measured by the MSIS.

The inability to make any conclusive remarks about the nature of the phase transition or magnetic phase highlight the utility of the MSIS in the study of NiPS_3 and its likely usefulness in studying others in the family of materials.

4.7 Future Work

The results presented here provide compelling reason to study other antiferromagnetic materials in the transition metal phosphorus trichalcogenide family, as well as carry out thickness-dependent measurements on NiPS_3 . Similar oscillations in T_2 were also found in MnPS_3 [17]. However, unlike NiPS_3 whose magnetic anisotropy can be well described by both the Heisenberg model [88] and by the XXZ model [90], the magnetic structure of MnPS_3 is only well described by the 2D anisotropic Heisen-

berg Hamiltonian [115]. MnPS_3 also differs from NiPS_3 in that its nearest-neighbor coupling is antiferromagnetic and dominates compared to the dominant third-nearest-neighbor AFM exchange in NiPS_3 [94]. The Néel type AFM order in MnPS_3 means that the inversion symmetry at the transition metal is not broken in the AFM phase; the sulfur atoms will always be coupling transition metal atoms with opposite spins [91]. In NiPS_3 , this is not the case—the sulfur atoms become distinguishable as bridging either aligned or anti-aligned nickel spins breaking local inversion symmetry at the nickel site. Since the spin and charge configuration of the sulfur atoms is influenced by the orientation of the nickel spins, the appearance of distinguishable sulfur ligands could explain a change in hybridization of the sulfur and phosphorus orbitals. If this is the case, we would expect to see little or no change in ω_{int} when MnPS_3 transitions from the PM to the AFM phase, since the local inversion symmetry at the transition metal site survives in the AFM phase. MnPS_3 would also provide insight into whether or not the excitons in the AFM phase of NiPS_3 play a major role in both the change in ω_{int} and in the increase in Γ_{int} , as theoretical work predicts a large binding energy of the excitons in MnPS_3 , as well as in FePS_3 [127].

FePS_3 , another member of the same family of materials, could also provide an interesting comparison when studying few-layer and monolayer NiPS_3 . In the 2D limit, the magnetic exchange interactions in NiPS_3 change in non-trivial ways, leading to an apparent vanishing of long-range order [92] whereas in FePS_3 , the Ising AFM order it displays in bulk survives down to the monolayer [88, 128, 129]. The MSIS would also be an effective tool in studying these materials in the 2D limit as multiple single- or few-layer flakes could be placed in a single NMR coil to achieve sufficient ^{31}P nuclei for a signal without the need to account for the relative orientation of their crystallographic or magnetic axes.

In conclusion, we used the MSIS to obtain a quantitative measure of the magnitude and distribution of the ^{31}P - ^{31}P interaction strength in both the PM and the

AFM phase. We found that ω_{int} changes abruptly at the magnetic transition, which signals a change in the orbital hybridization with magnetic ordering, supported by the concurrent change in electronic screening of the ^{31}P nuclei. The absence of any distribution in ω_{int} in the PM phase speaks to the uniformity of the interaction strength throughout the material above the transition, which precludes the presence of 2D correlations in this state. These results raise several questions as to the origin of the change in orbital hybridization at T_N , prompting the need to develop theoretical models to address these questions guided by the quantitative values obtained through the application of the MSIS to NiPS_3 . The results presented here indicate that the application of the MSIS to the rest of the transition metal phosphorus trichalcogenide family could be a very effective means of obtaining a more complete understanding of the microscopic nature of magnetism in these materials.

CHAPTER 5

NMR Investigation of CoNb_3S_6

Like NiPS_3 , CoNb_3S_6 is also a van der Waals antiferromagnetic material and was of interest to study with MTJ magnetic sensors. This material has a complicated and not well understood magnetic order, making it of particular interest to study with the MTJs, but also motivating the need to discern as much information about the system as possible prior to applying the MTJ sensors in order to have a better chance of understanding the MTJ results. To get a better idea of the nature of the magnetic order in this material, NMR measurements were conducted. The results of these measurements and the additional understanding they yielded on this material are presented in this chapter.

5.1 Sample

Bulk crystals grown at Brown University by the authors of Ref. [130] were used for all measurements reported here. The measurements taken at the LNCMI, which constitute most of the results presented here, were taken on the crystal sample shown in Figure 5.1(b) and (d). The sample measures $1.35 \times 2.45 \times 0.55$ mm and has a cobalt concentration of $x = 0.34$ as determined by the grower of the sample. The sample measured at Brown is comparable in size, but the cobalt concentration is unknown.

5.1.1 Crystal Structure

CoNb_3S_6 is a member of the intercalated transition metal dichalcogenide family. It is composed of triangular prismatic layers NbS_2 with a triangular lattice of cobalt atoms intercalated, all weakly coupled by the van der Waals force [19, 131]. CoNb_3S_6 has two distinct niobium sites, labeled Nb1 and Nb2. As shown in Figure 5.1(a) and (c), the Nb1 niobium site sits directly above or below the cobalt atoms and forms a hexagonal structure, with the Nb2 niobium site sitting symmetrically in the center. Sulfur atoms, sitting above and below the niobium plane, bridge the niobium atoms to each other and to the cobalt atoms. The crystallographic unit cell is shown in Figure 5.1(a) and (c) by the dashed gray lines.

The presence of intercalated cobalt atoms suppresses the superconductivity of the NbS_2 parent compound [132] and breaks space-inversion and mirror symmetries [133]. The relatively large distance between cobalt atoms means that their interactions are predominately mediated by itinerant electrons [134]. CoNb_3S_6 is in the non-centrosymmetric chiral hexagonal space group $P6_322$; it has six-fold screw symmetry along the c -axis with translation of $1/2$ the lattice constant along the symmetry axis and additional axes of symmetry perpendicular and parallel to the a - and b -axes [131, 135, 136].

5.1.2 Magnetic Order

CoNb_3S_6 is paramagnetic above its Néel temperature $T_N \approx 28$ K and antiferromagnetic (AFM) below [19, 130, 133]. The magnetic order in this material is not well understood, but several models have been proposed. It is well accepted to be a noncollinear, noncoplanar type AFM order with a weak out-of-plane ferromagnetic (FM) component [19, 130, 133, 137–139]. Recent resonant elastic x-ray scattering measurements suggest that it has double- Q magnetic structure with a noncollinear com-

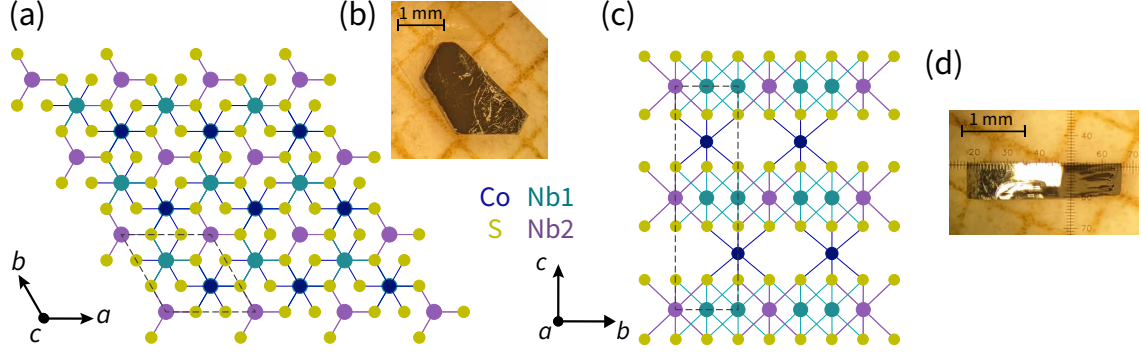


FIGURE 5.1: Crystal structure of CoNb_3S_6 with cobalt atoms shown in blue, niobium site Nb1 in green, niobium site Nb2 in purple, and sulfur in yellow looking along (a) the c -axis and (c) the a -axis. Pictures of the sample measured at the LNCMI showing the (b) ab -plane and (d) c -plane. The samples sit on a 1 mm^2 grid and the tick marks in (d) are 0.1 mm ticks shown at $\times 2$ zoom such that the tick spacing is actually 0.05 mm. Lattice parameters were determined from Ref. [136] and rendered using VESTA software package [98].

mensurate component and an incommensurate helical component that give rise to a staggered scalar spin chirality with either a modulated stripe pattern or a checkerboard pattern [130]. Early neutron scattering experiments found that the structure is either a multi-domain single- Q spin ordering with domains of each of the three possible directions of Q or a single domain with three- Q structure [137]. Polarized neutron scattering measurements have observed all-in-all-out type noncoplanar AFM order [133]. The magnetic order that most closely corresponds to the measured NMR spectra is Néel planar order, proposed by Ref. [137], which was determined by the analysis described in Section 5.4.

5.1.3 Anomalous Hall Effect

CoNb_3S_6 also exhibits a giant anomalous Hall effect (AHE) in the AFM phase, the origins of which are not well understood. There is good evidence that the weak FM component is at least partially responsible for the emergence of the AHE, but that it alone cannot account for the observed effect [19, 140]. Another possibility is that the AHE arises from the possible generation of a real-space Berry phase which arises

from the complex magnetic textures in the AFM phase [130, 141] or from a breaking of time reversal symmetry [140, 142]. The AHE was found to be very sensitive to the Co^{2+} content—excess cobalt was found to suppress the AHE and a deficiency was seen to enhance it and broaden the temperature range over which it is observable. The evolution of the strength of the AHE with Co^{2+} content revealed that disorder alone cannot account for the observation of the AHE and instead that it may be driven by an increase in frustration due to a more complex spin arrangement that arises from the cobalt deficiency [141].

In the paramagnetic state, the Hall resistivity in CoNb_3S_6 is linear, as expected for a normal conductor. When the system enters the AFM phase, additional contributions to the Hall resistivity appear. At 27 K ($< T_N = 28$ K) the anomalous Hall signal is small and increases in magnitude and field until it reaches a maximum at 23 K. The Hall resistivity continues to increase down to 20 K. At 15 K, the AHE is very small and found to be completely gone by 2 K [19]. This temperature dependence is consistent with changes seen in the NMR spectra, the results of which will be discussed in detail in this chapter.

5.2 Methods

We studied CoNb_3S_6 by probing the ^{93}Nb nuclei using standard nuclear magnetic resonance (NMR) techniques. Measurements were taken at both the Laboratoire National des Champs Magnétiques Intenses (LNCMI) in Grenoble, France, and Brown University. In both labs, the measurements were taken using a high-homogeneity superconducting magnet and state of the art lab-made spectrometers. The magnet at the LNCMI was a variable field magnet that could reach a maximum field of 15 T and the magnet at Brown was kept in a steady state mode at 7 T. Cryostats were used for temperature control; a variable temperature insert was used at the LNCMI, and a continuous-flow cryostat was used at Brown. Both systems used calibrated

Lakeshore Cernox thermometers mounted near the sample at comparable distances.

The sample was mounted on a lab-made probe in a single axis goniometer for sample rotation. The sample was initially aligned with the c -axis parallel to the static external field B_0 with an error of no more than $\pm 2^\circ$. The measurements taken at the LNCMI were further aligned to the $c \parallel B_0$ orientation by rotating the sample in the field to maximize quadrupolar splitting. The NMR coil used for measurements at Brown was made of copper, which has an isotope with a gyromagnetic ratio close to that of ^{93}Nb , so the coil used for measurements at the LNCMI was instead made of silver to avoid additional peaks from ^{63}Cu .

