Berry-Phase Interference in the Ni$_4$ Single-Molecule Magnet

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Abstract

Single-molecule magnets (SMMs) are a mesoscopic class of paramagnetic compounds that exhibit fascinating quantum properties while being easier to manipulate than the much smaller objects in the quantum realm. They can be approximated as a large ensemble of weakly interacting high-spin systems. SMMs are actively being researched for many different potential technological applications (e.g. as candidates of being used as qubits in a quantum computer) as well as for the many physical secrets we have yet to uncover. This thesis investigates one particularly compelling behavior – the Berry-phase interference in the quantum tunneling of magnetization of the magnetic spin in the Ni$_4$ SMM. Specifically, electron spin resonance techniques are used to drive and measure transitions in the $m = \pm 2$ spin states in order to observe how a changing transverse magnetic field along the hard plane of the crystal can exhibit interference effects. We present a home built design for a resonator probe assembly that allows in-situ rotation of the sample, enabling us to conduct our experiment quickly and reliably. The results of our experiment provide conclusive evidence of the Berry-phase interference in the quantum tunneling paths between the $m = \pm 2$ spin states.
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Chapter 1

Introduction

1.1 Motivation

Ever since the development of Quantum Mechanics early in the 20th century, humankind has been grappling with a huge problem - this theory, which so well predicts the behavior of atoms, electrons, photons, and other objects at the microscopic level, falters when it comes to observations of our classical, macroscopic world. It seems reasonable that a theory for the very small must then translate seamlessly into our theory for the macroscopic world. But alas, the lack of such physical systems prevented further research into the mesoscopic realm, where classical dynamics meets quantum uncertainty.

Largely ignored throughout the rest of the century, this problem has seen a tremendous return to the forefront of physical research in the past few decades with the discovery of molecular magnets in 1980 [1]. Single Molecule Magnets (SMMs), first termed as such in 1996 [2], are a class of fairly recently dis-
covered compounds that straddle this mesoscopic fence - large and complex enough to be considered classical, but also able to exhibit quantum-mechanical behavior in the way their magnetic spins can tunnel through angular space. This behavior, known as Quantum tunneling of magnetization, is classically forbidden. Since then, much more theoretical groundwork has been done on exploring these mesoscopic systems, and experimentation has developed enough to begin exploring this, and other, phenomena\(^1\).

This straddling of the classical and quantum realms makes investigation of SMMs an intriguing subject of research, not only for their physical secrets but also for their potential in technological advancement for use in quantum computers\(^2\). One of the unique characteristics of SMMs is that they have relatively long magnetic relaxation rates, which directly correlate to their quantum memory storage ability [5]. While this thesis does not focus on research relating to improving coherence times of SMMs, this example nevertheless explains the interest behind the useful and fascinating behavior of these molecules.

This brings us to the focus of my thesis - Berry-phase interference. Also called Geometric-phase interference, this physical phenomenon arises when two quantum spin tunneling paths interfere with each other, causing constructive or destructive interference in the tunneling rate. This interference can be tuned by various perturbations, creating oscillatory quenching effects in the magnetic relaxation rate of these SMMs. One of the most intuitive ways to analyze this behavior is to apply a magnetic field along the transverse axis of the

\(^1\)For more complete information on the progress made in this field, refer to [3]
\(^2\)For a more complete discussion on research into physical quantum computing systems, see [4]
molecule, which adds a Zeeman Splitting term to the spin Hamiltonian of the molecule. Anupam Garg showed in 1993 that this perturbation could be solved analytically to cause Berry-Phase interference for second-order anisotropy [6]. Using a similar method, Michael Foss-Feig showed that this interference effect could also be modulated using a uniaxial pressure perturbation for the four-fold symmetric Mn$_{12}$Ac SMM [7][8].

Previous research has been done to verify that the Berry-phase effect occurs in other SMMs. In 1999, Sessoli and Wernsdorfer observed this behavior for the first time in Fe$_8$ [9], and since then numerous other groups have managed to observe quantum phase interference in molecules like Mn$_{12}$ [10] and others [11] [12]. Interestingly enough, it has also been observed in half-spin SMMs [13], an antiferromagnetic SMM [14], as well as other systems that behave like exchange-coupled SMM dimers [15]. Many of these experiments have detected this quantum-phase interference by measuring the magnetization of the molecule, which can be challenging to interpret given that the dynamics involve multiple energy eigenstates. Measuring the ESR spectra of SMMs may prove to be a more direct method of observing the Berry-phase. In this experiment, I aim not only to observe Berry-phase interference in a different molecule, Ni$_4$, but also to examine this effect using spectroscopic techniques.

1.2 Two-State System

Before we advance into the more advanced background on Single Molecule Magnets, it is useful to step back and understand a simple two-state system.
Let us consider an arbitrary two-level spin system with a Hamiltonian given by

\[ \hat{H} = \frac{1}{2}(\epsilon S_z + \Delta S_x) \]  

(1.1)

where \( S_z \) and \( S_x \) are spin matrices and \( \epsilon \) and \( \Delta \) are parameters of the system. States \( |+\rangle \) and \( |−\rangle \) are the eigenstates of \( S_z \) and are the basis states for the matrix representation of this Hamiltonian. \( \epsilon \) is an external parameter that we can control, such as a static applied magnetic field, and \( \Delta \) is a fixed parameter inherent to the spin system. \( \Delta \) is called the tunnel splitting, and plays an important role in explaining tunneling between states in an SMM.

We can diagonalize the Hamiltonian in Eq. 1.1 to obtain

\[ E_{\pm} = \pm \frac{1}{2} \sqrt{\epsilon^2 + \Delta^2} \]  

(1.2)

and plot these energies as a function of \( \epsilon \), as shown in Fig. 1.4.

In the regime where \( \epsilon \gg \Delta \), the energy of the system can be approximated as

\[ E_{\pm} = \pm \frac{1}{2} \epsilon \]  

(1.3)

In Fig. 1.1, this linear dependence on \( \epsilon \) can be seen in Fig. 1.1 as \(|\epsilon|\) increases away from 0. It becomes clear that in this limit, the eigenstates are \( |\pm\rangle \).

In the regime where \( \epsilon \approx \Delta \), this approximation does not hold. The energy eigenvalues lose their linear dependence on \( \epsilon \) as it approaches 0. At \( \epsilon = 0 \), we see that the two eigenstates are separated by \( \Delta \) with energy
Figure 1.1: The Energy-level diagram for a two-state spin system of $m=\pm$ in the presence of an external perturbation. Each line shows the energy dependence of each spin-projection state on $\epsilon$. If $\Delta = 0$, the two states never mix into superposition states and each state would depend linearly on $\epsilon$ throughout its domain.

\[ E_{\pm} = \pm \frac{1}{2} \Delta \]  \hspace{1cm} (1.4)

In this limit, the energy eigenstates are $|\psi_{\pm}\rangle = \frac{1}{\sqrt{2}}(|+\rangle \pm |-\rangle)$.

We can show that in this regime, a starting state $|+\rangle$ can time evolve to the state $|-\rangle$. Let us begin with the state
\[ |+\rangle = \frac{1}{\sqrt{2}} [|\psi_+\rangle + |\psi_-\rangle] \quad (1.5) \]

If we are to understand how this system evolves over time, we must introduce the time evolution operator for this closed quantum system.

\[ |\psi(x, t)\rangle = e^{-iEt/\hbar} |\psi_0\rangle , |\psi_0\rangle = |+\rangle \quad (1.6) \]

\[ |\psi(x, t)\rangle = e^{-iE_{+}t/\hbar} |\psi_{+}\rangle + e^{-iE_{-}t/\hbar} |\psi_{-}\rangle \quad (1.7) \]

To find the probability of the system being in state |−\rangle, we find the probability amplitude

\[ \langle -n|\psi(x, t)\rangle = [\langle \psi_{+}| - \langle \psi_{-}|][e^{-iE_{+}t/\hbar} |\psi_{+}\rangle + e^{-iE_{-}t/\hbar} |\psi_{-}\rangle] \quad (1.8) \]

Referring back to Eq. 1.4, \( E_{\pm} = \pm \Delta \).

\[ = [\langle \psi_{+}| - \langle \psi_{-}|][e^{-i\Delta t/\hbar} |\psi_{+}\rangle + e^{i\Delta t/\hbar} |\psi_{-}\rangle] \quad (1.9) \]

\[ = e^{-i\Delta t/\hbar} + e^{i\Delta t/\hbar} \quad (1.10) \]

\[ = \cos \left( \frac{\Delta t}{\hbar} \right) \quad (1.11) \]

Therefore, the system oscillates between energy states as a function of time with a frequency of \( \Delta/\hbar \). The tunnel splitting \( \Delta \) is related to the tunneling frequency between |+\rangle and |−\rangle in this manner.

This kind of system is essentially the model we use to understand the spin states of SMMs, except extrapolated to more complicated Hamiltonians.
The following section will provide some further details on the history and characteristics of SMMs, as well as a more complete discussion of their energy states and behavior.

1.3 Background on Single Molecule Magnets

Single Molecule Magnets, as a class of compound, have certain important characteristics. First, they are usually composed of an inner magnetic core surrounded by a larger, usually organic, ligand structure that shields the magnetic cluster from the surrounding environment. As a result of the strong spin-spin coupling between these central metallic ions, the spins of the many individual metallic atoms can be treated as one collective, large spin. This Giant Spin Approximation has been widely applied in the study of SMMs [16]. While the intramolecular interactions are strong, however, the intermolecular exchange interactions are weak. Their relatively large separation in the crystal lattice means that dipole interactions are weak, and the sample behaves as a paramagnet. Because a crystallized SMM sample will contain $> 10^{15}$ molecules [17] with spin densities of $10^{20}$ spins/cm$^2$ [18], we can exploit the strong magnetizations of the sample as a whole to manipulate and model their behavior.

The first groundbreaking experiment to provide conclusive evidence showing that SMMs straddled the junction between quantum and classical realms was conducted by Friedman et al. in 1996 [20]. The process involved sweeping a magnetic field along the easy axis of a sample$^3$ of Mn$_{12}$ at several tempera-

$^3$[Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$O$_{12}$], first synthesized in 1980 by Lis in 1980 [1].
Figure 1.2: Magnetization as a function of field strength. Notice the steps in the thermal relaxation for each of the hysteresis curves; they occur at regular magnetic field intervals [19]. Reprinted with the permission of J.R. Friedman.

tures, resulting in the discovery that the classically determined hysteresis curve for thermal relaxation was not smooth, as expected, but rather showed quantized “steps” at regular magnetic field intervals. The closed hysteresis loops, shown in Fig. 1.2, reveal that while the magnetic relaxation of the sample must have had some thermal dependence, the unexpected step-like relaxation at regular intervals occurred at even intervals of the field.

To explain such behavior, the group proposed that the dynamics of Mn$_{12}$
could be modeled in the following way. The basic spin Hamiltonian for a spin-10 SMM like Mn_{12} can be written as

\[ \hat{H} = -D \hat{S}_z^2 - A \hat{S}_z^4 - g \mu_B \hat{J}_z + H'. \]  

(1.12)

The first term, with coefficient $-D$, represents an axial anisotropy that favors alignment of the molecule’s magnetization along a particular axis. We call this the “easy axis” of the molecule of the sample. The fact that the $\hat{S}_z$ operator is squared means that the energy eigenstates are degenerate and there is no preferred direction for the magnetization of the molecule at zero field; the spin vector can minimize energy by pointing along or antiparallel to the easy z-axis.

The first two anisotropy terms create a double-well potential, shown in Fig. 1.3, with the classical barrier between the wells defined by $U = DS^2 + AS^4$ when no field is applied. Given that Mn_{12} is a spin-10 molecule, there are $2S + 1 = 21$ magnetic spin states, from $m = -10, -9, ..., 10$. When a field is applied along the z-axis as represented by the Zeeman term, one side of the potential well shifts with respect to the other, making one direction lower in energy than the other. This causes a single spin direction to become preferred along the easy-axis.

The final term, $H'$, contains terms that do not commute with $S_z$. It usually contains transverse anisotropy and transverse field components that “break the symmetry” of the molecule. These additional terms allow for tunneling to occur from one spin state to another by introducing nonzero, off-diagonal matrix elements in the matrix representation of the Hamiltonian.
Figure 1.3: As a longitudinal field is applied to the Mn$_{12}$ sample, one well shifts relative to the other. As energy levels line up, $H'$ terms can induce tunneling between those two states; for example, the $m = S$ and $m = -S + 2$ states are mixed and therefore can allow tunneling between the potential barrier.

Figure 1.4: The energy levels of a pairs of states in an SMM that have formed an avoided crossing. While there are differences between the Hamiltonian for an SMM and a simple two-state system, they behave in similar ways.
This Hamiltonian can essentially be boiled down to the same kind of behavior described by the two-state system we investigated earlier. The first three terms are an analog of the $\epsilon S_z$ term in Eq. 1.1, while the $H'$ term is an analog of the $\Delta S_x$ term. The first three terms form the potential of the system with the Zeeman term raising or lowering one potential well relative to the other as shown in Fig. 1.3. When the spin states in one well line up with spin states in the other well, the $H'$ parameters dictate the allowed tunneling between the two spin states. These can be transitions from any $|m\rangle$ to $|m'\rangle$. This happens because $H'$ creates new eigenstates that are superpositions of $|m_s\rangle$ (the eigenstates of $\hat{S}_z$). For most field strengths, these superposition states are dominated by just one $|m\rangle$ state. However, just like for the two-state system where $\epsilon \approx \Delta$, these superposition states create so-called avoided level crossings where significant mixing of states occur. Fig. 1.4 is an example of an applied transverse field of strength $\epsilon$ creating this mixing of states between $m = \pm 2$. At the middle of the avoided crossing is the tunnel splitting $\Delta$, where the states are mixed with equal magnitudes $|\psi_\pm\rangle = \frac{1}{\sqrt{2}}(|2\rangle \pm |-2\rangle)$. The tunnel splitting is defined as the difference in energy between the two states $|\psi_+\rangle$ and $|\psi_-\rangle$.

Unlike the two-state system, SMM’s can have multiple energy level crossings depending on how the applied longitudinal field lines up the $|+m\rangle$ states to $|m'\rangle$ states. In this thesis, we will be focusing on the transition between the $|2\rangle$ and the $|-2\rangle$ states of Ni$_4$; more on this in the following chapter.

This kind of behavior proposed by Friedman et al. helped set the groundwork for investigating the behavior of SMMs. Using this framework for de-
scribing the energetics of molecular magnets, Wernsdorfer and Sessoli made another groundbreaking discovery in 1999 [9], observing another strange phenomenon in a different SMM, Fe₈. Their setup for this experiment is shown in Fig. 1.5, where θ = 90°.

![Diagram](image)

Figure 1.5: A diagram showing the basic premise of Wernsdorfer and Sessoli’s experiment. They set θ = 90° and rotated the field along the hard plane at different values of φ.

They turned the magnetic field away at increasing angles from the hard axis, observing the tunneling rate of magnetization as they changed the φ angle. One might expect that applying an increasing field in the hard plane would correlate to increasing tunneling rates in the molecule because it would break the S_z rotational symmetry of Fe₈. This happened to be the case at φ = 90°. With the field being aligned with the medium axis, the tunneling rate increased monotonically, as originally expected.

However, as they rotated the field closer to φ = 0°, as shown in Fig 1.6,
Figure 1.6: The final result of Wernsdorfer and Sessoli’s 1999 experiment. Notice that the berry-phase interference washes out as the field is turned from $\phi = 0^\circ$. Reprinted with permission from W. Wernsdorfer.

a strange oscillation in the splitting began to emerge. The surprising result was that when the field was aligned with the hard axis at $\phi = 0^\circ$, the tunnel splitting exhibited some periodic oscillation before returning to the expected monotonic growth. In fact, at certain fields, quantum tunneling of magnetization seemed to be dramatically quenched!

This effect, however, was not so mysterious after all. In 1993, Anupam Garg had shown analytically that there could exist a phenomenon called Berry-phase interference when a field is applied along the hard axis of an SMM with biaxial symmetry, like Fe$_8$. He showed that symmetry allows two tunneling paths between the two energy minima situated along the easy axes, each a reflection of the other across the plane of symmetry; and that these paths should interfere with each other, causing the quantum tunneling of magnetization effect to be quenched periodically as a function of field [6].
My thesis aims to explore a similar interference pattern in the Ni$_4$ molecule. At first, I aimed to utilize pressure as another means to “tune” the interference, much like the transverse field did in the 1999 experiment. In fact, uniaxial pressure was applied for the first time to Mn$_{12}$Ac in 2013 to examine the effect on its quantum tunneling of magnetization [21], so my project would have built upon their results, aiming to use pressure to observe a quantum phase interference effect. However, as I initially ran through simulations for Ni$_4$ by sweeping a transverse field at different orientations of $\phi$, I also saw Berry-phase interference through calculated ESR spectra. As a result, I turned my efforts towards experimentally verifying this phenomenon – towards identifying Berry-Phase Interference in the four-fold symmetric Ni$_4$ SMM.

1.4 Breakdown of Material

In Chapter 2, I will try to provide the theoretical groundwork of the concepts discussed in the Introduction. I will begin with a discussion of how we will use ESR to measure this behavior. I will then introduce Geometric Phase Interference in two-fold symmetric molecules, explaining the Garg’s results and how they would manifest in our experiment. I will then introduce and describe the four-fold symmetric Ni$_4$ SMM’s characteristics, extending Garg’s calculation to predict what should occur in our sample. Finally, I will discuss how applying a magnetic field and changing the orientation of the sample would induce oscillatory quenching behavior in molecules; this phenomenon manifests itself in energy level crossings for Ni$_4$. 

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In Chapter 3, I will go over the experimental setup of my probe, and the process involved in developing the hardware utilized to get the experiment running. I will also explain data-taking procedures and protocols, as well as sample mounting techniques.

In Chapter 4, I will go over the results of my experiment. I will provide the raw experimental data and illustrate the various steps in the analysis sequence. I will also provide some discussion of the final result with regards to the theoretical simulations covered in Chapter 2, pointing out sources of error and making some conclusive statements about our data.

In Chapter 5, I will provide a conclusion and remark on any further steps that may improve and expand upon our understanding of the results. I will also present other directions of research that may prove interesting.
Chapter 2

Theoretical Background

Berry-phase interference is a phenomenon that arises from the geometric properties of the Hamiltonian of a system. In single-molecule magnets, this effect can be seen in molecules that exhibit symmetry. Due to this symmetry, there exist pairs of spin tunneling paths that interfere with each other, with a phase difference that depends on the solid angle enclosed by the two paths. As the molecule increases its Berry phase, the tunneling oscillates between maximum tunneling to no tunneling at all. In two-fold symmetric molecules, there are two interfering paths; in four-fold symmetric molecules, there are four interfering paths.

In 1993, Garg showed analytically that Berry-phase interference could be found in two-fold symmetric spin systems. We will apply a generalization of that result to our four-fold symmetric Ni$_4$ SMM. We will first begin with a short discussion of ESR spectroscopy and how it can be applied to our SMM system. We will then move on to an explanation of Berry-phase interference,
beginning with two-fold symmetric molecules using Fe$_8$ as a model. Next, we further explore the background on Ni$_4$, developing the theory for Berry-phase interference in four-fold symmetric molecules and using EasySpin software to simulate our ESR experiment.

2.1 Electron-Spin Resonance

Before we even begin the theory behind Berry-phase interference, we need some robust method of experimentally determining whether it actually occurs. First discovered in 1944 by Yevgeny Zavoisky [22], Electron-Spin Resonance (ESR), also called Electron Paramagnetic Resonance, is invaluable for its easy implementation and straightforward results. We will begin with an analogy of a simple generic case of shining a beam of light at a sample of hydrogen gas.

Assume we bathe a sample of hydrogen gas in some light, each atom holding an electron with quantized energy levels. Because we know that only certain frequencies of photons can excite the gas from a low energy state to a higher energy state, the resonance condition is $\Delta E = hf$. Measuring the reflected power of the beam of light will provide a spectrum of absorption patterns, where frequencies of light that obey a resonance condition are absorbed, and are therefore missing (or less intense) than other frequencies of light.

Analogously, we will be bombarding our sample of Ni$_4$ molecules with electromagnetic radiation in the microwave region. Instead of flooding the sample with photons with a wide range of energies to produce a spectrum, however, we will use the electromagnetic radiation from a Loop-Gap Resonator (LGR,
more on this in Chapter III) to set a fixed resonance frequency. The way we produce a spectrum, then, is to take advantage of the Zeeman term by sweeping the magnetic field, producing a change in the energy levels of the molecular spins. When the energy difference between levels is on resonance with the frequency of photons being emitted by the resonator, there is net absorption of the photons by the Ni₄ molecules. In this way, we can produce an absorption power spectrum as a function of the field, with the dips in the spectrum correlating to the fields where the transitions occur.

![Figure 2.1: Level plot and spectra for the $|2⟩, |−2⟩$ avoided crossing. The red line indicates the energy of the rf field.](image)

Given a fixed microwave frequency from the LGR, we need to satisfy the
resonance condition:

$$\Delta E = hf$$  \hspace{1cm} (2.1)$$

where $f$ is the frequency of the driven rf field.

Fig. 2.1 shows the avoided crossing of two excited states, approximately $|2\rangle$ and $|-2\rangle$ away from the crossing for Ni$_{4}$, as a function of field in the upper plot and the corresponding predicted spectrum for $f=3.85$ GHz on the lower plot. It becomes evident that when the field tunes the energy difference between states to the energy of the rf field (shown on the energy level diagram as a red vertical line), the photons are absorbed by the Ni$_{4}$ crystal and result in a peak in the absorbed power spectrum.

A complete picture of performing ESR on a SMM can be given using the Hamiltonian given in 2.2:

$$\hat{H} = \hat{H}_{axial} + \hat{H}_{transverse} + \gamma \hat{H}_{0} \cdot \hat{S} + \gamma \hat{H}_{1} \cdot \hat{S}. \hspace{1cm} (2.2)$$

As in Eq. 1.12, the first axial anisotropy term defines the easy axis of the SMM, the next terms define the transverse anisotropy of the molecule, and the last two terms define the static and rf fields applied in ESR.

Solving for the eigenvalues of $\hat{H}$ in the basis of spin states $|m\rangle$ gives the energies and states of the system. Typically, transitions between states do not occur unless they obey a set of selection rules. These selection rules depend on the relation of the rf field to the quantization axis - whether it is perpendicular or parallel to the easy axis of the SMM. We will derive these selection rules for both cases. When the rf field is along the easy $z$-axis of the molecule, we
can take the matrix elements to be defined as:

$$\langle m'| S_z |m \rangle$$  \hspace{1cm} (2.3)  

$$m \langle m'|m \rangle$$  \hspace{1cm} (2.4)  

Since a matrix element only exists when $m' = m$, the resulting selection rule is that $\Delta m = 0$.