A standard spin-echo pulse sequence ($\pi/2 - \tau - \pi - \tau - \text{acquisition}$) was used for spectral and relaxation measurements. The ideal pulse length to tip the spins by $\theta = \pi/2$ was calibrated using the T_1 relaxation process described in Section 3.2.4. The pulse length was recalibrated as the temperature was changed to ensure that the ideal pulsing conditions were maintained throughout the experiment. In order to obtain the entire NMR spectrum, we need to sweep either the field or frequency while keeping the other parameter fixed, because ^{93}Nb has nuclear spin $I = 9/2$ and CoNb_3S_6 has two niobium sites, so its full spectrum contains 18 peaks that span a frequency range of over 10 MHz (or field range around 4 T). For the measurements taken at Brown, the pulsing frequency was swept at fixed field B_0 to get the entire spectrum. At the LNCMI, the spectra were taken by varying the static field and keeping the pulsing frequency fixed. Unless otherwise noted, spectra shown as a function of field represent spectra obtained by sweeping the field at a fixed pulsing frequency, and those shown as a function of frequency represent measurements taken while sweeping the pulse frequency at a fixed field.

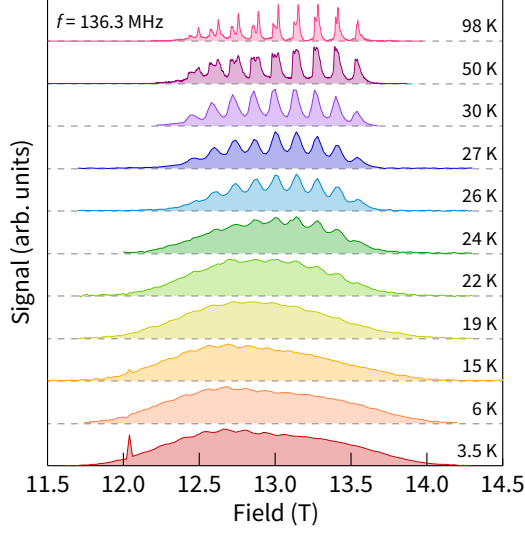


FIGURE 5.2: ^{93}Nb NMR spectra of CoNb_3S_6 at various temperature in the PM and AFM phase ($T_N \approx 28$ K). Spectra were taken at fixed frequency $f = 136.3$ MHz while the field was swept from around 14 T to around 11 T.

5.3 Results and Discussion

A characteristic representation of the NMR spectra of CoNb_3S_6 in the PM ($T > 28$ K), AFM+AHE ($28 \text{ K} > T > \sim 6$ K), and AFM ($T < \sim 6$ K) phase is shown in Figure 5.2. ^{93}Nb has nuclear spin $I = 9/2$, which produces eight satellite peaks symmetrically spaced around the central peak. Since CoNb_3S_6 has two distinct ^{93}Nb sites, each of which produces nine peaks, the full spectrum in the PM phase consists of 18 total peaks. In the AFM+AHE and AFM phases, only a single set of nine peaks belonging to one of the ^{93}Nb sites remains, but a broad background appears, which is due in part to the other ^{93}Nb site. This section will present more detailed results showing the evolution of the spectra of each ^{93}Nb site as a function of temperature, analysis of the field dependence of the spectrum, results of rotating the sample relative to the static field, and the temperature evolution of the spin-spin and spin-lattice relaxation rates.

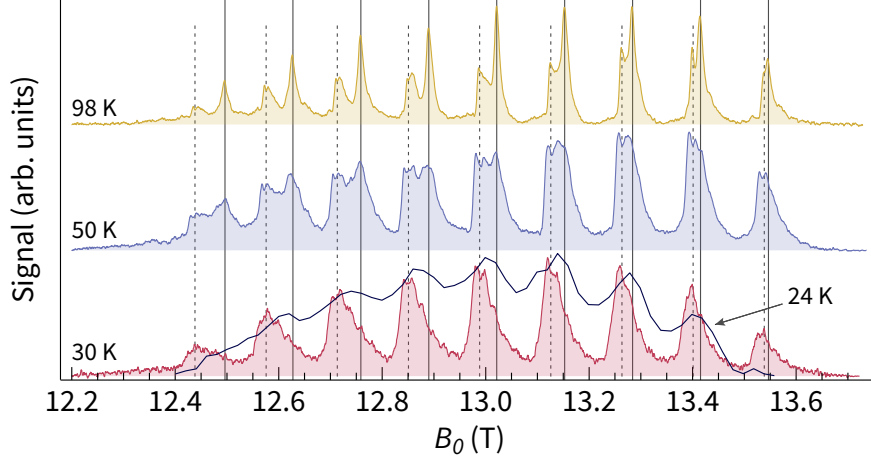


FIGURE 5.3: Peak splitting shown at three different temperatures in the PM state. The solid lines with splitting $\Delta B_0 = 0.131$ T denote the Nb1 site spectrum and the dashed lines with splitting $\Delta B_0 = 0.136$ T denote Nb2 site spectrum. The solid curve shows the spectrum at 24 K in the AFM state for comparison.

5.3.1 ^{93}Nb Site Allocation to Peaks

As previously mentioned, CoNb_3S_6 has two distinct niobium sites, which we will refer to as Nb1 and Nb2. The Nb1 site sits directly above or below a cobalt atom and the Nb2 site sits symmetrically in the center of a hexagon of Nb1 sites. A difference in local symmetry distinguishes the two sites and the resulting differences in the local environment of the ^{93}Nb nuclear sites result in individual spectra for each site. Determining which spectrum corresponds to which ^{93}Nb site is important in determining what the changes in the spectra correspond to physically.

One of the spectra has peak splitting $\Delta B_0 = 0.136$ T, which corresponds to $\delta_q \approx 1.42$ MHz for $^{93}\gamma/2\pi = 10.405$ MHz/T, and at 98 K the central peak is shifted from the resonant field (13 T) by -0.013 T which corresponds to a frequency shift of -0.135 MHz from resonant frequency (136.3 MHz) at 13 T. The peaks are shown by the dashed lines in Figure 5.3. The peak positions and linewidths change very little with a change in temperature in the PM phase. Investigating the spectrum measured with short ($\tau = 7$ μs) and long ($\tau = 18$ μs) decoherence times τ reveals that this is also the slower relaxing component of the signal, since only the peaks with splitting

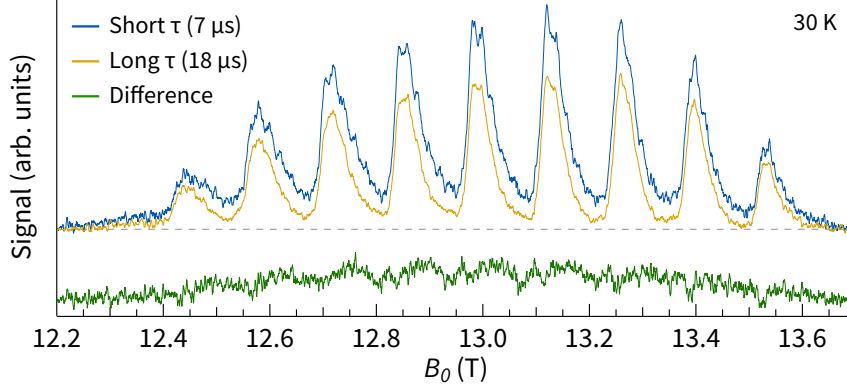


FIGURE 5.4: (Top) Full field sweep of the spectrum at 30 K taken with short τ (blue, 7 μ s) and long τ (yellow, 18 μ s). (Bottom) The short- τ spectrum subtracted from the long- τ spectrum showing the broad background signal at T_N is approached from above.

$\Delta B_0 = 0.136$ T remain with long τ , as shown in Figure 5.4. This remains true at and below the magnetic transition, where only these peaks remain distinguishable from a broad background signal. We believe that this is the Nb2 site.

The other set of peaks then corresponds to the Nb1 site, which has a cobalt atom either directly above or below it along the c -axis. The Nb1 site has a peak splitting of $\Delta B_0 = 0.131$ T ($\delta_q \approx 1.36$ MHz for $^{93}\gamma/2\pi = 10.405$ MHz/T) and a shift from the resonance field at 98 K of 0.021 T. Like the Nb2 site spectrum, the peak positions change very little with a decrease in temperature, but unlike the Nb2 site, it experiences significant linewidth broadening, clearly evident in the PM phase spectra shown in Figure 5.3 where the Nb1 site is marked by solid vertical lines. Furthermore, looking at Figure 5.4, it is clear that the Nb1 site relaxes much more quickly than the Nb2 site near the magnetic transition because the Nb1 peaks disappear almost completely for long τ . Subtracting the long- τ measurement from the short- τ measurement yields a broad peak that spans the full range of the spectrum, shown at the bottom of Figure 5.4. This broad peak probably corresponds to what remains of the quick-relaxing Nb1 signal. The Nb1 spectrum loses its distinct peaks completely in the magnetic phase but continues to contribute a broad background

signal that spans the width of the spectrum.

Our allocation of the peaks to each site is largely based on the difference in the local symmetry of the cobalt atoms at each site. The Nb2 site has three equidistance cobalt atoms above and below it with the two layers of cobalt offset from each other by a 60° in-plane rotation about the Nb2 site. In contrast, the cobalt atoms surround the Nb1 site in a tetrahedral formation; it has one cobalt atom sitting either directly above or directly below it and three cobalt atoms forming an equilateral triangle on the other side of the niobium plane. The Coulomb force between the cobalt atom and the Nb1 atom directly above/below it pushes the niobium atom slightly out-of-plane from the Nb2 atom, so there are two layers of Nb1 atoms offset from the plane of Nb2 atoms by $\pm 0.01545 \text{ \AA}$. Because of these differences in the local symmetry between the two sites, we find it more likely that the Nb1 site would experience a faster relaxation and be less likely to have a signal that survives in the magnetic phase. That being said, it is possible that we have allocated the sites incorrectly, in which case our analysis of possible AFM ordering in Section 5.4 would yield opposite results.

5.3.2 Field Dependence of Spectra

In order to determine the field dependence of the spectra in the PM phase, the central peak and outermost satellite on the low-frequency side for both sites were measured and compared to a field sweep at fixed frequency 136.3 MHz. By scaling the field sweeps at 98 K, 49 K, and 30 K with the two frequency sweeps at the central line and the outermost satellite, a value of $^{93}\gamma/2\pi = 10.495 \text{ MHz/T}$ was obtained at all three temperatures. The frequency sweeps at 50 K were taken at 13 T where the central peak (lower frequency, Nb2 site) is at 136.32 MHz. Repeating at 98 K and 30 K, also measured at 13 T, the same value of $^{93}\gamma_{eff}$ is obtained and no shift in the central peak position was observed, as shown in Figure 5.3(a). Comparing the peak splitting of the satellites across a full field sweep reveals that there is little effect on

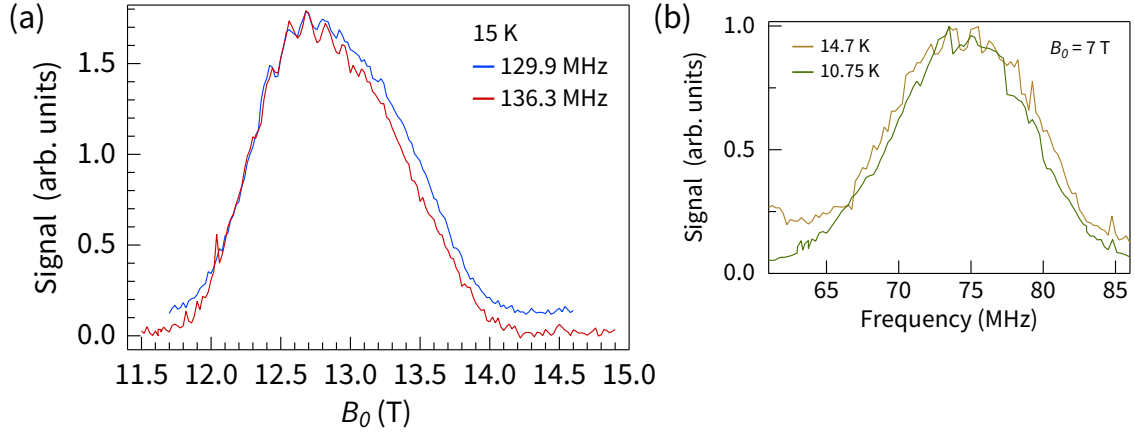


FIGURE 5.5: (a) Full spectrum field sweeps taken at different fixed frequencies, 129.9 MHz (blue) and 136.3 MHz (red), at 15 K showing the field dependence of the signal. The spectrum taken at 129.9 MHz is offset by +0.6 T and 0.12 in the y -direction. (b) Full spectrum field sweeps at 14.7 K and 10.75 K with $B_0 = 7$ T, normalized by amplitude to more easily see any asymmetry that may exist. It should be noted that the high-field region of a field sweep corresponds to the low-frequency region in a frequency sweep, so the asymmetry in the spectra in (b) should appear on the low-frequency side.

the quadrupolar splitting from the field in the PM state as the spacing of the peak splitting for both sites in Figure 5.3 are constant over the range of the field measured.