When the rf field is perpendicular to the easy axis, we can take the rf field to be in the hard plane of Ni$_4$. We can define the matrix elements to be

$$\langle m'| \hat{S}_x |m \rangle$$  \hspace{1cm} (2.5)  

We can substitute $\hat{S}_x$ with the raising and lowering operators, $\hat{S}_+$ and $\hat{S}_-$. 

$$\langle m'| (\hat{S}_+ + \hat{S}_-) |m \rangle / 2$$  \hspace{1cm} (2.6)  

After we distribute $|m\rangle$ among the operators, we get the result

$$\tilde{S}_+ \langle m'|m + 1 \rangle /2 + \tilde{S}_- \langle m'|m - 1 \rangle /2$$  \hspace{1cm} (2.7)  

where

$$\tilde{S}_+ = \sqrt{(s - m)(s + m + 1)}$$  \hspace{1cm} (2.8)  

$$\tilde{S}_- = \sqrt{(s + m)(s - m + 1)}$$  \hspace{1cm} (2.9)  

Since a matrix element only exists when $m' = m + 1$, or $m' = m - 1$, the selection rule is that $\Delta m = \pm 1$.  

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Returning to Fig. 1.4, we are interested in one transition – one that appears to involve a transition from $|\pm 2\rangle$ to $|\mp 2\rangle$. At first glance, these transitions do not follow the selection rule because $\Delta m$ is clearly not changing by 0 or $\pm 1$. These classically forbidden transitions become possible due to transverse anisotropy parameters in the Hamiltonian of Ni$_4$. These allow the $|2\rangle, |-2\rangle$ states to mix into superposition states: $\psi_{\pm} = \frac{1}{\sqrt{2}}(|2\rangle \pm |-2\rangle)$. These states are, to a good approximation, eigenstates of $\hat{H}$. We then evaluate the transition matrix elements between these states. In our experiment, the rf field is aligned with the easy axis, or the quantization axis. Since the rf field is a much stronger perturbation than the static field, we must show that transitions between the $\psi_{\pm}$ states have a nonzero matrix element.

\[
\langle \psi_+ | \hat{S}_z | \psi_- \rangle
\]

\[
\frac{1}{\sqrt{2}}(\langle 2 | + \langle -2 |) \frac{1}{\sqrt{2}}(\hat{S}_z | 2 \rangle - \hat{S}_z |-2 \rangle)
\]

After distributing the $S_z$ operator, factoring out a two, and distributing the bras through the kets, we get the result that

\[
\langle \psi_+ | \hat{S}_z | \psi_- \rangle = 2,
\]

showing that this transition is indeed allowed under this excitation. We can therefore be assured that our experiment, where we align the rf field along the easy axis of Ni$_4$, should induce the expected transitions between states.
2.2 EasySpin

EasySpin is a Matlab-based computation software package, containing extensive ESR functionality for simulating, fitting, and modeling ESR spectra [23]. As the primary computational package for spectral analysis of ESR simulations, it contains numerous functions – for pulsed ESR, SQUID magnetometry, slow motion ESR, least-squares fitting of data – but for our purposes the function we are looking for is solid state continuous wave (cw) ESR. There are two primary functions in EasySpin that we use to model the behavior of Ni$_4$. We can calculate both field-swept and frequency-swept cw ESR spectra for spin systems like Ni$_4$. And we can compute the cw resonance line positions (field values), widths, and amplitudes for either field-swept or frequency-swept spectra.

I will not go through the specifics of EasySpin programming, but I will provide a basic outline of how it works.

EasySpin takes in the molecule’s spin Hamiltonian, experimental parameters, and several options, outputting an array of magnetic fields and another vector with the calculated spectrum. The experimental parameters that must be passed into the function are the temperature, the microwave frequency of the resonator, the crystal orientation with respect to the lab frame, and the excitation mode of the experiment.

EasySpin defines the excitation modes as the orientation of the microwave field relative the external field; parallel mode means that the rf field is applied along the static field, and perpendicular mode means that the rf field is applied perpendicular to the static field. We will be using perpendicular mode in
our simulations and experiment. The orientation of the crystal within this framework is given by user-defined Euler Angles $\theta, \phi,$ and $\psi$. In addition to the experimental parameters, it is possible to manually determine the level pairs used in the spectrum e.g. to isolate the $|2\rangle, |-2\rangle$ spin states.

The most important piece of information that we obtain from EasySpin is the central field of each absorption line, which allows us to identify the field at which the microwaves will drive the tunneling transition. We also obtain the intensity of each spectral feature – the more intense, the more powerful the transition.

More information about EasySpin software can be found on the EasySpin website, at www.easyspin.org.

2.3 Berry-Phase in Two-Fold Symmetric SMM

This section will explain the basic theory behind Berry-phase interference, and discuss the important results of Garg’s calculation of the tunneling frequency using path integrals. For concreteness, the discussion will focus on the Fe$_8$ SMM.

Fe$_8$ is composed$^1$ of iron ions linked by $O^{2-}$ and $OH^-$ bridges. As seen in Fig. 2.2, its inner metallic structure is composed of 8 spin-$5/2$ Fe$^{3+}$ ions. With two spin-down ions, and six spin-up ions, the Giant Spin Approximation allows us to assign it a total spin of $S = 10$. This allows for $2S + 1 = 21$ states of the system, which is split into 10 doublet states and one singlet state (the

$^1$The full chemical name is $[(tacn)_6Fe_8(O_2)(OH)_{12}(H_2O)]$, where (tacn) is the organic ligand 1,4,7-triazacyclononane. This was first found to exhibit SMM-like behavior in 1995 [24].
Figure 2.2: The molecular model of a molecule of Fe₈. The brown balls represent Fe atoms, with arrows indicating their spins. Red circles are O, blue circles are N, and grey circles are C. H, Br, and ligands are not shown. Taken with permission from J.R. Friedman [3].

The highest energy state, \( m = 0 \). When the field is applied along the x axis (see below), its Hamiltonian can be represented as

\[
\hat{H} = k_1 \hat{J}_x^2 + k_2 \hat{J}_y^2 - g \mu_B \perp (\hat{J}_x \cos(\phi) + \hat{J}_y \sin(\phi)) + B_z \hat{J}_z
\]  

(2.13)

Remembering some terminology from Chapter I, the easy and hard axes are the axes along which the energy is the least and the most, respectively. In this case, they are set by the coefficients \( k_1 \) and \( k_2 \). Taking \( k_1 > k_2 > 0 \), the
first $\hat{J}_x$ term means that $x$ is the hard axis, the $\hat{J}_y$ term represents the medium axis of the molecule, and the lack of a $\hat{J}_z$ term means that the $z$-axis will be the easy axis. The third term represents the Zeeman effect caused by a field applied along the hard axis; this causes a modulation in the energy splitting as a function of the magnetic field. This will be expanded upon in Section 2.

Figure 2.3: The Energy Landscape of a two-fold symmetric SMM at 0 field. The saddle points indicate the quantum tunneling paths of least action. Obtained from J.R. Friedman.

Ground state tunneling takes place from $+z$ to $-z$. Taking a look at Fig. 2.3, an energy landscape representation of the Fe$_8$ Hamiltonian, it is clear that there is a two-fold reflection symmetry in the $xz$ plane.

As shown in Fig. 2.3, there are two equally energetically favorable paths that arise from this symmetry. Interference between these paths arises from Berry’s geometric phase. Garg solved for the “imaginary-time” path that the spin would take in going from $+z$ to $-z$. We can represent this path as the
trace along the energy landscape left by the spin vector $\vec{S}$ as it tunnels from $+z$ to $-z$. The least-action path carved out by $\vec{S}$ is along the two saddle points in the $\pm y$-direction. It becomes simple to visualize, then, that as you apply an increasing magnetic field along the hard axis, the energy landscape will gain more energy in the $-x$ direction while losing energy in the $+x$ direction due to the Zeeman term in the Hamiltonian. As this happens, the two symmetric saddle points - and therefore the shortest paths in the energy landscape - shift towards the $-x$-axis.

Garg showed that of all the “imaginary-time” (instanton) paths that the molecule could take to reverse its spin, the only paths that have a substantive weight to them were these two least-action paths along the saddle points [6]. He calculated the actions for these instanton paths, which have real and imaginary parts associated to them. While the real part of this action, $S_R$, is identical for both paths, the imaginary part $S_I$ is not. The tunnel-splitting can be shown to be the sum of all of these actions:

$$\Delta \propto \sum e^S.$$  \hspace{1cm} (2.14)

$$\Delta \propto e^{S_R+iS_I} + e^{S_R-iS_I}$$  \hspace{1cm} (2.15)

$$\Delta \propto e^{S_R \cos(S_I)}$$  \hspace{1cm} (2.16)

The result can be shown to be
\[ \Delta \propto e^{S_R \cos \left[ J\pi \left[ 1 - \frac{B}{B_c} \right] \right]} , \]  (2.17)

where \( S_R \) are the real and imaginary components of the action and the critical field \( B_c \) is defined as

\[ B_c = \frac{2k_1}{g\mu_b} \sqrt{1 - \frac{k_2}{k_1}} \]  (2.18)

It becomes clear that the tunneling is quenched whenever the argument of the cosine function is at odd multiples of \( \pi/2 \). With \( J = 10 \) for Fe\(_8\), there should exist 10 such quenches as the field is swept to its critical field \( B_c \). Because the argument of the cosine is linear with the static field strength, these quenches should be evenly spaced. When \( B > B_c \), the tunnel splitting increases monotonically with the strength of the field perturbation.

A more intuitive way to understand this formulation is to think of the relative phase of the two least-action paths as being proportional to the solid angle bounded by them. As the field causes these least-action paths to change, the solid angle decreases, causing the tunnel splitting to oscillate as defined by Eq. 2.17. This final result is that the tunnel splitting is quenched \( J \) times and oscillates as a function of the static field \( B \).

With this result in mind, we can try to predict the behavior of the spin paths as we change the orientation of the magnetic field with respect to the molecular axes. Let us begin by switching the field from being applied along the hard axis, or the x-direction, to the medium axis, or the y-direction. Referring back to Fig. 2.3, it becomes apparent that the path along the y-axis
becomes less energetically favorable while the path along the +y-axis becomes more energetically favorable. Therefore, the latter path will dominate over the former, and that one path becomes the preferred for tunneling. In this case, there is no interference between paths.

Geometrically speaking, if the field is turned an angle \( \phi \) away from the x-axis, a small component of the field will be along the y-direction. As \( \phi \) increases, the field component along the y-direction also increases. This causes one tunneling path to become preferred over the other, washing out the interference effect between the two paths. This was the result that Wernsdorfer and Sessoli experimentally obtained in 1999.

Let us now visualize the effect of applying a field along the z axis. This is a wholly different scenario than applying a field in the hard plane, as applying a z-oriented field will tilt the energy potential wells in relation to each other, causing one to be higher energy than the other. This means that the solid angle between the two paths no longer depends on the field strength - the paths can no longer be tuned by the field. Therefore, there is some interference between paths, but this interference does not depend on field strength.

We can extend this result to four-fold symmetric molecules. We will first delve into some information on the Ni\(_4\) SMM before exploring how Berry’s phase can be mapped out by studying this four-fold symmetric molecule.
2.4 Background on Ni$_4$

The Ni$_4$ SMM was found to be a molecular nanomagnet in 2002 [25]. It has a full chemical name of [Ni(hmp)(dmb)Cl]$_4$, where hmp is the anion of 2-hydroxymethylpyridine and dmb is 3,3-dimethyl-1-butanol [26]. The core is composed of four spin-1 Ni$^{2+}$ ions, which yield a Giant Spin Approximation of $S = 4$ at low temperature for the molecule. Therefore, the number of states that it can occupy is given by $2S + 1$, or a total of 9 spin states ranging from $m = -4$ to $+4$. The core is surrounded by the hmp and dmp hydrocarbon compounds, which minimize the intermolecular interactions in a sample. Its Hamiltonian is given by

$$\hat{H} = -D\hat{S}_z^2 - B\hat{S}_z^4 + C(\hat{S}_+^4 + \hat{S}_-^4) + g\mu_B\hat{B}_x,$$

and pictures of its molecular and crystal form are given in Fig. 2.4 and Fig. 2.5.

The first term, with coefficient $-D$, represents the axial anisotropy that biases the magnetization of the molecule in one of two ways, defining the easy axis of the sample. The two intermediate terms represent additional anisotropy terms that indicate other structural symmetries of the molecule; Ni$_4$ has a four-fold symmetry with two hard axes, the x and y axes. The last term is the Zeeman interaction term, which represents the effect of an external magnetic field applied along the hard axis direction, and breaks the four-fold symmetry.

The Ni$_4$ SMM is an ideal system for investigating several phenomena. It is

\footnote{The process for synthesizing these crystals is given in [27].}
Figure 2.4: The molecular model for the Ni$_4$ SMM. The colors of the balls indicate the following: green, chloride; cyan, nickel(II); black, carbon; red, oxygen; blue, nitrogen; Hydrogen atoms are not shown [25]. Adapted with permission from [28].

Figure 2.5: The macroscopic form of a 100% sample of Ni$_4$. Notice its four-fold symmetric square bipyramidal structure. Adapted with permission from [26]. Copyright 2008 American Chemical Society.
a model system for investigating the validity of the Giant Spin Approximation - how the GSA arises from the microscopic multispin Hamiltonian as well as its limitations [29]. It is also a system in which the tunneling rate is faster than the decoherence rate. Decoherence occurs when states lose their energy to their environment (i.e. modes of a lattice or nuclear spins in an SMM). Studying Ni$_4$ provides useful information on the upper bounds of the decoherence rate of high-spin states that are superimposed in a SMM [30].

Another phenomenon that occurs in Ni$_4$ is the observation of highly forbidden transitions between states that are enabled by tunneling. It has shown that the absorption of a single photon can permit a reversal in its macrospin, violating the $\Delta m = \pm 1$ selection rule; indeed, this is what we are doing in this experiment.

At low temperatures, Ni$_4$ transitions into two distinct ligand conformational states [17]. Each isomer has slightly different energies, resulting in double the features in the ESR spectra [26]. This difference in energies arises from slight variations in anisotropy parameters - for one state, $D_1 = 15.13(4)$ GHz, $B_1 = 0.136(2)$ GHz, and $C_1 = 0.0053(2)$ GHz while the other state parameters $D_2 = 15.55(4)$ GHz, $B_2 = 0.138(2)$ GHz, and $C_2 = 0.00645(3)$ GHz [28]. We shall refer to the former as State 1 and the latter as State 2.

There are two samples of Ni$_4$ that we have been working with - a pure, 100% sample of Ni$_4$ and a compound of 5% Ni$_4$ diluted with 95% Zn$_4$ that reduces the intermolecular dipole interactions within the sample by increasing the space between Ni$_4$ molecules. This manifests itself in the data as narrower,

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sharper peaks in the resonance spectra that make it possible to distinguish
the peaks of each conformational state[17]. In the 100% sample, the peaks are
much broader and it is nearly impossible to distinguish between the two states,
as they generally blend together into one large absorption peak. The process
for diluting the Ni$_4$ is provided in [17]. We obtain both of these samples from
Rafael A. Cassaro from the Institute of Chemistry, Universidade Federal do
Rio de Janeiro in Brazil.

Figure 2.6: The energy landscape for a four-fold symmetric SMM at 0 field.
Notice that there are now four saddle points. Obtained from J.R. Friedman.

We can extend the predictions for Berry-phase interference from the two-
fold symmetric molecule to four-fold symmetric molecules like Ni$_4$.$^4$ Fig. 2.6
shows an energy landscape for a four-fold symmetric molecule. Notice here
that there are four symmetric saddle points corresponding to four tunneling
paths of least energy. As we apply a field along one of the hard axes, one
symmetric pair of paths immediately become preferred over the other pair.

$^4$A full mathematical prediction of this behavior was presented in 2002 by Park and
Garg[31] and independently by Kim[32].
The interference, then, occurs as a function of the magnetic field as it changes the solid angle between the two paths. As we shift the field by some angle $\phi$ from a hard axis, the interference effect is lifted as one path becomes preferred over the other.

![Magnetic Field v. Energy at 0 Pressure](image)

Figure 2.7: Energy Level Diagram for the 2$^{nd}$ state of the Ni$_4$ SMM, calculated using the QuTip package in Python [33]. Notice the Zeeman splitting, as well as the crossing in the $|2\rangle$, $|-2\rangle$ transition.

It is possible to see the Berry-phase interference from a simple calculation of the energy of each state as a transverse field is applied to the Ni$_4$ SMM. Figure 2.7 shows an Energy Level diagram of the 2$^{nd}$ state of Ni$_4$, with the Zeeman term causing a splitting in the energy levels of the $|m\rangle$, $|-m\rangle$ pairs when the field is applied along a hard axis. The interference effect can be seen
Figure 2.8: Energy level diagram and tunnel splitting for the $m=\pm 2$ energy states in state 2 of Ni$_4$. Notice that the levels cross at 0.325 T.

Figure 2.9: Energy level diagram and tunnel splitting for the $m=\pm 3$ energy states in state 2 of Ni$_4$. Notice that the levels cross at 0 and 0.875 T.
most clearly in the $|2\rangle, |−2\rangle$ transition, where the yellow and purple curves are distinctly apart at 0 Tesla and meet at around 0.32 Tesla. At this point, we see that the avoided crossing has disappeared and that the tunnel splitting is now 0. The point where they meet is where complete destructive interference occurs and tunneling is quenched. Although not as visible for the $|3\rangle, |−3\rangle$ and $|4\rangle, |−4\rangle$ transitions, the energy level pairs also exhibit this oscillatory interference pattern until gradually reaching a point where the levels begin to diverge monotonically.

A somewhat clearer picture emerges when looking at the energy difference within a pair. Let the tunnel splitting be defined as $\Delta = E_{|\psi_+\rangle} - E_{|\psi_-\rangle}$. Fig. 2.8 and Fig. 2.9 explicitly show the oscillatory quenching effect of the tunnel splitting for the $m = \pm 2$ and $m = \pm 3$ energy states. We see that the tunnel splitting is quenched for different values of B field, and that these quenches correlate to the crossings between the pairs of states in the energy level diagram. The result is similar to the result produced by Wernsdorfer and Sessoli in Fig. 1.6. As the field increases in magnitude to 0.3 Tesla, the tunnel splitting decreases to $\Delta = 0$, signaling that the magnetization tunneling frequency between the $m = 2$ to $m = −2$ states has dropped to 0.

Fig. 2.10 shows a progression of how the quenched crossing becomes an avoided crossing as the $\phi$ angle is turned away from 0. Because of the destructive interference, there are two observable ESR transitions marked by the red lines in the upper subplot of Fig. 2.10 and the resonance spectra in the lower subplot. These two transitions serve to track the effect of changing $\phi$. As we turn the sample away from the hard axis and eliminate the destructive
Figure 2.10: This collection of plots shows the level crossings and resonance spectra for several values of $\phi$ at $\theta = 90^\circ$. At $\phi = 0^\circ$, there is complete destructive interference between paths and tunneling is quenched. As $\phi$ increases, the avoided crossing forms and the two transition peaks move closer together until they disappear.

Berry-phase interference, the two transitions begin to move closer, eventually blinking out of existence just after $\phi = 24^\circ$ in the figure. Because Ni$_4$ is four-fold symmetric, this interference effect is $90^\circ$ periodic.

Fig. 2.11 shows a more complete picture of how the transitions change as a function of $\phi$. With the transitions furthest split when the field is aligned at $\phi = 0^\circ$ along a hard axis, we see that these transitions eventually blink out of existence at around $\phi = 25^\circ$. This simulation depicts the Berry-phase interference effect in the Ni$_4$ SMM, and is precisely the behavior I aim to
Figure 2.11: These plots show how the resonance transition peaks behave as a function of $\phi$ for the $m = \pm 2$ states. It also shows the intensity of the transition - the larger the dot, the more intense the spectral resonance.

corroborate through my experiment.
Chapter 3

Experimental Design and Procedure

The theoretical predictions of Berry-phase Interference in Ni$_4$ have provided us with a seemingly straightforward method of experimentally gathering information to verify this phenomenon. This chapter will provide a detailed outline of the setup, procedures, and protocols implemented to gather experimental results. I will present two different probes built throughout the course of the year - the first when I was still hoping to use pressure to tune the Berry-phase, and the second when I decided to pursue the $\phi$ dependence of the Berry-phase more thoroughly. Because our experiment hinges on performing ESR spectroscopy to obtain data, we will begin with an introduction of the setup for a typical ESR measurement using a Loop-Gap Resonator (LGR). This setup involves a cryogenic apparatus, called the Physical Property Measurement System (PPMS).
3.1 Physical Property Measurement System

It is common to have an experimental setup that integrates ESR with a cryogenic system. For the goal of observing Berry-phase interference, such an apparatus is crucial. Transitions in the spin states of SMMs are only observable at sufficiently low temperature, because the thermal energy at room temperature would cause all of the spin states to be equally populated. Because the strength of an ESR signal depends on the population difference between these states, we would obtain weak (almost nonexistent) signals.

The cryostat that we utilize in our experiment is the Physical Property Measurement System\(^1\) by Quantum Design. This system essentially has two parts. One component is a probe consisting of detection equipment and electromagnet where the sample is placed inside, shown in Fig. 3.1. The other component is a nitrogen-jacketed dewar that houses the probe inside a bath of liquid helium. The layer of liquid nitrogen between the liquid helium bath and the superinsulation layer, shown in Fig. 3.2, significantly reduces the amount of helium consumed in maintaining the system.

The probe is composed of a superconducting electromagnet wrapped around the sample space. The magnet produces the static field necessary for our Berry-phase experiment. It can be set to persist at a certain field or to sweep across a range of fields, can generate a field of up to 9T, and can sweep the field at rates ranging from 10.8 Oe/sec to 199.9 Oe/sec. The probe also contains insulating chambers, heat shields, thermometers and pressure gauge, and other precision detectors. The PPMS controls the temperature by using the cold

\(^1\)All figures and specifications in this section come from the PPMS manual [34].
Figure 3.1: A detailed diagram of the features of the PPMS probe. The diagram was copied from the PPMS hardware manual with permission from Quantum Design [34].

Figure 3.2: A detailed diagram of the design of the PPMS dewar. The diagram was copied from the PPMS hardware manual with permission from Quantum Design [34].
helium vapor in the dewar to cool the space to as low as 4.2 K. From 4.2 down to 1.8 K, the PPMS lowers the boiling point of the liquid helium inside the cooling annulus by using an external pump. The total range of temperatures that can be set by the PPMS is 1.8K-400K.

Using the PPMS does constrain the experimental design of our probes. These physical constraints will play a role in selecting the kind of resonator we use as well as the physical design of the probe itself. However, its dual functionality of both temperature and field control makes it invaluable in creating the proper conditions for experimentation on SMMs, and so these constraints are rather minor when compared to the benefits of using the PPMS.

### 3.2 ESR

![Figure 3.3: A crude diagram of our ESR experimental design.](image)
We begin with the diagram in Fig. 3.3, which shows the overview for a typical ESR experiment. The electromagnets at the bottom of the figure can induce either a static or sweeping magnetic field in the positive z-direction. At the midpoint of the coils, where the field is the strongest and uniform, we place a resonator of some sort - in our experiment, we use an LGR inside a shield.