To investigate any possible field dependence in the spectra in the AFM phase, the static field B_0 was swept at 15 K for two fixed frequencies, the results of which are shown in Figure 5.5. The effective $^{93}\gamma$ was determined by aligning the peaks central transition ($1/2 \leftrightarrow -1/2$) as the central line remains unchanged under the quadrupolar effect and dividing the change in frequency by the shift in field required to align the peaks:

$$\Delta f = 136.3 \text{ MHz} - 129.9 \text{ MHz} = 6.4 \text{ MHz}$$

$$\Delta B_0 = 12.69 \text{ T} - 12.09 \text{ T} = 0.60 \text{ T}$$

$$^{93}\gamma_{\text{eff}}/2\pi = 6.4 \text{ MHz}/0.60 \text{ T} = 10.667 \text{ MHz/T}$$

The spectrum taken at 129.9 MHz is offset by +0.6 T and 0.12 in the y -direction to

align the central peak with that of the spectrum taken at 136.3 MHz. The left-hand (low field) sides of the spectra align well, but the right-hand (high field) sides do not. It is unclear if the peaks on the high field side align or not as they are not easily distinguished from the broad background, but it is clear that there is some field dependence to the asymmetry in the spectrum that develops below the magnetic transition. The precise nature of this field dependence is unclear with only two sweeps over slightly different field ranges. To get a better idea of the nature of the field dependence, additional field sweeps at over different field ranges should be done.

The field dependent nature of the asymmetry is further supported by the data shown in Figure 5.3(b), which was taken at Brown University at a fixed field while sweeping the frequency. There appears to be no significant asymmetry in the line shape of these spectra. It should be noted that the precision of these measurements was not good enough to distinguish the Nb2 site peaks, so additional fixed-field measurements should be taken to confirm these results. Despite the low resolution of these measurements, it is likely that the asymmetry in the line shape would still be apparent to some degree, especially at 10.75 K where the asymmetry of the line shape in the field-swept data is significant. This asymmetry will be discussed further in the next section, but these results merit further investigation into the field dependence of this asymmetry.

5.3.3 Temperature Dependence of Spectra in AFM Phase

As discussed in the previous section, there is some asymmetry in the spectral line shape that has some dependence on the static magnetic field B_0 . Normalizing the spectra by area makes the change in linewidth with decreasing temperature much clearer, as shown in Figure 5.6(a). It is apparent that the linewidth broadening increases a bit just below the magnetic transition, which was determined to be around 26 K, but the most significant feature of this plot is the temperature range over which

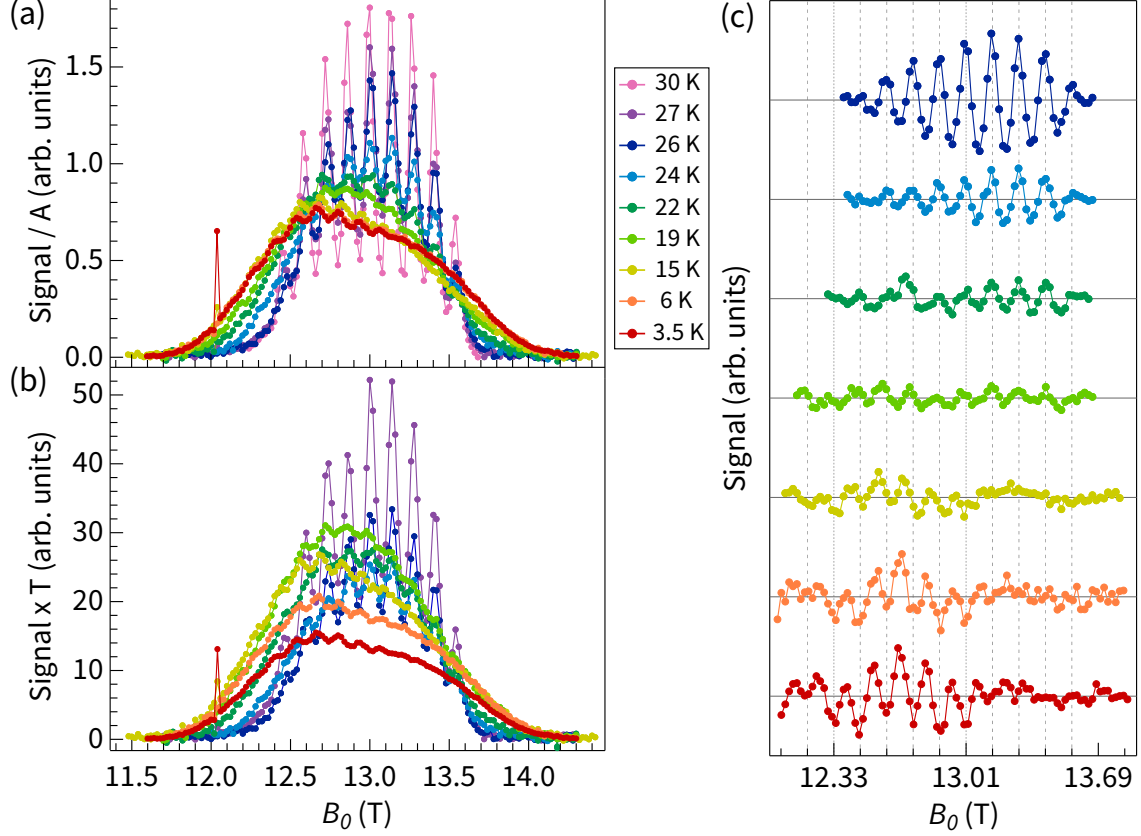


FIGURE 5.6:]

The full spectra normalized by (a) their respective areas to show the relative linewidth broadening with temperature and (b) their respective temperatures to remove the Boltzmann contribution to the signal. (c) The spectral peaks extracted from the broad magnetic background by subtracting a multi-order polynomial function fit to the signal. The dashed lines have splitting equal to the peak splitting of the Nb2 site, $\Delta B_0 = 0.136$ T.

the aforementioned asymmetric linewidth broadening increases. The asymmetry begins to become apparent around 24 K and becomes increasingly prominent until 6 K, at which point it appears to remain constant with decreasing temperature. This increase in asymmetry occurs over the same temperature range as the decrease in the strength of the anomalous Hall effect [19]. The fact that this asymmetry increases as the AHE decreases points to its relation to the AHE, and further investigation of its field dependence could shed light on the origins of the AHE in this material, which at present are not well understood.

To further investigate this temperature region, the spectra are normalized by their

temperature, the results of which are shown in Figure 5.6(b). The amplitude of an NMR signal is correlated with the population difference between adjacent energy levels—a large signal amplitude means that there is a large population difference between adjacent energy levels and a small signal amplitude means there is a small population difference. The magnetization is proportional to the population difference which is described by the Boltzmann distribution,

$$M \propto \frac{N_-}{N_+} = \exp\left(-\frac{\Delta E}{k_B T}\right) = \exp\left(-\frac{\hbar\omega}{k_B T}\right), \quad (5.1)$$

where N_- represents the population of the lower energy level and N_+ represents that of the higher energy level. The population difference is, in part, determined by the temperature of the system; as the temperature increases, the exponential in Eq. (5.1) approaches zero and the population difference decreases ($N_-/N_+ \rightarrow 1$). By multiplying the spectra by the temperature, the contributions to the population difference due to thermal effects are removed, so the change in amplitude is instead due to the quantum mechanical properties of the system.

Near the magnetic transition, the increase in spin fluctuations as the magnetic order develops decreases the population difference and attenuates the signal. Once the magnetic order develops, the magnetic fluctuations decrease again, so by normalizing the spectra by temperature, a decrease and subsequent increase in the signal amplitude indicates the transition into the magnetic state. This behavior is seen in the spectra plotted in Figure 5.6(b). The signal amplitude is most attenuated at 24 K, but the drop in amplitude between 26 K and 27 K is very large which indicates the true minimum, and the magnetic transition, actually occurs somewhere just below 26 K. From 24 K, the signal amplitude increases again until 19 K at which point it drops and continues to decrease to the lowest temperature measured.

At 19 K, there is also a shift in the peak position, shown in Figure 5.6(c). The

shift in peak position was extracted by subtracting a 7th order polynomial (9th order for 6 K and 3.5 K data) fit to the full spectrum to remove the broad background introduced by the magnetic order. This isolated the peaks, making the shift in their position easier to identify and shows that the first shift in the peak position from the position in the PM phase is at 19 K (the dashed lines in Fig. 5.6(c) denote the peak position in the PM phase). The onset of magnetic order generally causes a shift in the NMR spectrum as a result of local fields that develop at the nuclear site due to the magnetic order. In this material, since there is a net ferromagnetic component along the *c*-axis, we would expect to see a shift in the peak position at the magnetic transition. No such a shift occurs, which could provide some insight into the AHE in this material. The AHE was found to be very weak at 15 K, so it's possible that the onset of a shift in the peak positions is due to the weakening of the AHE. The subsequent decrease in signal amplitude and the shift in peak position at 19 K indicate the presence of some change in the quantum mechanical behavior of this system around 19 K.

Previous work found that the anomalous Hall effect (AHE) is strongest around 23 K and that it weakens with decreasing temperature, becoming very weak at 15 K and disappearing completely at 2 K [19]. All of these changes are consistent with our data. The peak positions stay the same until below 22 K where they start shifting and then stop shifting at 6 K. The asymmetric linewidth broadening starts around 22 K and stops at 6 K. Likely, we are seeing the magnetic phase transition through the attenuation of the signal just below 26 K, a weakening of the AHE around 19-15 K through the Knight shift and asymmetric spectral broadening, and its complete disappearance around 6 K below which these effects remain constant.

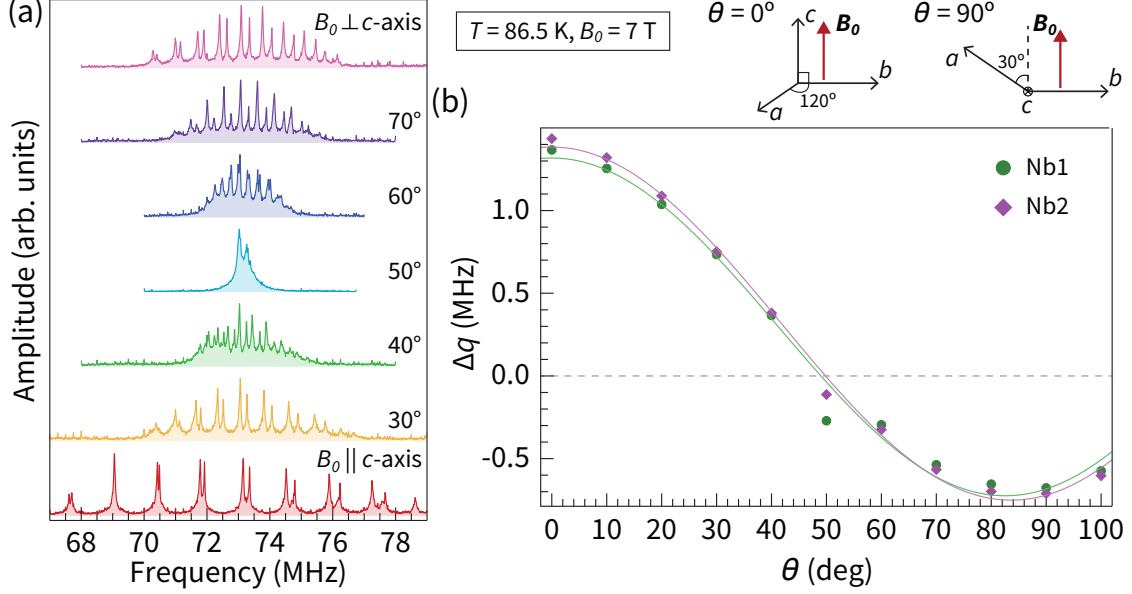


FIGURE 5.7: (a) Spectra at 86.5 K (PM) as the sample is rotated in the out-of-plane direction. (b) Peak splitting Δq as a function of rotation angle extracted from (a). Solid lines are Eq. (5.2) fit to data. The quadrupolar interaction strength was found to be $\nu_q = 1.32 \pm 0.06$ MHz for site Nb1 and $\nu_q = 1.38 \pm 0.03$ MHz for site Nb2.