In order to gather data, we must have some frequency source to produce these microwaves. These microwaves are coupled to the cavity with an antenna that propagates the microwaves to the cavity, transferring power. At the resonant frequency of the LGR, the maximum power is transferred from the antenna to the cavity as the radiation is absorbed by the resonator and transformed into a radiative field, and the reflected power reaches a minimum. We call this minimum a resonance peak. As we measure this, we see in Fig. 3.4 that the power reflection as a function of frequency forms a Lorentzian curve that we can use to detect the $Q$-value, the minimum reflected power, the central frequency of the resonance, and other features.

To recap, we need a source to emit some frequency of electromagnetic radiation into the cavity and to measure the reflected power. In our experiment, we will use a vector network analyzer (VNA) to serve this dual purpose. This instrument generates electromagnetic waves over a controllable range of frequencies and measures the phase and magnitude of the reflected signal. It also is able to measure many different network parameters, such as the Voltage Standing Wave Ratio (VSWR), etc. Some useful features include allowing us to get an instant measure of the $Q$ by detecting the resonance peak center and
Figure 3.4: A resonance peak of a \(\sim 4.41\) GHz microwave resonator captured by the VNA. This can be fitted with a Lorentzian function to find \(Q\) and the resonance frequency.

setting a bandwidth, being able to save several configurations to the memory, and more. In our experiment, we use the KEYSIGHT E5063A vector analyzer, which can produce electromagnetic waves in the frequency range between 100 kHz and 18 GHz at powers ranging from \(-20\) dBm to 0 dBm [35].

In order to prevent microwaves from leaking away, it is imperative that the resonator is encased inside a metallic shield - usually one that will fit inside the PPMS. The use of an LGR and shield is critical in this experiment due to the relatively weak signals associated with ESR. The LGR stores electromag-
netic energy when microwaves form standing waves inside it at its resonant frequency. We use the LGR to concentrate the electromagnetic radiation applied to the sample, which is mounted inside the loop of the resonator. The LGR and shield are able to increase the sensitivity of the measurement by focusing the microwave power to a small, confined area.

3.3 Loop Gap Resonators

Resonators, for all the reasons outlined in the previous section, have been shown to be useful and relevant to experiments such as ours. The particular resonator that we will use is called the Loop-Gap Resonator (LGR), shown in Fig. 3.5. The LGR is a flat metallic disk with an inductive loop and capacitive gap, and has been shown to produce a large homogenous magnetic field inside the loop. This field is concentrated at the inducting loop, while much of the electric field is concentrated at the gap [36]. The shield itself is also an important part of the resonator. In general, the shield is metallic, and is usually rectangular or cylindrical in shape. Because its sole purpose is to confine the electromagnetic waves and prevent and radiation loss, it will be discussed later.

Loop-gap resonators also have many other advantages over other kinds of resonators. For my experiment, the first and foremost advantage of using an LGR was its size. Because one of the physical constraints of using the PPMS is that the resonator probe must fit inside the cylindrical hollow tube, it is imperative that our resonator be small. Furthermore, a good resonator
must be small compared to the length of the microwaves that it is being
bombarded with. One of the advantages of the LGR is that its size can be
on the order of tenths of inches - an extremely attractive feature especially in
low temperature ESR experiments like ours. In addition to the favorable size
of these resonators, LGRs have great design flexibility. Not only can they be
reshaped to fit into varying probe designs, they can quickly be redesigned and
machined to have different electromagnetic properties to shift the resonance
frequency by changing the loop size and the gap width. Or it can be made
to have a stronger magnetic field at the loop without changing the resonance
frequency. The possibilities are endless, and because of their relative ease to
machine, the turnaround time on designing and producing one of these LGRs
are on the order of mere hours. The following subsection will describe the
general theory for describing the behavior of an LGR.

### 3.3.1 LGR Properties

Before getting to the specific design of my resonator, it is important to under-
stand how its physical properties translate to its electromagnetic properties.
These design parameters are given in Fig. 3.5. Much of the information in
this section was obtained from Chapter 2 of [36], which contains the published
design equations for an LGR. We begin with the resonant frequency of the
resonator, which depends on the inductance and capacitance of the resonator
as follows:

$$ \omega_0 = \frac{1}{2\pi\sqrt{LC}} $$

(3.1)
Figure 3.5: General template design for our resonator. The two unlabeled holes are for screws that will secure the LGR into a plate or wall.

where $\omega_0$ is the resonant frequency, $L$ is the inductance, and $C$ is the capacitance. $L$ and $C$ depend respectively on the loop and the gap of the LGR. An estimation for $L$ and $C$ can be found from the following physical parameters:

$$L = \frac{\mu_0 \pi r^2}{Z + 0.9r} \quad (3.2)$$

$$C = \frac{\epsilon W Z}{D} \quad (3.3)$$

where $\mu_0$ is the permeability of free space, $r$ is the radius of the loop, $Z$ is the thickness of the resonator, $\epsilon$ is the permittivity of free space, $W$ is the width
of the gap, and $D$ is the gap separation.

The next important electromagnetic property is the $Q$. The $Q$ is a measure of the energy lost in the system. The higher it is, the less microwave radiation is lost. The $Q$ can be found with the following equation:

$$Q = \frac{\pi \omega_0 L}{R}$$

(3.4)

where $R$ is the resistance. $R$ depends on the skin effect, which is the tendency of an AC current to distribute most of its current density near the surface of the conductor. This means that the effective cross-sectional area decreases at high frequencies, resulting in an increased resistance of the conductor. $R$ can be described as:

$$R = 2 \left( \frac{\pi r + W/3}{Z} \right) \sqrt{\frac{\mu_0 \pi \omega_0}{\sigma}}$$

(3.5)

where $\sigma$ is the conductivity of the metallic resonator.

In addition to the LGR, the shield is an essential part of the resonator as well. Because we worked with two different probes throughout the course of this thesis, we used two different shields. We will go into detail into the two designs later in this chapter; for now, the important thing to know is that the geometry and the dimensions of the shields are largely set by physical restraints of the PPMS. As a result, our shields have a cylindrical shape to fit inside the sample space of the PPMS. They also have a small ventilation hole that allows the pressure inside the shield to equalize with the outside environment - otherwise, the inside of the probe may retain some air after
the purging process which could condense as the system is cooled, lowering the $Q$. It is important that the hole be small so as to not allow the relevant wavelengths to be radiated out of the probe. Generally, we set the diameter of the hole to be much smaller than the appropriate wavelength of the microwave radiation.

An essential part of designing a shield involves considering a way of supporting and coupling the resonator to the rest of the system - ultimately, to obtain a signal that can be read on the VNA. Both of our probe designs involve a cap that either threads directly into the shield body or uses screws to securely hold the resonator in place inside the shield. For both designs, an antenna sticks out into the shield body as a means of capacitively coupling the resonator to the microwave radiation.

To create the antenna, we use a semi-rigid coaxial cable with the outer conductor and insulator machined off at one end. We position the antenna so that it is parallel to the electric field inside the gap. The antenna then works to radiate microwaves that are coupled to the gap of the resonator. In general, the closer the antenna is to the gap, the better coupled the system will be and the lower the $Q$.

In practice, it is often difficult to position the antenna in such a way to attain critical coupling. Because the antenna is flexible, some adjustments can be made by bending the antenna closer to the gap or through other means. Much of the coupling process is trial and error; it involves adjusting the antenna relative to the LGR by a tiny amount, hooking it up to the VNA, and checking the reflective spectra to see if the coupling is improved. The goal is to
at least get a reflective resonance dip that is visible throughout the background reflection. Because the resistance of the LGR does depend on temperature (the skin effect causes the resistance to increase at low temperature), the coupling does tend to improve at low temperatures if the resonator is undercoupled to the antenna at room temperature.

### 3.3.2 LGR Design

Referring back to Fig. 3.5, the design parameters for our resonator are:

\[ W=0.422 \text{ in.}, \quad R=0.030 \text{ in.}, \quad D=0.020 \text{ in.}, \quad \text{and} \quad Z=0.020 \text{ in.} \]

Unfortunately, the LGR design equations are not as accurate as one might expect. In obtaining these relationships, some mathematical approximations were made and certain effects were not taken into account (such as the effect of the shield, other objects like screws and washers in the resonator probe, etc.). As a result, while the equations do generally describe the relative electromagnetic behavior based on the LGR’s physical properties, they are very limited in providing an exact prediction for every resonator design.

In order to more accurately model the behavior of a resonator, it is desirable to use simulation software to model and estimate \( \omega_0 \) and \( Q \). The software we use in the laboratory is called the High Frequency Structural Simulator (HFSS). Given a 3-dimensional model of the shield, LGR, and other macroscopic objects in the resonator probe, it can solve Maxwell’s equations with the given boundary conditions to arrive at a virtual reflection measurement for the resonator. HFSS was used as a preliminary check in designing my LGR.
before sending my design to be produced in the CNC machine in the machine shop.

Once the LGR is machined successfully, it must go through a polishing step to minimize the scratches on the resonator. This is done by slowly but firmly running both sides of the LGR on extremely fine sandpaper in a direction along the length of the gap. The $Q$ and the resonance frequency can be tested immediately once the LGR is machined and polished. There are likely to be several issues - not seeing a resonance peak at all, not finding the correct resonance peak, having a sub-par $Q$. It is also useful to know how to manipulate the resonance frequency using a piece of sapphire. The following section will elaborate on this stage of production and troubleshooting.

### 3.3.3 Resonator Testing and Troubleshooting

After obtaining a polished LGR and assembling it with the rest of the probe, we want to experimentally test its resonance frequency and $Q$ through a reflection experiment. We use the VNA to measure the power reflected by the resonator. The reflected power should become a minimum at the resonant frequency, where much of the radiated microwaves are absorbed by the resonator. This should form a Lorentzian dip in the signal on the VNA. We can locate the resonance peak by sweeping through the GHz frequency range until we see such a dip. Once we do, we must test to make sure that the observed resonance is really due to our resonator and not some spurious parasitic reflection. We can do this by placing a piece of absorbent foam to the loop or gap of the resonator to see if it eliminates the resonance dip. We can also insert a piece of dielectric
in the gap of the LGR to shift the resonance frequency of the observed peak. This shift occurs because placing the dielectric between the two capacitive plates increases the capacitance $C$ of the capacitor. According to Eq. 3.1, increasing $C$ will have the effect of decreasing the resonance frequency. For our purposes, we use slivers of sapphire as our dielectric material. If the peak indeed shifts down to a lower frequency, then we have found the resonance peak and can begin using it for experimentation. The sapphire can be used to control the resonance frequency of the resonator to a certain extent, allowing some flexibility in its usage.

Once we have found the resonant frequency of our resonator, we can measure the $Q$ by using cursors on the VNA to find the peak minimum and setting a bandwidth around the peak to automatically calculate the FWHM (Full Wave at Half Maximum) of the peak. In spectroscopy, the HWHM (Half Wave at Half Maximum, henceforth called $\gamma$) is more commonly in use. By definition,

$$FWHM = 2\gamma$$  \hspace{1cm} (3.6)

For more formal, rigorous methods of calculating $Q$, we can fit the data to a Lorentzian function of the following form:

$$P = \frac{(\gamma)^2}{(\omega - \omega_0)^2 + (\gamma)^2}$$  \hspace{1cm} (3.7)

The biggest problem that may arise is if the resonance peak is not visible at all. If this is the case, there is likely a coupling issue. It is usually the case that the LGR is undercoupled to the antenna, and so needs to be adjusted to
be closer. This is done multiple ways - by using washers between the LGR and its holder to move it closer to the antenna, by bending the antenna to be closer to the gap of the LGR, by moving the antenna to a different location of the gap, etc. This coupling process is a rinse-and-repeat process until the resonance peak is found, which can then be tested using the method described previously.

### 3.4 Angle Control

A sample probe holder must be used to hold the sample in place inside the PPMS. It must be able to fit into the ∼1-inch diameter cylindrical cavity inside the cryostat, with a length of ∼40 inches to reach the uniform magnetic field produced by the electromagnetic coils. Specific designs vary depending on the purpose of the experiment - throughout my thesis, I have had to use two different probe holders. As mentioned previously, I had originally begun my thesis with the intent to examine the effect of pressure on the Berry-phase of Ni$_4$. It was only after going through some interesting simulations that I decided to turn my investigation towards something else: The effect of sweeping a transverse field across the hard plane of Ni$_4$, or investigating the effect of $\phi$ on the interference.

As a result, my initial probe prototype was built using a probe designed to be used in a pressure experiment. After spending an exhaustive amount of effort only to gather sub-par data, we decided to focus on building a whole new, in-situ rotator probe. This involved switching to another apparatus,
which granted us much more design freedom than using the pressure probe. This section will provide details on both the prototype Phi probe and the final in-situ rotator probe.

### 3.4.1 Initial Phi Probe Design

![Figure 3.6](image1.png)

Figure 3.6: A birds-eye view of the prototype phi probe holder. The VNA connects via the SMA port towards the left, and the resonator and shield are on the right.

![Figure 3.7](image2.png)

Figure 3.7: A dissassembled view of the shield and resonator. The antenna is bent to align with the electric field of the gap.
Fig. 3.6 shows the probe for my first design. It is made of a stainless steel shield welded onto a thick tubular rod that runs up the length of the PPMS sample space. The T tube clamps onto the top of the sample space, sealing it from the outside environment. The VNA sends a signal down the coax cable, which connects to the resonator antenna via an SMA connector. A groove along the metal washers and the shield have been machined to house the cable, allowing the probe to fit within the diameter of the cylindrical PPMS sample space.

In the close-up picture of the resonator shown in Fig. 3.7, there are several important features. The first is the white 3D printed LGR holder made with ABS plastic. It houses our LGR, attached via nylon 0-80 screws, and is held onto the shield cap with heavy-duty double-sided tape. The antenna fits through a hole on the bottom of the LGR holder. This entire system is then slotted into the shield and threaded into place. One small feature that is not shown is a small hole, ∼1mm in diameter, that was drilled into the shield cap to allow air pressure to equalize between the resonant chamber and the outer cavity.

Fig. 3.8a shows the rotation design of this initial prototype probe. The LGR holder has a cylindrical hole drilled into the back to allow for a rotator puck to be inserted. This puck serves the dual purpose of holding the sample and serving as a manual rotation device to induce the $\phi$ rotations. Once we have a crystal mounted onto the puck, we use a razor to score a groove through the center of the cylindrical bottom of the puck, assigning an arbitrary $\phi = 0$ baseline. We also have scored a vertical reference line (marked with blue
Figure 3.8: (a) shows the crystal mount and rotator. This fits into the back of the plastic LGR holder, as shown in (b). This allows us to manually turn and keep track of the $\phi$ angle.

marker) on the back of the plastic LGR holder. We can then measure the relative angle of the notch on the rotator puck to the reference line on the LGR holder to find the $\phi$ angle. This allows us to manipulate $\phi$ by hand. Fig. 3.8b shows the sample at $\phi = 31^\circ$.

3.4.2 In-Situ Control

The main flaws were related to the fact that because we had to disturb the probe every time we wanted to change the $\phi$ orientation of the crystal, there was significant chance for error. Every time we took the probe out of the cryostat and took it apart to rotate the puck, there was a chance that we had
changed the orientation (or something else!) without accounting for such a perturbation. Because the system wasn’t necessarily fixed from data set to data set, it was extremely unlikely that the only independent variable was $\phi$, making the entire experiment flawed. If we could just keep the Phi probe in an isolated environment as we rotated the crystal, we would not have to worry about any of these unknown perturbations of the system because the ONLY change to the system would be due to the rotator.

After the anticlimactic result from the initial Phi probe design, we decided that we should endeavor to create an in-situ design for the $\phi$ orientation of the sample. This would fix the aforementioned experimental flaws, as well as speeding up the troubleshooting and data-taking process by more than an order of magnitude. The cooling and warm-up process of the cryostat takes time, and the fact that we would not have to go through that procedure for EVERY rotation means that we would be able to take data for anywhere from 4-10 $\phi$ orientations in the time it took to take data for just one $\phi$ measurement with thePhi probe. It also provided us the opportunity to automate the entire process, meaning that we could run the data-taking program overnight. The benefits we would reap from designing such a mechanism were immense.

This section provides the production details for the In-Situ Phi Probe, including the automation scheme for the rotator.

**In-Situ Phi Probe Design**

Fig. 3.9 shows a picture of the home-built probe designed by former student Spencer Adams and modified by various students and post-doctoral researchers
through the years. We begin with the top of the probe holder comprised of two T-tubes that fully seal onto the sample space of the PPMS. At the very top of the holder is a sealed cap that has a hermetic SMA adapter that allows the microwaves to be passed to and from the system. A long, semi-rigid coaxial cable then connects the top of the probe to the bottom of the probe, where the cable attaches via SMA to the antenna in the resonator shield cap.

The probe holder also has two rods made of G10 epoxy that also can be attached to the shield cap. These are held in place by white spacers that
help keep the cable and rods in place and also enhance cooling efficiency by preventing thermal convection. One of the rods attaches to the shield cap to keep the resonator steady at the bottom of the probe, while the other, longer one is used as part of the rotating mechanism. From here on, I will distinguish between the latter from the former by referring to it as G10’. Because this rod spans the length of the holder and even goes through the top cap of the probe holder, it is perfect for functioning as a way to manipulate the orientation of the sample in-situ.

Figure 3.11: A Solidworks assembly of the parts designed to fit inside the shield. The gear has a central rod that sticks into the loop of the LGR, which is where the sample is placed. The worm gear allows for manipulation of the sample by mating to the gear.

Fig. 3.11 shows the 3D printed design for the rotator mechanism. Inside is a base plate that can be screwed into the base of the shield. We use two nylon 0-80 screws to accomplish this. Because we are aiming to perform perpendicular-mode ESR, the LGR is mounted on the side of the vertical wall using two more 0-80 nylon screws. On the other side of the vertical wall is the two-in-one
gear+mount, a support structure for the gear, and a space for a worm gear to slot into. The gear+mount serves the important functional purpose of being the rotating mechanism for the sample that is mounted onto it. The gear has a protruding cylindrical rod that slots through the wall into the loop of the LGR. The end of the rod (which is inside the LGR loop) has a small hole where the sample is to be mounted. This gear mount serves as the rotating mechanism when coupled with the worm gear.

The worm gear couples to the gear with a ratio of 1:40 (40 turns of the worm gear to one complete rotation of the gear), and has threads that allow it to attach to G10'. This means that for every 10 turns of the gear worm, the crystal rotates by 90°. We can thus rotate the worm gear and therefore the gear by turning the G10' rod sticking up from the top of the probe holder. Because we are using threads to keep the rod and the worm gear attached, it must be rotated in the clockwise direction - one drawback is that it cannot be rotated counterclockwise, else the rod and worm gear may uncouple. Of course, a way around this potential drawback is to apply some grease on the threads, which should act as a glue at low temperature.

When attached directly to the G10' rod, we discovered a design flaw. Because the threaded end of G10' was tapered, as the rod was rotated it kept trying to thread deeper into the soft plastic of the worm gear. After several turns, the worm gear split and rendered the rotating mechanism useless. To solve this problem, I designed the adapter shown in Fig. 3.12, which threaded into the worm gear with a straight thread and also provided a female receptor for the G10' rod to thread into. Because the adapter was made of brass, it
Figure 3.12: A Solidworks design of a brass adapter used to fix some problems with the connection between the G10 rod and the worm gear. The bottom threads are straight and bottom out on the worm gear, and the bronze material prevents the piece from splitting due to torque from the G10 rod.

Figure 3.13: (a) shows the design for the shield body, made of copper. (b) shows the design for the shield cap, made of brass. Both figures were designed in Solidworks.
Figure 3.14: An assembly of the shield, shield cap, LGR, and 3D printed rotation device. Front view.

Figure 3.15: An assembly of the shield, shield cap, LGR, and 3D printed rotation device. Rear View.
would have no issues of splitting.

Fig. 3.13 illustrates the final design for the shield body and top for the resonator. The diameter of both is a little more than an inch, about the size of the sample space in the PPMS. The shield body is made of copper, while the shield top is made of brass, and are held together by four 0-80 copper screws. The shield cover has three main features. The first is an antenna that has been soldered to the top, which connects to the rest of the electronics via an SMA connector. This antenna comes down on the LGR side of the vertical base plate to couple with the gap of the LGR. The second feature is a hole that allows the worm gear to attach to the G10’ rod. The third feature is another threaded hole for the other G10 rod to thread into - this is solely to help stabilize the probe.

When the individual pieces are all put together properly, we have the assembled product shown in Fig. 3.14 and Fig. 3.15. When we tested this probe,
we found that it worked spectacularly, making this entire endeavor well worth the time and effort.

**Rotator Automation**

In the previous section, the possibility of automating the in-situ rotation device was mentioned as a possibility for speeding up the data-taking process. By setting up a motor that would perform that task, I was able to improve and streamline the entire experimental process. Instead of having to monitor the apparatus to turn the rotator G10’ rod every 30 minutes, it became feasible to just set the program running and work on modeling data and other tasks, or to have the program run overnight so I could return in the morning to loads of data. The following provides a brief guide on how I implemented the automation scheme.

Stepper motors are common in everyday machines - printers, scanners, computer and 3D printers, CD drives, for precision positioning equipment in optics experiments, and more. They are simple, rugged, low-cost electromagnetic devices that convert DC currents into mechanical rotation. They are generally composed of four electromagnetic coils arranged like the Cardinal directions on a compass. These are organized into “phase” groups that, when charged in sequence, causes the motor to rotate in steps. Motors are grouped into “unipolar” or “bipolar” motors. Unipolar drivers can only energize two opposite poles at once, while bipolar drivers can energize both pairs of electromagnets with alternating polarity, increasing the torque of the motor. A Data-Acquisition Device or an arduino can be used to allow a computer to
communicate with the motor. For our automation design, we use the four-step PM55L-048-HP69 stepper motor produced by NMB. While this can be configured in both unipolar and bipolar modes, we use the unipolar mode for ease of set-up (and because we do not need the extra torque).

Figure 3.17: The circuit diagram for the stepper motor. We use a (POWER SOURCE NAME?) as a power supply and the NI-USB-6008 to control the rotator from the computer using LabView.

A simple circuit using a breadboard, power source, and transistors was used to power the motor. We used the National Instruments USB-6008 data acquisition device to communicate with the computer. Because the current output
from the USB-6008 was very low (on the order of .05 amps), transistors were necessary to produce enough current to power the electromagnets. Fig. 3.17 shows the circuit diagram for the motor, showing the circuit connections for each electromagnetic coil.

Figure 3.18: A side-profile picture of the mechanical setup of the motor. The motor is fixed by a gripper clamp, which is held up by a framework of clamps and rods attached to the PPMS setup.

After getting the stepper motor to work, I set up a mechanical framework using some preexisting clamps and rods to position the motor above the probe holder. Fig. 3.18 shows a photo of this setup. Jim designed a simple coupling
device to allow the motor to couple directly onto the G10’ rod of the probe. I then created a LabView VI in which I could set the number of turns as well as the turn interval. At the end of each data run, it would rotate the sample by a set amount until it reached the upper limit that I had set for the number of turns. This integration with the software marked the success of our goal of completely automating our data-taking process.