5.3.4 Sample Rotation and Anisotropy in EFG

In the measurements taken at Brown ($B_0 = 7$ T), we rotated the sample relative to the static field around the b -axis so that the c -axis went from parallel to B_0 ($\theta = 0^\circ$) to perpendicular to B_0 ($\theta = 90^\circ$) and the a -axis ended 30° off-axis from B_0 , as shown in the diagram in Figure 5.7. The spectra are shown in Figure 5.7(a). There is a high symmetry angle somewhere around $\theta = 50^\circ$ where all the peaks collapse into only two peaks. Near this angle could be a good place to retry the multi-modal spectroscopy since the quadrupolar splitting is much smaller and therefore on a time-scale that will be easier to detect.

The strength of the quadrupolar interaction ν_q and the anisotropy of the electric field gradient (EFG) η can be determined from the change in quadrupolar splitting as the angle θ between the static field B_0 and the principal component of the EFG, V_{zz} , is varied. The peak splitting Δq as a function of θ is plotted in Figure 5.7(b)

and fit to the following equation,

$$\Delta q(\theta) = \frac{\nu_q}{2} [3 \cos^2(\theta) - 1 + \eta \cos(2\phi) \sin^2(\theta)] \quad (5.2)$$

where ϕ is the standard azimuthal angle of a spherical coordinate system, the anisotropy $\eta \equiv |V_{xx} - V_{yy}|/V_{zz}$, and $\nu_q \equiv (eQ)V_{zz}/2h$, for nuclear quadrupolar moment eQ [72]. From these data, the quadrupolar interaction strength was found to be $\nu_q = 1.32 \pm 0.06$ MHz for site Nb1 and $\nu_q = 1.38 \pm 0.03$ MHz for site Nb2. For site Nb1, $\eta = 0.099 \pm 0.076$ and for Nb2, $\eta = 0.085 \pm 0.039$ for $\varphi = 90^\circ$, indicating that the principal component of the EFG is along the c -axis with virtually no anisotropy. If ϕ is left as a fitting parameter and η is fixed to 1, $\phi = 47.85 \pm 2.17^\circ$ at Nb1 and $\phi = 47.43 \pm 1.12^\circ$ at Nb2, which also indicates a near-zero anisotropy in the EFG. This is consistent with DFT calculations and symmetry analysis carried out in Ref. [138], which found $\eta = 0$ and $V_{zz} \parallel c$ -axis.

5.3.5 Relaxation Measurements

The spin-lattice relaxation rate as a function of temperature is shown in Figure 5.8(a). The peak in $T_1^{-1}(T)$ is at 28.44 K which is close to the value of $T_N = 28$ K cited in most of the literature [19, 130, 133]. The value of T_1^{-1} measured at room temperature is marked on the plot by a dashed line that shows that the spin-lattice relaxation at the lowest temperatures measured is smaller than that measured at room temperature. T_1^{-1} decreases exponentially below the transition, but there may be a slight bump or plateau just above 15 K, around the same temperature range over which the shift in spectral frequency was observed.

During spin-lattice relaxation, excited nuclear spins transfer energy to the lattice in order to relax back to their equilibrium state. Therefore, to properly determine the rate at which that energy transfer occurs, and thus relaxation back to equilibrium,

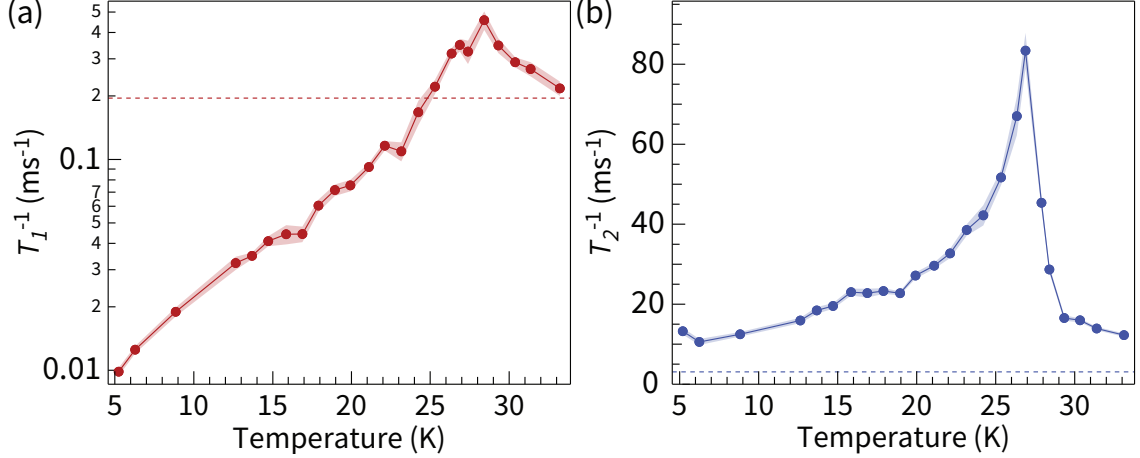


FIGURE 5.8: (a) Spin-lattice relaxation rate T_1^{-1} and (b) spin-spin relaxation rate T_2^{-1} as a function of temperature, measured at $B_0 = 7$ T. The dashed lines in both plots denote their respective values measured at room temperature.

one must first accurately describe the initial condition of the system. A well-defined initial condition is set by the initialization pulse in a T_1 pulse sequence and is described by the resulting population difference of adjacent levels. For an accurate description of population differences in the specific system under investigation, it is important to know which transition is being saturated for systems with quadrupolar splitting ($I > 1/2$).

In the PM phase, the quadrupolar splitting is large enough that a single transition can be probed, so an accurate description of the relaxation process can be determined. The ^{93}Nb nuclei have spin $I = 9/2$, so for a train pulse sequence $(\pi/2 \text{ (x10)} - t - \pi/2 - \tau - \pi - \tau)$ saturating the central transition, the magnetization recovery profile can be described by the following equation:

$$M_{-1/2 \leftrightarrow 1/2}(t) = 1 - 0.3628e^{-45t/T_1} - 0.192e^{-28t/T_1} - 0.1538e^{-15t/T_1} - 0.1515e^{-t/T_1} - 0.1399e^{-6t/T_1}. \quad (5.3)$$

Appendix A has recovery profiles for additional transitions as well as for a full saturation inversion recovery sequence, and details on how Eq. (5.3) was calculated.

In the AFM phase, the spectrum of the Nb2 site maintains some structure with visible, although not very well defined, peaks. The Nb1 spectrum becomes a broad potato-like background signal over the entire frequency range, making it impossible to saturate a single transition. Therefore, an equation like Eq. (5.3) that relies on a single transition being saturated can no longer be used to describe the spin-lattice relaxation process. Instead, we must use an approximate description of the magnetization recovery that states that the longitudinal magnetization has recovered when it is at $[1 - (1/e)] \approx 63\%$ of its initial value after the initialization pulse. The values plotted in Figure 5.8(a) are the magnetization at 63% of the total magnetization recovery curves.

The spin-spin relaxation rate T_2^{-1} as a function of temperature is shown in Figure 5.8(b). There appears to be a slight plateau between 20 K and 15 K, but additional data must be taken to be certain. $T_2^{-1}(T)$ peaks at 26.89 K, close to where the transition was estimated by changes in the spectral shape. The value of T_2^{-1} at room temperature is shown by the dashed line and is of the same order of magnitude as that found for the lowest temperature measurements.

The MSIS measurement technique was attempted on this material, but there were no apparent oscillations or plateau in the T_2 decay curves. This is likely because the quadrupolar splitting is on the order of megahertz, meaning that the oscillations would occur on a time scale of a single microsecond to hundreds of nanoseconds, which is very difficult to resolve on the timescale of NMR spectroscopy.

5.4 Analysis of Possible Magnetic Order

As discussed in Section 5.1.2, multiple models have been proposed to describe the magnetic order in CoNb_3S_6 . It is well understood to be antiferromagnetic with a small ferromagnetic component along the c -axis, but the exact form of AFM order remains unknown. In an attempt to discern more information about the magnetic

order in CoNb_3S_6 , we calculated the NMR spectra for each ^{93}Nb site, adjusting the values of the local field felt by the nuclear site until the calculated spectrum matched the measured spectrum as best possible.

5.4.1 Method

As discussed in Section 3.1.2, the total hyperfine interaction contains contributions from the dipolar hyperfine interaction and the transfer hyperfine tensor. The dipolar interaction matrix can be calculated from Eq. 3.11 since the position of the cobalt atoms relative to the ^{93}Nb site of interest is known. Calculating the transfer hyperfine interaction tensor requires exact knowledge of the electronic wavefunction of the interacting electron and nucleus, so it is much more simple to determine based on experimental results.

The diagonal elements of the tensor can be extracted from a Clogston-Jaccarino plot as described by Eq. 3.12. The off-diagonal terms of the hyperfine tensor in the PM phase were determined from the local field at each ^{93}Nb site extracted from fits of calculated NMR spectra to the data. The spectra were calculated using a Python program that diagonalizes the total Hamiltonian at the nuclear site being probed to determine the energy splitting and thus the position of the peaks in the NMR spectra. This is described in more detail in Appendix B.

The internal field parallel and perpendicular to the static field B_0 was varied to best fit the measured spectra. The contributions to the total local field from the parallel versus perpendicular components were determined by comparing the calculated results to the measured data with the static field B_0 oriented in various directions relative to the crystallographic c -axis of the sample. Once the local field at each ^{93}Nb site was determined, the total hyperfine tensor was calculated using the relationship in Eq. (3.8), assuming the spins are randomly oriented and that the effective magnetic moment of cobalt is $3\mu_B/\text{Co}$ [19, 134].

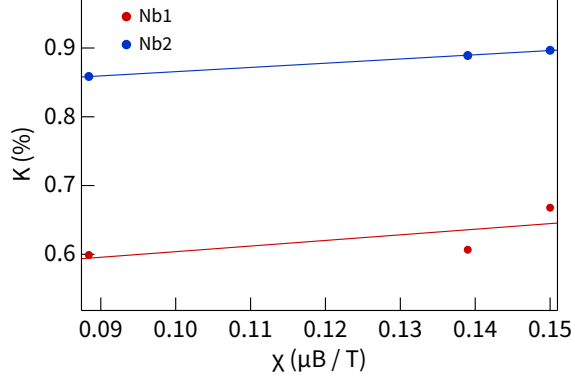


FIGURE 5.9: Clogston-Jaccarino plot showing the Knight shift as a function of susceptibility in the PM phase. The susceptibility data was taken from Figure 3(a1) in Ref. [140]. Knight shift values were obtained from the position of the center line of both sites at 98 K, 50 K, and 30 K.

Calculating the hyperfine coupling tensor in the AFM phase is more complicated since the magnetic order is not well understood. The symmetry of the hyperfine tensor can be inferred by the local symmetry of the spin structure at the ^{93}Nb site [143, 144] and thus will be different for each proposed magnetic order. By adjusting the angle of the cant and the off-diagonal terms of the hyperfine interaction tensor to obtain local field values determined based on fits to the data, we expect to be able to gain insight into the nature of the AFM order. Determining the hyperfine coupling tensor for each proposed magnetic order is the subject of future work.

5.4.2 Diagonal Components of Hyperfine Interaction Tensor

The diagonal components of the hyperfine interaction tensor were determined from the Clogston-Jaccarino plot in Figure 5.9 [71]. Magnetic susceptibility was obtained from Figure 3(a1) in Ref. [140] and plotted against Knight shift data obtained from our NMR measurements in the PM phase taken at the LNCMI. Assuming the g -factor is isotropic and all diagonal elements of $\mathbb{A}$ are equal, $A_{ii} = 0.409 \pm 0.4 \text{ T}/\mu_B$ for the Nb1 site and $A_{ii} = 0.307 \pm 0.007 \text{ T}/\mu_B$ for the Nb2 site.

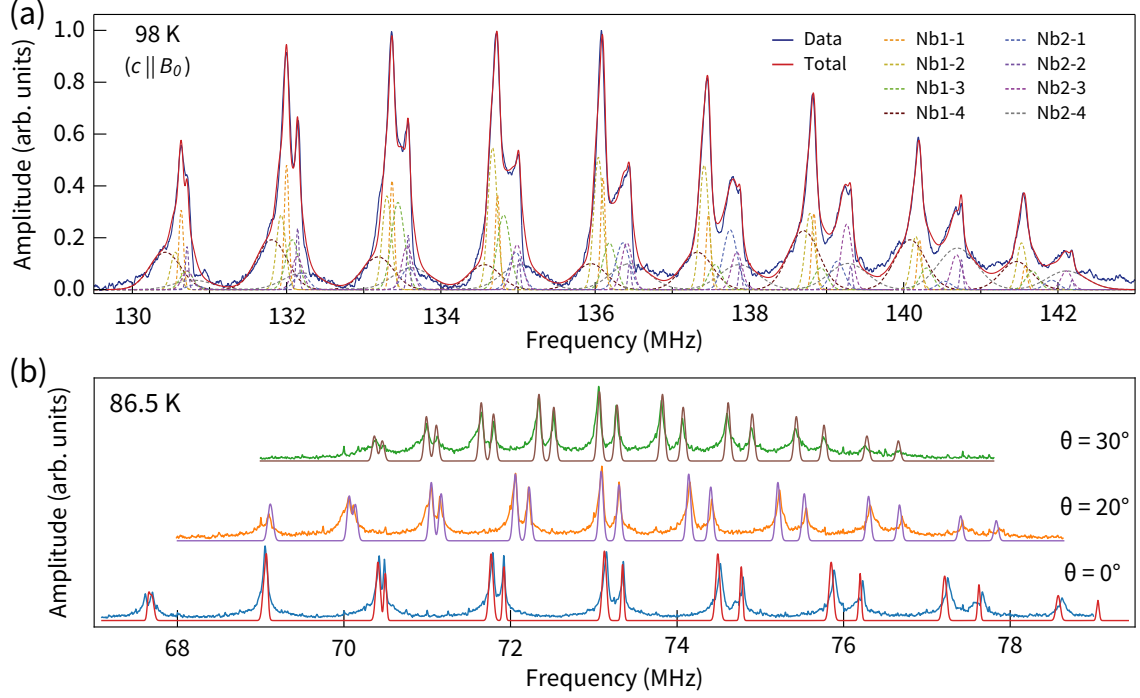


FIGURE 5.10: Measured paramagnetic phase spectrum of CoNb_3S_6 compared to spectra calculated based on the local environment of each ^{93}Nb site. (a) Spectrum at 98 K showing the number of Gaussians required to fully fit the measured data. Each Gaussian curve represents a different local field environment of the ^{93}Nb site, likely due to domains or stacking faults in the layered material. (b) Spectrum at 86.5 K where rotation data was used to verify that the perpendicular and parallel contributions to the local field were determined correctly. Note that the data in (a) and (b) were taken on different crystals and the data in (a) is a field sweep converted to a frequency sweep ($f_0 = 136.3$ MHz, $B_0 = 13$ T, $^{93}\gamma = 10.405$ MHz/T) measured at the LNCMI and (b) is a frequency sweep at fixed field ($B_0 = 6.994$ T) measured at Brown.

5.4.3 Calculations of PM Spectra

To determine the off-diagonal components of the hyperfine coupling tensor in the PM phase, the local field at both ^{93}Nb sites was extracted by fitting the measured data to the simulated NMR spectra. The simulated NMR spectra are Gaussian distributions whose peak position and distribution are determined by the local field felt at each site. The satellite peaks introduced due to the quadrupolar interaction of the $I = 9/2$ ^{93}Nb nuclei have peak splitting determined by the strength of the EFG.

In order to obtain a good fit to any peak in the spectrum, multiple Gaussian

Nb1 site	$h_{\parallel}$ (T)	$h_{\perp}$ (T)	ν_q (MHz)	Nb2 site	$h_{\parallel}$ (T)	$h_{\perp}$ (T)	ν_q (MHz)
Nb1-1	0.0645	0.64	1.373	Nb2-1	0.1037	0.5	1.438
Nb1-2	0.071	0.3	1.373	Nb2-2	0.11	0.0	1.425
Nb1-3	0.082	0.4	1.373	Nb2-3	0.105	0.0	1.39
Nb1-4	0.065	0.05	1.373	Nb2-4	0.1	0.6	1.42

TABLE 5.1: Local field parallel ($h_{\parallel}$) and perpendicular ($h_{\perp}$) to $B_0 \parallel c$ -axis in the PM phase (98 K) and the strength of the quadrupolar interaction ν_q for all of the Nb1 and Nb2 domains. Note that there is no particular correlation to the way the Nb1 and Nb2 domains were labeled.

distributions were required, which indicates that there are domains of the sample where the ^{93}Nb nuclei feel slightly different local field, likely due to either impurities or stacking faults. In order to account for all features of the spectrum, eight total Gaussians, four for each site, were necessary. All Gaussian distributions and the total fit, a sum of individual curves, are shown in Figure 5.10(a). The corresponding local field values are given in Table 5.1. Probably, the values listed in Table 5.1 result in an accurate spectral shift for each domain, but there is likely some discrepancy between the contributions to the spectra due to the parallel and perpendicular components of the local field.

From the local fields described in Table 5.1, the hyperfine coupling tensors were calculated for each domain. The resulting hyperfine tensors are listed in Table ???. Very little difference is found between $\mathbb{A}$ calculated from the various Gaussian fits.

To get an idea of how well contributions to the total local field were determined from the perpendicular versus parallel local fields, and what effect this would have on $\mathbb{A}$, a single Gaussian was fitted to the rotation data taken at 86.5 K and $B_0 = 6.994$ T, shown in Fig. 5.10(b). Using the rotation data made it easier to determine the correct values for $h_{\parallel}$ and $h_{\perp}$, which is made more apparent by the equations used to determine the NMR spectra given in Appendix B. A more complete fit is the subject of future work.

The local field at each site and the resulting $\mathbb{A}$ tensors are shown in Table 5.3. The

Nb1 site	$\mathbb{A}$ (T/ μ_B)	Nb2 site	$\mathbb{A}$ (T/ μ_B)
Nb1-1	$\begin{pmatrix} 0.409 & -0.145 & -0.194 \\ -0.145 & 0.409 & -0.212 \\ -0.194 & -0.212 & 0.409 \end{pmatrix}$	Nb2-1	$\begin{pmatrix} 0.307 & -0.108 & -0.144 \\ -0.108 & 0.307 & -0.158 \\ -0.144 & -0.158 & 0.307 \end{pmatrix}$
Nb1-2	$\begin{pmatrix} 0.409 & -0.178 & -0.198 \\ -0.178 & 0.409 & -0.207 \\ -0.198 & -0.207 & 0.409 \end{pmatrix}$	Nb2-2	$\begin{pmatrix} 0.307 & -0.156 & -0.151 \\ -0.156 & 0.307 & -0.151 \\ -0.151 & -0.151 & 0.307 \end{pmatrix}$
Nb1-3	$\begin{pmatrix} 0.409 & -0.168 & -0.197 \\ -0.168 & 0.409 & -0.208 \\ -0.197 & -0.208 & 0.409 \end{pmatrix}$	Nb2-3	$\begin{pmatrix} 0.307 & -0.156 & -0.151 \\ -0.156 & 0.307 & -0.151 \\ -0.151 & -0.151 & 0.307 \end{pmatrix}$
Nb1-4	$\begin{pmatrix} 0.409 & -0.201 & -0.202 \\ -0.201 & 0.409 & -0.203 \\ -0.202 & -0.203 & 0.409 \end{pmatrix}$	Nb2-4	$\begin{pmatrix} 0.307 & -0.100 & -0.142 \\ -0.100 & 0.307 & -0.160 \\ -0.142 & -0.160 & 0.307 \end{pmatrix}$

TABLE 5.2: The hyperfine coupling tensor $\mathbb{H}$ for each peak in the calculated spectrum.

hyperfine coupling tensors are very similar to those found from the 98 K measurements which indicate that either the local field components were well determined or that they have little effect on the coupling tensor. Note that this is a different crystal than was measured to produce the data at 98 K. A more detailed analysis could be done on the 86.5 K data to better determine the coupling tensor in each domain, but these results indicate that it is unlikely to provide additional significant information.

For the rotation data, the orientation in the plane of the static field ϕ was set to 90° since the sample was mounted so that it rotated about the b -axis (see Figure 5.7). The in-plane orientation of the spins φ was found to be $\varphi = 45^\circ$, where $\varphi = 0^\circ \parallel x$ -axis and $\varphi = 90^\circ \parallel y$ -axis. In the 98 K spectrum, the angle of ϕ is irrelevant since $\theta = 0^\circ$ and changing φ produced no significant change in the calculated spectrum. For both fits, the electric field gradient is isotropic ($\eta = 0$) and its principal component V_{zz} is parallel to the c -axis [138].

Some likely errors in the hyperfine coupling tensor should be noted. Firstly, the parallel components were determined from the slope of a line with only three data points, so it is not possible to say that they are highly accurate. Additionally, the

Site	$h_{\parallel}$ (T)	$h_{\perp}$ (T)	ν_q (MHz)	$\mathbb{A}$ (T/ μ_B)
Nb1	0.015	0.52	1.372	$\begin{pmatrix} 0.409 & -0.155 & -0.196 \\ -0.155 & 0.409 & -0.212 \\ -0.196 & -0.212 & 0.409 \end{pmatrix}$
Nb2	0.036	0.52	1.437	$\begin{pmatrix} 0.307 & -0.105 & -0.145 \\ -0.105 & 0.307 & -0.160 \\ -0.145 & -0.160 & 0.307 \end{pmatrix}$

TABLE 5.3: Local field parallel ($h_{\parallel}$) and perpendicular ($h_{\perp}$) to B_0 in the PM phase (86.5 K), the strength of the quadrupolar interaction ν_q for the Nb1 and Nb2 sites, and the hyperfine coupling tensor in the PM phase calculated from these local fields and the Clogston-Jaccarino plot.

local field values obtained probably also contain some errors. Due to the complicated nature of the spectra, basic computational fitting algorithms could not be applied, so the values were determined through trial and error. The rotation data that were used to estimate the contributions of the local field from the perpendicular versus the parallel components of the local field were definitely subject to some slight error in the rotation angle. Most of this error was accounted for in the fitting, but more thorough rotation data would likely yield more precise results.