3.5 Euler Angles and Sample Mounting

![Euler Rotations](image)

Figure 3.19: A figure illustrating the Euler Rotations. Adapted from original creation by Lionel Brits in Wikipedia under Creative Commons License.
In order to run the experiment properly, we must first define some physical orientation parameters regarding the lab frame and the crystal frame orientations. We can use Euler Angles to define the orientation of the crystal frame relative to the lab frame.

Let the xyz coordinate system in Fig. 3.19 represent the lab frame, with the static magnetic field applied along the +z direction. The Euler angles describe three consecutive rotations of this xyz system that align it to an arbitrary ABC coordinate frame - in our case, the crystal frame. The rotations work as such:

1. Rotate xyz counterclockwise around the z axis by $\psi$.
2. Rotate counterclockwise around the N axis by $\theta$.
3. Rotate counterclockwise around the Z axis by $\phi$ to get XYZ.

![Figure 3.20: Ideal orientation of the sample, where $\psi = 0^\circ$, $\theta = 90^\circ$, and $\phi$ is our rotation angle.](image_url)
In an ideal situation, we aim to mount our sample of Ni₄ in this orientation, where $\psi = 0^\circ$, $\theta = 90^\circ$, and $\phi$ is our rotation angle. In this orientation, the easy axis of the sample would point in the direction of the x-axis as shown in Fig. 3.20 and so changing $\phi$ would give us our desired perturbation.

### 3.5.1 Sample Mounting

We aim to orient the sample of 100% Ni₄ as described in the previous section. Fig. 3.21 shows a picture of a crystalline sample of Ni₄, and its easy axis indicated by the thin black line. As we’ve stated before, the goal is to align this easy axis along the x-axis of the laboratory frame, as shown in Fig. 3.20.

![Figure 3.21: A 100% sample of Ni₄, with the easy axis indicated by the black arrow.](image)

In practice, we do this by first picking out a crystal with a length of around 1 mm that has a visibly nice, bipyramidal structure. While the resonator is fastened to the 3D-printed piece, we apply some grease to the gear crystal holder and use a needle to gently place the crystal inside it. We then connect the printed piece to the shield with the 0-80 nylon screws. In order to
make finer adjustments to the crystal, we look at this configuration under a microscope, as shown in Fig. 3.22.

It is extremely difficult to set the easy axis of the crystal to $\theta = 90^\circ$, or exactly perpendicular to the resonator. It helps to take pictures similar to what is shown in Fig. 3.20 and use computer software to find the angle between the easy axis of the sample and the resonator. However, because the view under microscope only presents a 2-dimensional image, it is difficult to have $\theta = 90^\circ$ for all angles of $\phi$.

The way I tried to align the crystal was to look at one orientation and use
the needle to lightly adjust the crystal towards $\theta = 90^\circ$. Then I rotated the crystal $90^\circ$ in $\phi$, lightly adjusting the crystal again towards $\theta = 90^\circ$. I then rotated it back to its original orientation to check if the crystal had shifted off $\theta = 90^\circ$. I continued this until I felt that the crystal was reasonable aligned in the two orthogonal viewpoints, and then assembled the probe for data-taking.$^2$

### 3.5.2 Misalignment

Unfortunately, in practice, it is extremely difficult to align the sample in such a way as to get the easy axis aligned precisely along the x-axis. As such, it is incredibly likely that any kind of data we take will have some sort of misalignment error as shown in Fig. 3.23.

![Figure 3.23: The easy axis is supposed to align directly along the x-axis, but it is off by some misalignment angle $\psi$. As a result, we are not rotating $\phi$ as we turn the rotator probe, but some other orientation parameter $\xi$.](image)

$^2$The data taking procedure is outlined in Appendix A.
In order to account for this problem, we can adjust our Euler Angles by introducing a new angle, $\xi$, to represent the rotation that we were performing experimentally. The $\psi$ angle would then account for the misalignment angle. In this scenario, as we experimentally rotate $\xi$, we would change both $\theta$ and $\phi$. Notice that if $\psi = 0^\circ$, then $\xi = \phi$ and we have the ideal case we presented at the beginning of this section, where the easy axis is aligned perfectly along the x-axis. Since there are three degrees of freedom in the motion of the crystal, we model the behavior of our experimental rotation with $\psi$, $\phi$, and $\xi$, setting $\theta$ to initially be exactly $90^\circ$. In the results, we use this correction to represent our rotation in terms of $\xi$, not $\phi$. 
Chapter 4

Results and Interpretation

This chapter will present the results of performing perpendicular-mode ESR on the Ni$_4$ SMM using the in-situ rotator probe. We will assume that we were unable to attain perfect crystal alignment with the x-axis, and so we utilize the correction we made at the end of Chapter III by assigning our rotation angle as $\xi$. Therefore, all of our data will be as a function of $\xi$, not as a function of $\phi$. If the crystal is properly aligned, then $\xi$ should be the same as $\phi$ and we should solely see four-fold symmetric behavior.

4.1 Results

Fig. 3.4 is the primary source of data that we obtain from the apparatus. It is a measure of the reflected radiation from the resonator as detected by the VNA. From this peak, we can find the resonant frequency of the resonator and characterize it by measuring its quality factor $Q$, the power reflected at the central frequency $f_c$, and the minimum $P_{\min}$. This resonance peak is sensitive
to driven transitions on the mounted sample - as the field approaches the appropriate magnitude determined by Eq. 2.1, photons are absorbed by the molecule and transitions between states are driven. This net absorption of photons acts as a load to the LGR. This causes the $Q$ to drop. The $P_{\text{min}}$ is another measure of how we measure the reflected power. If we imagine the LGR as a load on the coax cable, if the two are critically coupled then all of the emitted power from the coax antenna will be absorbed by the LGR, meaning none is reflected - the resonance peak will be at its deepest. If the impedances are imperfectly matched and the load increase due to the magnetic spins of the SMM causes this impedance to go further away from critical coupling, then the reflected power increases. If the load causes the impedance to go towards critical coupling, then the reflected power decreases.

We want to see how this signal changes as we sweep the magnetic field, which should change as microwaves are absorbed and transitions are driven in the sample. We can characterize these changes in the Lorentzian by seeing how the field changes the $Q$, $P_{\text{min}}$, and $f_c$. In order for us to do this uniformly and conveniently for each raw set of data, we use a curve fitting program that fits a Lorentzian curve to the signal and outputs these parameters.

Of the three parameters, the $Q$ is the most easily interpreted because unlike the $P_{\text{min}}$, it doesn’t depend on the coupling, and unlike $f_c$, the exact transition field can be read more easily from the $Q$ minima rather than at an inflection point. Once we have $Q$, we can plot it against the entire range of the field, giving us the plot like the one in Fig. 4.1. This graph shows the $Q$ v. $B$ plot at 5 turns of the rotator, which roughly correlates to a 45° $\xi$ rotation of the
Figure 4.1: Q v. B graph taken at T=2 K with an LGR with a resonance frequency of 3.78 GHz. This was the basic measurement we took as a result of fitting the Reflected Power v. f data from the VNA as we swept the field.

Figure 4.2: EasySpin simulation modeling the Hamiltonian in Eq. 2.19 in the 2nd conformational state of Ni$_4$. Notice the two small peaks at $\sim 200$ mT and $\sim 360$ mT, and the large peak at 960 mT. Compare to the features in Fig. 4.1 located in the same field locations (1 mT=10 Oe). The largest dip at $\sim 2300$ mT is not shown because its intensity dwarfs out the other three peaks in this figure.
sample. The dips in $Q$ indicate when the transitions are being driven in the crystalline sample of Ni$_4$.

Fig. 4.2 contains a level plot diagram in the upper subplot indicating the fields at which transitions should occur (the vertical green lines) and the associated simulated spectral features in the lower subplot. We can therefore directly compare our results in Fig. 4.1 to the simulation in 4.2 to see whether the dips in the $Q$ are located at the same field as the peaks in the power density spectrum. As we can see, the data in Fig. 4.1 seems to match up to the simulation of the sample oriented at $\theta = 90^\circ$ and $\phi = 20^\circ$.\footnote{In this comparison, we see that the peak near 0 field does not appear in the simulation. We can use this information, along with the observation that this feature does not change as we rotate the sample, to reason that it is merely an artifact and not a meaningful signal from the sample.}

As we changed the $\xi$ angle by rotating the probe in increments of either .5 or 1 Turn, we saw the dips in the $Q$ v. B plots shifting in field. Fig. 4.3 illustrates how the central peak fields move as a function of $\xi$. The plot on the left shows the larger shifts of the higher field transitions. It also indicates the first inkling of some alignment error - notice how the rightmost peak increases in magnitude as we increase $\xi$. This shows that the field is inducing stronger transitions in the Ni$_4$ crystal. Optimally, at $\theta = 90^\circ$, this should not be occurring - more on this issue in the next section.

\footnote{This comparison is not completely correct, as the prediction was for a rotation in $\phi$, not $\xi$, but the main point of this illustration is to show that our data can be modeled well by these simulations.}

\footnote{The degrees $\rightarrow$ changxi/Turn ratio is $9^\circ$/Turn, which is given by the gear ratio of our rotator design.}
Figure 4.3: Several sequential experimental spectra at a resonance frequency of 3.78 GHz plotted to show the progression of data as we change $\xi$. Data is labeled in terms of the number of turns (roughly $9^\circ \xi$/Turn.) Dots indicate the peaks positions. Spectra have been inverted and manipulated for spacing - the y-axis does not necessarily correspond to the actual $Q$ values of the data.

The zoomed-in figure on the right shows the lower-field $m = \pm 2$ transitions that we are specifically interested in. The dots represent the maximum of each transition peak. Notice that these dots seem to follow an interesting shift in field. After seeing this pattern emerge, we took data for 41 turns of the rotator probe, enough to complete a full $360^\circ$ cycle of $\xi$. As a quick aside, this process follows our data-taking and analysis procedure for $T=2$ K. We followed the same steps in order obtain data for the same sample at $T=10$ K.

Fig. 4.4 illustrates a full field sweep taken from -12k Oe to 12k Oe. Notice that the data is not symmetric about 0 field as it should be, but rather shifted by a slight amount to the right. These offsets occur because of the inductive “lag” in the swept field due to Lenz’s Law. In order to correct this issue, I reflected the negative field points so that they were overlaid on top of the positive field points and shifted them by some constant offset field $\epsilon$ until
Figure 4.4: A field sweep from -12000 Oe to 12000 Oe at T=2 K. The plot should be symmetric about $B = 0$, and we can use this fact to find the field offset.

The absorption peaks were exactly symmetrical about $B = 0$, and the peak features lined up. In this way, I found $\epsilon = 204 \pm 16$ Oe for the 10 K data and $\epsilon = 186 \pm 32$ Oe for the 2 K data. We can subtract off these values from the appropriate data sets to obtain data free from this systematic error.

We plot the central fields of each experimentally obtained reflection peak in the spectroscopic spectra as a function of $\xi$ at 2 K and 10 K respectively in Fig. 4.5 and Fig. 4.6.

Note that there are some missing points on the graph, or that several points seem randomly disordered. Because some of the data sets that we took for each angle of $\xi$ did not have clear minimum peaks, it was difficult to obtain an accurate central field measurement for them, so I either omitted them or
Figure 4.5: Final results for our experiment for Ni$_4$ at T=2 K. Notice the behavior of the $m = \pm 2$ avoided crossing at low field.
Figure 4.6: Final results for our experiment for Ni$_4$ at T=10 K. Similar behavior to the T=2 K data is found, except the $|4\rangle,|-4\rangle$ transitions at high field doesn’t have the odd 180° periodic dips in the central B field.
measured them to the best of my ability. Furthermore, the two data sets at T=2 K and T=10 K did not start at the same angle of ξ so they will differ by some phase shift.