5.4.4 Initial Analysis of Proposed Magnetic Orders

Three different magnetic orders were considered in this analysis, shown in Figure 5.11. To begin the process of determining which magnetic order is most likely to correspond to our experimental results, the number of different local spin structures at each site for each magnetic order is determined. This provides information on possible orders because the spectral linewidth is directly related to the distribution of fields felt at the ^{93}Nb sites across the sample. Since we see significant linewidth broadening for the Nb1 spectrum and no significant increase in the linewidth for the Nb2 spectrum with magnetic ordering, we expect there to be a large distribution in the local field at the Nb1 sites and little distribution in the local fields at the Nb2 sites across the sample. It should be noted that if the sites were incorrectly allocated,

the opposite would be true. This is simply a first step in exploring the insight that our measurements can provide on the proposed magnetic order, and it is likely that calculation of the hyperfine interaction tensor will be a much more insightful analysis.

The first order considered is a stripe AFM order with a slight cant out-of-plane and effective magnetic moment $\mu_{eff} = 3\mu_B$, shown in 5.11(a). The spin vectors for this order are,

$$\begin{aligned}\mathbf{S}_1 &= \mathbf{e}_x \cos \theta \cos \phi - \mathbf{e}_y \cos \theta \sin \phi + \mathbf{e}_z \sin \theta \\ \mathbf{S}_2 &= -\mathbf{e}_x \cos \theta \cos \phi + \mathbf{e}_y \cos \theta \sin \phi + \mathbf{e}_z \sin \theta,\end{aligned}\tag{5.4}$$

where $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ are unit vectors along the $[110]$, $[1\bar{1}0]$, and $[001]$ crystal axes respectively. This order creates a single unique local environment for the Nb1 site: each Nb1 atom is surrounded by two cobalt spins described by $\mathbf{S}_1$ and two described by $\mathbf{S}_2$. There two unique environments for the Nb2 site: the Nb2 atoms are surrounded by either four $\mathbf{S}_1$ spins and two $\mathbf{S}_2$ spins or two $\mathbf{S}_1$ spins and four $\mathbf{S}_2$ spins. This results in a distribution in the local field felt at the Nb2 sites across the sample, but no distribution in the local fields at the Nb1 sites. This is inconsistent with our NMR measurements.

The second magnetic order that we analyzed was the all-in-all-out order described in Ref. [133, 138, 139] and shown in Figure 5.11(b), where the circles represent spins pointing out of the page, along the c -axis. This is a $3\mathbf{q}$ magnetic order with four normalized spin vectors:

$$\begin{aligned}\mathbf{S}_1 &= \mathbf{e}_z, \\ \mathbf{S}_2 &= \mathbf{e}_y \sin \theta + \mathbf{e}_z \cos \theta, \\ \mathbf{S}_3 &= \mathbf{e}_x \frac{\sqrt{3}}{2} \sin \theta - \mathbf{e}_y \frac{1}{2} \sin \theta + \mathbf{e}_z \cos \theta, \\ \mathbf{S}_4 &= \mathbf{e}_x \frac{\sqrt{3}}{2} \sin \theta - \mathbf{e}_y \frac{1}{2} \sin \theta + \mathbf{e}_z \cos \theta.\end{aligned}\tag{5.5}$$

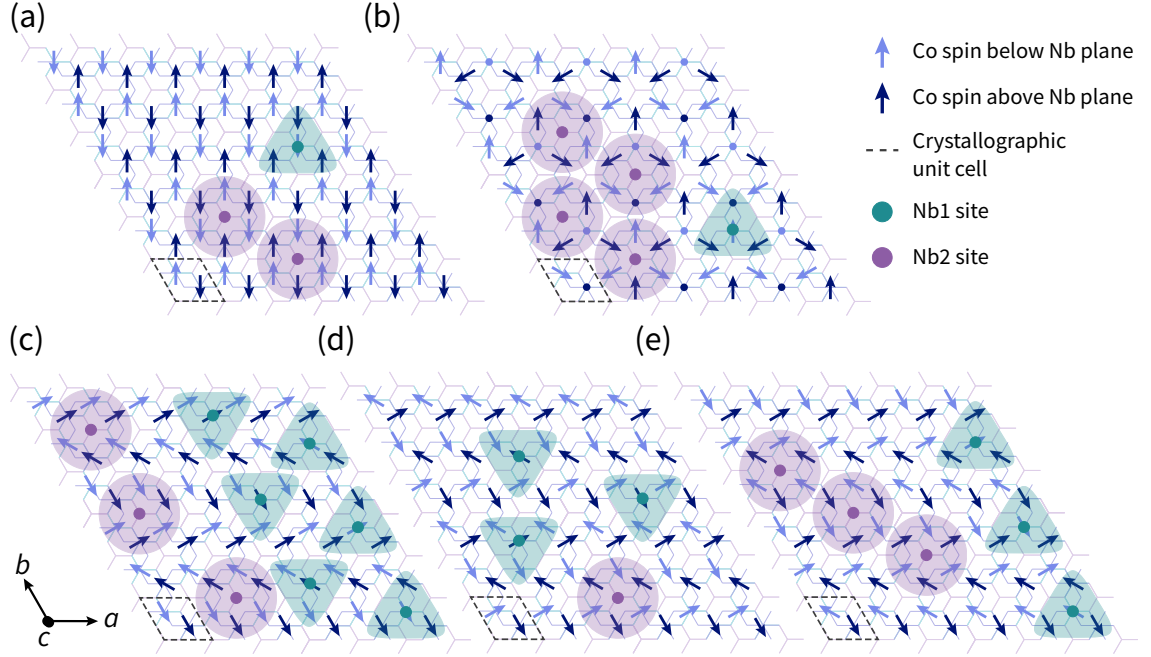


FIGURE 5.11: Possible magnetic orders in CoNb_3S_6 including (a) stripe AFM order proposed by Ref. [137], (b) all-in-all-out AFM order proposed by Ref. [133, 138, 139], and (c-d) planar Néel order as described by Ref. [145] with different amounts of offset between cobalt layers above and below the niobium plane. The crystallographic unit cells are shown by dashed gray diamonds and unique local spin structures for the Nb1 and Nb2 sites are shown by shaded teal and purple shaded regions, respectively, around the ^{93}Nb site.

This order produces the same local environment for all the Nb1 sites across the sample: each Nb1 site is surrounded by four cobalt atoms with one of each of the four spin vectors. For the Nb2 site, there are four possible local environments: the six surrounding cobalt atoms have spin vectors of either two with $\mathbf{S}_1$, $\mathbf{S}_2$, and $\mathbf{S}_4$; two with $\mathbf{S}_2$, $\mathbf{S}_3$, and $\mathbf{S}_4$; two with $\mathbf{S}_1$, $\mathbf{S}_2$, and $\mathbf{S}_3$; or two with $\mathbf{S}_1$, $\mathbf{S}_3$, and $\mathbf{S}_4$. This again produces different local fields at the Nb2 site across the sample and not at the Nb1 site, which is counter to what we would expect from our data.

The third magnetic order we analyzed is the $3\mathbf{q}$ planar Néel order described in Ref. [145] and shown in Figure 5.11(c-e). This order is described by the following

spin vectors,

$$\begin{aligned}
\mathbf{S}_1 &= \mathbf{e}_x \cos \theta \cos(\phi + \pi/6) + \mathbf{e}_y \cos \theta \sin(\phi + \pi/6) + \mathbf{e}_z \sin \theta \\
\mathbf{S}_2 &= \mathbf{e}_x \cos \theta \cos(\phi + 5\pi/6) + \mathbf{e}_y \cos \theta \sin(\phi + 5\pi/6) + \mathbf{e}_z \sin \theta \\
\mathbf{S}_3 &= \mathbf{e}_x \cos \theta \cos(\phi + 3\pi/2) + \mathbf{e}_y \cos \theta \sin(\phi + 3\pi/2) + \mathbf{e}_z \sin \theta.
\end{aligned} \tag{5.6}$$

These equations describe the order of the cobalt spins in a single plane, but changing the offset of this order between adjacent cobalt planes produces different local environments for the niobium atoms between them. These different offsets are shown in Figure 5.11(c-e).

In Figure 5.11(c), the two sublattices are not offset from each other, which means that the spin vectors of the two cobalt atoms in each crystallographic unit cell are the same. This creates six unique local environments for the Nb1 site and three for the Nb2 site. The two sublattices offset by one crystallographic unit cell, as shown in Figure 5.11(d), creates three unique local environments for the Nb1 sites and only a single local environment for the Nb2 sites. With the two sublattices offset by two crystallographic unit cells, shown in Figure 5.11(e), there are three unique local environments for both sites. The first two options (the two sublattices offset by zero and one crystallographic unit cell) both produce a larger distribution in local environments of the Nb1 site than for the Nb2 site, but since we see very little change in the spectral linewidth of the Nb2 site peaks with magnetic order, as can be seen in Figure 5.6(a), it is most likely that the order without a distribution in local environments of the Nb2 sites best describes the magnetic order in this material.

5.4.5 AFM Phase Fits to Spectrum

Without consideration of the hyperfine coupling tensor or specific magnetic orders, the local field at the Nb1 and Nb2 site was determined by fitting the calculated NMR spectra to the measured data at 3.5 K. At 3.5 K, the AHE is expected to have

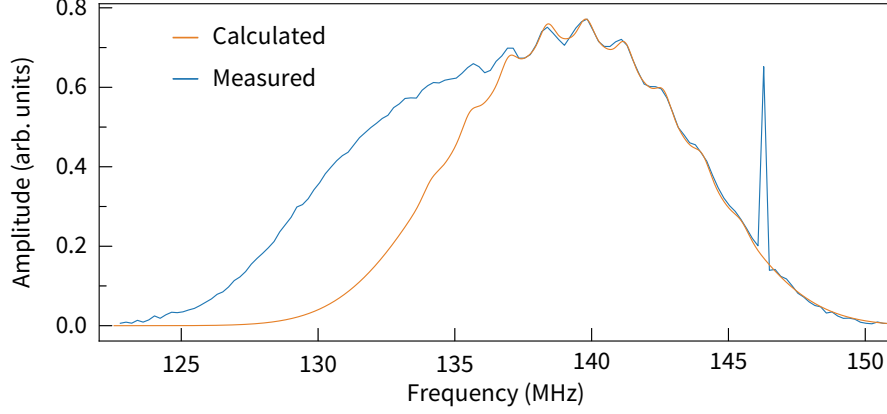


FIGURE 5.12: Calculated NMR spectrum in the AFM phase compared to the measured data at 3.5 K where no AHE is present. Note that this spectrum was measured by sweeping the field at constant frequency 136.3 MHz and was converted to an equivalent frequency sweep at fixed field $B_0 = 13$ T using $^{93}\gamma = 10.405$ MHz/T to compare to the spectrum.

completely disappeared, so the local field values should only be due to the magnetic order. These values will help in determining the hyperfine coupling matrix and the cant angle of the spins in future work.

The calculated spectrum compared to the measured data at 3.5 K is shown in Figure 5.12. It was not possible to determine local field values that fit both the left- and right-hand sides of the spectrum. Since the left-hand side of the spectrum (low frequency/high field) is where the asymmetry develops with decreasing contributions from the AHE, the local field was determined based on the best fit to the right-hand side (high frequency/low field) of the spectrum.

Attempts to account for the asymmetry in the calculated spectrum were made to no avail. Since the asymmetry is likely field dependent, as was previously discussed, and the 3.5 K data is a field sweep that was converted to a frequency sweep for the sake of the fits, it is likely that the asymmetric contribution to the signal can be accounted for by an asymmetric Gaussian distribution. We tried convoluting the spectra without the asymmetry with an asymmetric Gaussian distribution centered on the central transition but were not able to find an asymmetric Gaussian distribution

that correctly fit the measured data. We also tried adding an asymmetric Gaussian to the spectrum for both sites instead of performing a convolution, but similarly were not able to reproduce the measured data. Additional measurements and theoretical models will be needed to determine the origin of this asymmetry.

5.5 Future Work

The work presented here shows the initial NMR measurements of CoNb_3S_6 . Additional measurements and supporting theoretical work are needed to obtain a more complete understanding of the system under investigation. It is likely that signatures of the AHE are visible in the NMR spectra in the expected temperature range for those effects, as described by Ref. [19], providing significant motivation for additional measurements and theory to confirm. The AHE is very sensitive to the concentration of cobalt in the material [141], so repeating these measurements on a sample with a slightly different concentration of cobalt would provide significant insight into whether the effects observed here are from the AHE.

The cobalt concentration of the sample that produced the results in Figure 5.6, which show features that can likely be attributed to the AHE, was $x = 0.34$ (ideal $x = 0.33$). The AHE is expected to be slightly suppressed for $x > 0.33$ and more prominent for $x < 0.33$, so an enhancement of the effects seen in Figure 5.6 with a sample with $x < 0.33$ would provide strong evidence for attributing them to the AHE. Further investigation of possible field dependence on the asymmetric nature of the spectral line in the AFM phase may also provide insight into the nature and origins of the AHE in CoNb_3S_6 .

More detailed measurements of the Knight shift in the PM phase along each crystallographic axis, as well as susceptibility data that can be more accurately determined at each temperature, would provide more accurate values of the diagonal components of the transfer hyperfine interaction tensor $\mathbb{A}$. A better algorithm for fit-

ting the spectra to multiple Gaussian distributions would also improve the accuracy of the calculated hyperfine interaction in the PM phase. Determining the hyperfine interaction matrix for the proposed AFM orders from the symmetry of the local spin structure and the local fields at each ^{93}Nb site due to the magnetic order will also provide insight into the nature of the AFM order in this material.

Other members of the same family of materials could also shed some light on the results obtained for CoNb_3S_6 . For example, CoTa_3S_6 is another material that displays a large spontaneous Hall effect in the AFM phase, although it also has a second magnetic transition below the initial PM-AFM transition [133]. Cr_xNbSe_2 with $x \geq 0.33$ is ferromagnetic and displays oscillations in the spin-spin relaxation curves like those seen in NiPS_3 [132]. Fe_xNbS_2 has a magnetic state that is similarly complicated to that of CoNb_3S_6 and has a strong dependence on the concentration of iron [134, 146, 147]. This could provide interesting ground on which to investigate the effects of different magnetic orders with different iron concentration.

CONCLUSION

In this thesis, we presented an experimental set-up and techniques to enable the measurement of the electronic noise of magnetic tunneling junctions as a means of unobtrusively detecting spin fluctuations of materials in their immediate proximity. Several experimental techniques were discussed, including using a lock-in amplifier to measure noise spectral densities, our method of supplying a voltage bias to the MTJs while maintaining the ability to measure the voltage-dependent MTJ resistance while minimizing spurious noise, and the technique developed to perform cross-correlation of noise spectral densities measured with the lock-in amplifier. The benefits of implementing a low-temperature amplifier to amplify the MTJ noise signal as close to the source as possible were discussed, and several low-temperature amplifiers were characterized. Although no low-temperature amplifier meets all the needs of our MTJ-based magnetic sensors, *i.e.* has low intrinsic noise, high-gain, wide-bandwidth, and can operate from room temperature down to 4.2 K or lower, the HBT-based low-temperature amplifiers presented a good option that could be further improved by optimizing the amplification circuit to increase their operational frequency range.

The design, build, and performance of a highly sensitive cryogenic probe was also presented. Measurement of the transmission of the probe with a $50\ \Omega$ microstrip mounted on our sample holder yielded a -3 dB point of transmission loss at 4.2 K of 550 MHz, which increased to above 1 GHz when the sample holder was removed, likely due to the absence of wire bonds that were used to mount the microstrip to

the sample holder. The results of thermal and shot noise measurements of the MTJs using this probe and the HBT low-temperature amplifier indicated that the biggest challenge these measurements still face is increasing the operational frequency range of the system as a whole. Although we were unable to extract a precise value for the shot noise of the MTJs due to excessive low-frequency noise and a roll-off frequency around 600 MHz, we were able to confirm that what we were measuring was the MTJ shot noise because the noise changed with the bias voltage as expected.

The results presented in this thesis are merely the first steps in creating a functional quantum magnetic sensor from an array of magnetic tunneling junctions. This work provides insight into the most important limitations of the current system that need to be addressed in order to realize these quantum sensors; namely increasing the operational frequency range of the system as a whole. The noise measurement techniques and steps taken to mitigate spurious noise signals will hopefully be helpful in efforts to implement these sensors and in using MTJ noise as a means of quantum sensing.

Obtaining a direct measure of the spin-spin interaction strength of the ^{31}P - ^{31}P dimer in NiPS_3 provided previously inaccessible information about this material and demonstrated the utility of the MSIS measurement technique. The most striking result was the change in the ^{31}P - ^{31}P interaction strength with magnetic ordering. This change in interaction strength points to a change in hybridization of the orbitals involved in the nickel exchange pathways with the onset of magnetic order. The precise cause of this change in hybridization is yet unknown, but it could be related to the exciton quasiparticle observed in this material. The gradual change in interaction strength was found to be due to a coexistence of the PM and AFM phases, indicating that the magnetic phase transition has characteristics of a first-order transition.

One of the most unique characteristics of the MSIS measurement technique is its ability to measure not only the strength of spin-spin interactions but also its dis-

tribution. In NiPS_3 , this provided insight into conflicting results between different measurement techniques with regard to the presence of quasi-2D short-ranged correlations above the magnetic transition. Our results found that the distribution in the ^{31}P - ^{31}P interaction strength was zero above the magnetic transition, which provides strong evidence for the absence of short-ranged correlations in this temperature region. If such correlations were present, they would result in a change in the ^{31}P - ^{31}P interaction strength of the ^{31}P nuclei neighboring the correlated nickel atoms, which would produce some distribution in the interaction strength.

Overall, these results provide insight into the nature of the spin-spin interactions in this material and demonstrate the benefits of applying the MSIS technique to such magnetic systems. The application of this technique to other members of the transition metal phosphorus trichalcogenide family should be a subject of future work, as it is likely to similarly provide previously inaccessible information about the materials as well as help in better understanding the NiPS_3 results. For example, MnPS_3 has antiferromagnetic order that does not break the local symmetry at the transition metal site, so whether or not we see a similar change in hybridization with the onset of magnetic order in MnPS_3 would provide valuable insight into whether the breaking of that local symmetry in NiPS_3 is related to the observed change in hybridization. Furthermore, the development of magnetic models that include the phosphorus atoms would help better understand the cause and nature of the change in ^{31}P - ^{31}P interaction strength.

Standard NMR measurements of the van der Waals antiferromagnet CoNb_3S_6 revealed several changes in spectral features in conjunction with the temperature range over which previous work detected the anomalous Hall effect. Specifically, the resonance frequency of the ^{93}Nb sites being probed shifted and the spectral line shape became increasingly asymmetric over the same decreasing temperature range where the AHE was found to weaken and eventually die out. Additionally, field sweeps

at two different fixed frequencies showed a change in the strength of the asymmetry, and frequency sweeps at fixed field displayed no asymmetry, pointing to the likelihood that this feature has some field dependence.

Through estimates of the local fields at the ^{93}Nb sites by simulating NMR spectra and analysis of the change in the position of the spectral line with magnetic susceptibility, we were able to determine the hyperfine interaction tensor for both ^{93}Nb sites in the PM phase. We were also able to estimate the local fields at the ^{93}Nb sites in the AFM phase, but were unable to identify a model that accounted for the asymmetry observed in the AFM spectra. By analyzing the distribution in local fields that would arise from a range of proposed magnetic orders and comparing them to the difference in spectral linewidth between the two ^{93}Nb sites in the AFM phase, we were able to determine that the Néel planar order best describes our NMR results.

These results point to the possibility that a complete NMR study of CoNb_3S_6 could provide insight into the nature of the antiferromagnetic order and the microscopic origins of the anomalous Hall effect that arises in the magnetic phase of this material. Additional field sweeps at a range of fixed frequencies and at different temperatures throughout the AFM phase would be necessary to fully understand the field dependence of the asymmetry in the spectral line shape. Because AHE was found to be highly sensitive to the concentration of intercalated cobalt, measuring samples with a concentration slightly different from that present in the sample measured here could provide valuable insight into which features are tied to the possible microscopic origins of the AHE effect. Finally, more detailed measurements of the spectral shift in the PM phase and a better fitting algorithm for determining the local field at the ^{93}Nb sites in the PM phase would likely produce a more accurate hyperfine coupling tensor. Determining the hyperfine coupling tensor in the AFM phase would also allow us to compare calculated values of the local fields felt at the ^{93}Nb sites as a result of different magnetic orders to the measured local field values. This could provide

additional insight into the nature of the AFM order in this material.

The MSIS and standard NMR techniques presented in this thesis have significant applications to current topics of condensed matter physics research. The high sensitivity that NMR has to local magnetic fields allows it to be incredibly useful in the study of magnetism in low-dimensional systems, monolayers, and materials with complicated magnetic order. The ability of the MSIS technique to independently quantify different environmental contributions to the NMR signal could be incredibly beneficial for detecting coexisting quantum phenomena. Additionally, since it can measure both the strength and distribution of spin-spin interactions, its resolution essentially extends to every site in the material, allowing interactions that do not include enough nuclei to contribute significantly to the average to be detected, as well as effects that average to zero across the sample. Overall, this work fits more broadly in the field by demonstrating the utility of these techniques in studying materials that are currently of interest because of their technological applications and the exotic quantum phenomena that are predicted to arise in materials with similar crystal and magnetic structures.

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APPENDICES

APPENDIX A

Derivation of I=9/2 Recovery Profiles

The spin-lattice relaxation rate describes how quickly the spins in the system relax back to their equilibrium state from their excited state following an rf excitation pulse. To properly extract the relaxation rate from this process, the initial conditions of the system, which in this case means the distribution of spins across the accessible spin energy levels and the probability of transitioning between energy eigenstates induced by relaxation, must be known. The relaxation of the spin system towards thermodynamic equilibrium is given by:

$$\frac{d}{dt}\mathbf{P}(t) = \mathbb{W}[\mathbf{P}(t) - \mathbf{P}(0)] \quad (\text{A.1})$$

where $\mathbf{P}(t)$ is the population vector of different energy levels with equilibrium value $\mathbf{P}(0)$ and $\mathbb{W}$ is the $(2I + 1)$ -dimensional relaxation matrix [148]. The elements of $\mathbb{W}$, W_{mn} , represent the transition probability from state m to state n which are induced by magnetic fluctuations. For nuclear spin I with $m = -I, \dots, I$ possible states,

$$W_{m \rightarrow n=m \pm 1}^{mag} = W(I \mp m)(I \pm m + 1). \quad (\text{A.2})$$

The transition probabilities W themselves are proportional to the spectral density of the fluctuating random field at Larmor frequency ω_0 [149]. The probability of transitioning from state m to n is expected to be the same as that of transitioning from n to m . [75] We are assuming here that the primary contributions to the spin-lattice relaxation are magnetic and not quadrupolar and thus we do not include the quadrupolar contribution to the transition probability.

We can define the population of level m as P_m , the population difference between adjacent levels as $p_m = P_{m+1} - P_m$, and the equilibrium value of p_m as $n_0 = P_{m+1}(0) - P_m(0)$. Now, we can construct a vector $\mathbf{N}$ with elements $N_m = p_m - n_0$ to describe the deviation of the population difference from equilibrium. Equation (A.1) can be rewritten in terms of $\mathbf{N}$,

$$\frac{d}{dt}\mathbf{N} = \mathbb{R}\mathbf{N}, \quad (\text{A.3})$$

where $\mathbb{R}$ is the $2I$ -dimensional reduced relaxation coefficient matrix. The matrix $\mathbb{R}$ is composed of the transition probabilities of each state such that, for transition j between $m \rightarrow (m+1)$, the change in the population difference is

$$\frac{d}{dt}N_j = W_{(m+1) \rightarrow m}N_{(j+1)} - [2W_{m \rightarrow (m-1)}]N_j + W_{(m-1) \rightarrow m}N_{(j-1)}. \quad (\text{A.4})$$

The relaxation coefficient matrix can be obtained from Eq. (A.2) and Eq. (A.4).

The solution of Eq. (A.3) for transition j takes the form:

$$N_j(t) = \sum_i [(\mathbf{E}^T)^{-1}\mathbf{N}(0)]_i E_{ij} \exp(t\lambda_i) \quad (\text{A.5})$$

where $\mathbf{E}$ is the eigenvector matrix of $\mathbb{R}$, λ_i are the eigenvalues of $\mathbb{R}$, and $\mathbf{N}(0)$ is the population vector describing the initial condition of the spin system prepared by a given pulse sequence.

Knowing the time-dependent population difference between adjacent levels for

transition j $N_j(t)$ allows us to write the time-dependent magnetization $M_j(t)$ measured by the NMR experiment as the two quantities are proportional,

$$M_j(t) = M(\infty) \left[1 - \sum_i a_i \exp(t\lambda_i) \right], \quad (\text{A.6})$$

where a_i are given by:

$$a_i = -\frac{1}{n_0} [(\mathbf{E}^T)^{-1} \mathbf{N}(0)]_j E_{ij}. \quad (\text{A.7})$$

From Eq. A.6, it is clear that the spin-lattice relaxation rate $1/T_1 = \lambda$. It should also be noted that $1/T_1 = 2W$.

In order to obtain Eq. A.6, the prepared initial condition of the spin system must be known. Two different means of initializing the spin system will be discussed here. The first is the saturation recovery sequence in which a single $\pi/2$ pulse is applied selectively to one transition after which a standard spin echo is applied after a time t . This is the most direct way of measuring T_1 . The system must be in equilibrium before the initial $\pi/2$ pulse is applied, which means that there must be a rest time $T_R > 5T_1$ between each average to ensure that all the spins are fully relaxed back to their thermal equilibrium state before the initialization pulse is applied. For systems with a long T_1 , this method can significantly increase the experiment time, so it is most often applied to systems with shorter T_1 values and strong signals to reduce averaging. The saturation recovery method is often particularly useful when measuring T_1 near a transition as T_1 often sees a drastic decrease near a critical temperature due to an increase in fluctuations and the long rest time between averages minimizes sample heating from the rf pulses which could otherwise unknowingly move the sample temperature above the transition temperature.

The second method of initializing the spin system is the train pulse sequence in which the selected transition is saturated by a series of repeated pulses separated by a time $5T_2 < \tau < T_1$. This series of pulses completely saturates the spins, effectively

“killing the signal”. Using a train pulse sequence greatly decreases the measurement time compared to the saturation recovery sequence, since the rest time T_R can be reduced to a time of the order of 10’s of milliseconds, but it can also create significant heating in the sample which can be especially problematic at low temperatures or near phase transitions.

We can now apply this to the specific case of $I = 9/2$. Knowing m takes values from $-I$ to I , we obtain the following reduced relaxation coefficient matrix,

$$\mathbb{R}_{9/2} = W \begin{bmatrix} -18 & 16 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 9 & -32 & 21 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 16 & -42 & 24 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 21 & -48 & 25 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 24 & -50 & 24 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 25 & -48 & 21 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 24 & -42 & 16 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 21 & -32 & 9 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 16 & -18 \end{bmatrix}. \quad (\text{A.8})$$

The initial condition prepared by the full saturation recovery sequence for a spin-9/2 system when the central transition ($-1/2 \leftrightarrow 1/2$) is irradiated can be described as follows:

$$N_{(-1/2 \leftrightarrow 1/2)}^{\text{full sat}}(0) = \begin{bmatrix} 0, & 0, & 0, & 1, & -2, & 1, & 0, & 0, & 0 \end{bmatrix}. \quad (\text{A.9})$$

If instead the first satellite, ($\pm 3/2 \leftrightarrow \pm 1/2$) is irradiated, the initial condition becomes,

$$N_{(\pm 3/2 \leftrightarrow \pm 1/2)}^{\text{full sat}}(0) = \begin{bmatrix} 0, & 0, & 0, & 0, & 1, & -2, & 1, & 0, & 0 \end{bmatrix}. \quad (\text{A.10})$$

If the spin system is prepared by the train pulse sequence, the initial condition for a spin-9/2 system whose central transition is being irradiated can be described as

follows:

$$N_{(-1/2 \leftrightarrow 1/2)}^{\text{train}}(0) = \begin{bmatrix} 0, & 0, & 0, & 0, & -1, & 0, & 0, & 0, & 0 \end{bmatrix}. \quad (\text{A.11})$$

The full recovery profiles for $I = 9/2$ with the excitation pulse selectively applied to several transitions with both initial conditions described are written below.

Full Saturation Inversion Recovery Sequence for Spin-9/2

Pulse sequence: $\pi - t - \pi/2 - \tau - \pi - \tau - \text{acquisition}$

Central transition ($-1/2 \leftrightarrow 1/2$):

$$\begin{aligned} M_{-1/2 \leftrightarrow 1/2}(t) = & 1 - 1.3061e^{-45t/T_1} - 0.43e^{-28t/T_1} - 0.1846e^{-15t/T_1} \\ & - 0.0121e^{-t/T_1} - 0.0671e^{-6t/T_1} \end{aligned} \quad (\text{A.12})$$

First satellite ($\pm 3/2 \leftrightarrow \pm 1/2$):

$$\begin{aligned} M_{\pm 3/2 \leftrightarrow \pm 1/2}(t) = & 1 - 0.907e^{-45t/T_1} - 0.6168e^{-36t/T_1} - 0.0067e^{-28t/T_1} \\ & - 0.297e^{-21t/T_1} - 0.0321e^{-15t/T_1} - 0.0787e^{-10t/T_1} \\ & - 0.0121e^{-t/T_1} - 0.0076e^{-3t/T_1} - 0.0421e^{-6t/T_1} \end{aligned} \quad (\text{A.13})$$

Second satellite ($\pm 5/2 \leftrightarrow \pm 3/2$):

$$\begin{aligned} M_{\pm 5/2 \leftrightarrow \pm 3/2}(t) = & 1 - 0.2962e^{-45t/T_1} - 0.8056e^{-36t/T_1} - 0.5616e^{-28t/T_1} \\ & - 0.0242e^{-21t/T_1} - 0.1282e^{-15t/T_1} - 0.1399e^{-10t/T_1} \\ & - 0.0121e^{-t/T_1} - 0.0303e^{-3t/T_1} - 0.0019e^{-6t/T_1} \end{aligned} \quad (\text{A.14})$$

Train Pulse Sequence for Spin-9/2

Pulse sequence: $\pi/2$ (x10) - t - $\pi/2$ - τ - π - τ - acquisition

Central transition ($-1/2 \leftrightarrow 1/2$):

$$M_{-1/2 \leftrightarrow 1/2}(t) = 1 - 0.3628e^{-45t/T_1} - 0.192e^{-28t/T_1} - 0.1538e^{-15t/T_1} - 0.1515e^{-t/T_1} - 0.1399e^{-6t/T_1} \quad (\text{A.15})$$

First satellite ($\pm 3/2 \leftrightarrow \pm 1/2$):

$$M_{\pm 3/2 \leftrightarrow \pm 1/2}(t) = 1 - 0.2419e^{-45t/T_1} - 0.2056e^{-36t/T_1} - 0.0029e^{-28t/T_1} - 0.1697e^{-21t/T_1} - 0.0256e^{-15t/T_1} - 0.0944e^{-10t/T_1} - 0.1455e^{-t/T_1} - 0.0303e^{-3t/T_1} - 0.0841e^{-6t/T_1} \quad (\text{A.16})$$

A python notebook to calculate the magnetization recovery profiles for nuclear spins $I = 1/2, 3/2, 5/2, 7/2$, and $9/2$ for both the train and full saturation recovery pulse sequences can be found at the following link: <https://github.com/calvin-bales/Magnetization-Recovery-Profiles>.

APPENDIX B

Analytical Determination of Local Fields

This Appendix outlines the details of the method used to determine the local field at the ^{93}Nb sites by fitting calculated NMR spectra to the data in the PM and AFM phase. The spectra were calculated from a basic NMR Hamiltonian with a Zeeman term and quadrupolar term. The Zeeman term accounts for all fields felt at the nuclear site, including the static external field and all local fields, and takes the form:

$$\mathcal{H}_Z = -\gamma (D_{h_x}\mathbf{I}_x + D_{h_y}\mathbf{I}_y + D_{h_z}\mathbf{I}_z), \quad (\text{B.1})$$

where γ is the nuclear gyromagnetic ratio, $\mathbf{I}_i$, $i = (x, y, z)$ is the $2I + 1$ -dimensional spin matrix for nuclear spin I , and D_{h_i} is the local field in spherical coordinates,

$$\begin{aligned} D_{h_x} &= (B_0 + h_{\parallel}) \sin \theta \cos \phi + h_{\perp} (\cos \varphi \cos \theta \cos \phi + \sin \varphi \sin \phi) \\ D_{h_y} &= (B_0 + h_{\parallel}) \sin \theta \sin \phi + h_{\perp} (\cos \varphi \cos \theta \sin \phi - \sin \varphi \cos \phi) \\ D_{h_z} &= (B_0 + h_{\parallel}) \cos \theta - h_{\perp} \cos \varphi \sin \theta, \end{aligned} \quad (\text{B.2})$$

where $h_{\parallel}$ and $h_{\perp}$ are the components of the local field parallel and perpendicular to the static field B_0 respectively, θ is the angle between the out-of-plane axis (c -axis) of the sample and the static field B_0 , ϕ is the standard azimuthal angle that describes the orientation of the static field B_0 along the ab -plane, and φ is the in-plane orientation of $h_{\perp}$.

The quadrupolar component of the Hamiltonian takes the form:

$$\mathcal{H}_Q = \frac{\nu_q}{6} \left[3(\mathbf{I}_z^{EFG})^2 - I(I+1)\mathbb{I} + \eta \left((\mathbf{I}_x^{EFG})^2 - (\mathbf{I}_y^{EFG})^2 \right) \right] \quad (\text{B.3})$$

where $\mathbb{I}$ is the $2I + 1$ dimensional identity matrix, ν_q is the quadrupolar interaction strength which can be extracted from the peak splitting, and

$$\mathbf{I}_i^{EFG} = \mathbf{I}_x \cos(V_{ii}^x) + \mathbf{I}_y \cos(V_{ii}^y) + \mathbf{I}_z \cos(V_{ii}^z) \quad (\text{B.4})$$

where i denotes the x , y , or z component and $V_{ii}^{x,y,z}$ describes the orientation of the principal axes of the EFG with respect to the crystal axes which are defined in a right-handed coordinate system.

The eigenvalues of the resulting $2I + 1$ dimensional Hamiltonian are calculated and sorted in ascending order. The difference between consecutive sorted eigenvalues ω_0 gives the position of the spectral peaks. The peaks are assumed to be Gaussian, so each peak takes the form:

$$f(\omega) = A \exp \left[- \left(\frac{\omega - \omega_0}{\sqrt{2}\sigma} \right)^2 \right], \quad (\text{B.5})$$

where σ is the width of the distribution and A is the signal amplitude which is given by the population difference between adjacent levels. For $I = 9/2$, A is the diagonal values in Eq. (A.8) where the center value corresponds to the amplitude of the central peak. For spectra with satellite peaks, as is the case for $I = 9/2$, each curve calculated

from Eq. (B.5) is summed together to form the full spectrum.

Once the full spectrum is calculated, the local field values $h_{\parallel}$ and $h_{\perp}$ are manipulated until the calculated spectrum well describes the measured spectra.