Let us begin with features that are common to both the T=2 K and T=10 K graphs. The first important feature is that all of the data oscillates with a period of around 90° in ξ. Second, the low field data shows the transition peaks moving apart, then coming back closer until the transition either disappears or collapses back into one transition. Third, notice that the higher field peaks are narrower than the lower field peaks in the \( m = \pm 3 \) transitions at \( \sim 1000 \) mT. Furthermore, in Figs. 4.7 and 4.6, the \( m = \pm 4 \) transitions do not oscillate uniformly, but seem to exhibit a two-fold symmetry pattern in their amplitudes. In the 2 K data Fig. 4.7, the peak amplitudes at \( \xi = 70° \) and 260° are lower in amplitude than the peaks at \( \xi = 170° \) and 350°. In the 10 K data in Fig. 4.8, the peaks at \( \xi = 50° \) and 240° are much smaller in amplitude than the peaks at \( \xi = 150° \) and 330°.

The 2 K data has two other features that the 10 K data does not exhibit. The first are the bumps in the \( m = \pm 4 \) field transitions at \( \xi = 70° \) and 250° in Fig. 4.7. Clearly, this behavior is not symmetric as it does not appear again at \( \xi = 160° \) and 340°. The second feature is that the high field transitions at \( \xi = 110° \) in Fig. 4.5 seem to split before joining back into one transition.
Figure 4.7: A close up of the $m = \pm 4$ transitions.

Figure 4.8: A close up of the $m = \pm 4$ transitions.
4.2 Discussion of Results

In this section, we provide an interpretation for this data under our theory outlined in Section II. We also aim to produce explanations for several aberrant behaviors not explained by the theory that were perhaps a result of a design or a crystal-mounting flaw. We provide crude fittings that indicate that this behavior indeed corroborates our predictions, and indicate further directions for research.

Overall, these results almost undeniably exhibit the Berry-phase interference pattern that we have predicted in Section II. Referring back to Fig. 2.10, we see that as the $m = \pm 2$ energy crossing becomes a widening avoided crossing, the two transitions grow closer together. We observe this pattern in our data, in the low-field regime. In fact, when comparing Fig. 2.11 to both 2 K and 10 K data, we see that not only do the transitions shift in the same way, but they occur in almost exactly the same field regime.

For the mid- and high-field regimes, we did not expect to find transitions on both sides of the crossing as we did for the low-field regime. However, we did expect the transition to shift up to higher fields and back down as we rotated the crystal, changing the tunnel splitting between states. Furthermore, we expected all of this behavior to repeat periodically every 90°, as the sample is four-fold symmetric.

While the experimental data clearly shows evidence for the theoretical behavior predicted by our simulations, there are multiple points of aberration that did not align with our simulations. All of the features that we described at the end of the previous section as being 180° periodic (two-fold symmetric)
are abnormalities, in addition to the 2 K-specific features.

These behaviors were most likely caused by the slight misalignment in the crystal-mounting process. With the easy axis of a four-fold symmetric sample aligned perpendicular to the field, we would expect the spectrum to show a four-fold pattern as a function of $\phi$. If the sample is misaligned, as shown in Fig. 3.23, we would expect some two-fold pattern to emerge as the easy axis precesses about the x-axis. From Chapter II, we’ve seen that the Berry-Phase effect is most sensitive to changes in $\theta$, and so even a small deviation from $\theta = 90^\circ$ would cause a noticeable aberration - which we indeed see in our results.

After adjusting for the misalignment through the Euler Angles mentioned at the end of Chapter III, I created a function\(^3\) that would use a least-squares regression to best fit the simulation to our data using three parameters - $\phi$, $\psi$, and the phase offset. The $\phi$ and $\psi$ parameters are self-evident, while the phase offset makes sure that the fits begin at our initial experimental $\xi$ orientation. Because it was tricky to fit all three transitions in the fit function at the same time, I only used the high-field $m = \pm 4$ data to find the fitting parameters, and used them to plot a best fit simulation in Fig. 4.9. At first, the results from the fittings were:

- 2 K: $\phi = -14.7954, \psi = 0$, offset=17.5439\(^\circ\)
- 10 K: $\phi = -40.1835, \psi = 0.3169$, offset=-115.4583\(^\circ\),

However, this discrepancy in $\phi$ and $\psi$ should be impossible; we did nothing

---

\(^3\)Refer to Appendix B for the appropriate Matlab scripts used to analyze the data and perform fittings.
Figure 4.9: Our fit of the 2 K data using Least-Squares Regression. Notice the $180^\circ$ variation in amplitude.

Figure 4.10: Our fit of the 10 K data using Least-Squares Regression. Notice the $180^\circ$ variation in amplitude.
Figure 4.11: Experimental data overlaid with simulation results using the fit parameters found from Fig. 4.9.

Figure 4.12: Experimental data overlaid with simulation results using the fit parameters found from Fig. 4.10.
to change the orientation of the crystal besides warming the probe up to 10 K. This discrepancy indicates that the fitting algorithm has not actually yet found a true best fit, and likely has converged on a false minimum in the Least Squares Regression. To try to obtain a reasonable fit for both sets of data, I used the fit from the 2 K data and applied it to the 10 K data, and vice versa. The parameters that output a believable fit for each set were the ones from the 2 K data. Therefore, I took the fit parameters from the 2 K data, used them to fix the $\phi$ and $\psi$ parameters of the sample, and only fit the phase offset parameter to the 10 K data, obtaining an offset of $-0.3171^\circ$. These fits are shown in Figs. 4.9 and 4.10.

As shown in Figs. 4.11 and 4.12, the simulations do a remarkable job of reproducing the essential, overall behavior of the data. The curves all roughly fit the general oscillations of the transitions for each of the $m = \pm 2$, $\pm 3$, and $\pm 4$ states. In addition, the orientation angles and phase offset were the only parameters used in the fitting - the anisotropy parameters were taken from published values without modification. The fact that the simulation and data agree to this extent indicates that the spin Hamiltonian works extraordinarily well for modeling this system.

To produce our final fit results, I used these fitting parameters to produce a best fit curve on top of the experimental results. However, the fitting leaves much to be desired. The fact that the fit parameter $\psi = 0$ indicates that our sample was fully aligned and that this entire Euler formulation was unnecessary - nevertheless, there are features in the data that prove otherwise. The $180^\circ$ periodic features strongly show that the sample is misaligned. This
indicates that our fitting needs further development.

Despite the shortcomings of our least squares regression fitting in explaining the abnormal features in our data, it ultimately allows us to make certain conclusions. First and foremost, we see that the data exhibits almost exactly the behavior predicted by the Theory presented in Chapter 2. As we turn the field away from the hard axis of Ni$_4$ by rotating the crystal an angle $\phi$, we find that $\Delta$ changes for the $m = \pm 2$ crossing. This causes the transitions in the ESR spectra to oscillate, with the field separation at its maximum when $\Delta = 0$ and no field separation at all when $\Delta$ becomes large.

Being able to distinguish between conformational states would have allowed for much more accurate analysis to be performed on the results. Our experimental results turned out to resemble the behavior of the 2$^{nd}$ conformational state, but the broader peak lines of the 100% sample make it impossible to tell how much of the behavior is due to just the 2$^{nd}$ state. This may have been a factor in being unable to obtain a fit that more closely models our data. Knowing the behavior of each state could have helped immensely in modeling and fitting our data to theoretical calculations.

In order to obtain data that would remedy this problem, we dedicated a considerable effort to obtaining data from a 5% sample of Ni$_4$. We were able to get signals when the crystal was oriented so that $\theta = 90^\circ$, but as we rotated the probe, the signal was lost, presumably because the easy axis had precessed away from $\theta = 90^\circ$. Ultimately, aligning the sample by hand at precisely the orientation we needed proved too difficult. However, this provides a clear path for further studies - devising a method to align the sample properly along its
easy axis. One idea is to encase a 5% sample in some uncured epoxy and apply
a magnetic field to orient the crystal along its easy axis.

Once we have some 5% data, it would be more fruitful to do further analy-
sis work in the hopes of obtaining better parameter fits. This would involv-
ing using more sophisticated analysis packages (i.e. the Matlab Curve Fitting
Toolbox), using a different kind of regression, and otherwise exploring other
options in terms of fitting techniques.
Chapter 5

Conclusion

This thesis was an attempt to experimentally verify the Berry-phase interference effect in the Ni$_4$ single-molecule magnet using ESR spectroscopy. Beginning with a simple two-state system, we saw how an avoided crossing created by a non-commuting parameter caused the states of the system to mix and form a superposition state, enabling tunneling. After a brief introduction to the properties and history behind SMMs, we applied our knowledge of the avoided crossing to these more complicated molecular systems and found that these states exhibited Berry’s phase due to molecular symmetries.

In Chapter 2, we took this phenomenon and found out the theoretical cause of this interference effect, using the Fe$_8$ two-fold symmetrical SMM to get a better understanding of the phenomenon. We then expanded this formulation to our four-fold symmetric Ni$_4$ SMM, learning about its unique properties. Furthermore, we discovered that using Electron-Spin Resonance spectroscopy to measure this interference pattern was theoretically not only feasible, but
was extremely simple to interpret.

Chapter 3 covered the experimental design of taking these ESR measurements. The properties of the loop-gap resonator were instrumental in enabling us to design a resonator probe to perform low-temperature ESR experiments. In order to perform our experiment, there needed to be some method of changing the orientation of the crystal relative to the applied static field. Our first prototype used the LGR and a probe holder that allowed us to adjust this orientation manually. However, this design took too long to troubleshoot issues, had serious margins for error, and was overall too cumbersome. To save time and to reduce the error susceptibility, we designed a resonator probe that allowed us to change the \( \phi \) orientation of the sample in-situ. Moreover, we were able to automate the data-taking process using a stepper motor to enable faster, more efficient troubleshooting - which, in the end, paid off. This successful endeavor allowed us to attain useful data, showing that ESR could indeed be used to exhibit Berry-phase interference in Ni\(_4\).

We presented these results with some analysis in Chapter 4. The data provided conclusive evidence that magnetic spin tunneling was indeed being quenched at certain intervals of \( \phi \). However, we also saw signs of other errant behavior that had not been predicted by the theoretical simulations. This was thought to be a result of some misalignment error that caused the easy axis of the crystal to precess around the x-axis as we changed \( \xi \). Unfortunately, even after accounting for this error in fitting our data, we were unable to obtain results that exactly matched our experimental data.

These strange effects could be attributed to several problems. The glaring
issue with analysis is the quality of our fitting program. There are sundry methods of obtaining a fitting, and we were only able to try a least-squares regression fit using EasySpin to narrow in on these set orientation parameters. Needless to say, this did not work as well as we hoped. However, there may other possible reasons for these unaccounted-for features in our data. Perhaps there may be other systematic complications (such as the probe’s orientation being slightly off-axis) that we did not realize was impacting our system that we could try to account for in our fitting. It is also feasible that certain characteristics could be due to unknown perturbations to the sample - for example, the strange dips occurring at 180° intervals in the ground state energy pair of Ni₄.

Thinking of and fixing these issues of experimentation and fitting errors are one direction that this project could head towards. Another possible course this research could head towards is to try to obtain data from a 5% sample of Ni₄, which would allow for more precise data. This would allow us to really pin down the behavior of both conformational states, which is what may be causing some murkiness in the results of this thesis. After several weeks of facing frustration trying to mount the 5% sample successfully at θ = 90°, I suggest a more systematic way of orienting the crystal to make sure that the easy axis of the sample is properly aligned and does not precess. Perhaps using the method described in [21] in which the crystal is encased in some freshly-mixed epoxy and set inside a magnetic field in order to align the crystal as the epoxy cures is worth pursuing.

This project could also head in a new direction, towards tuning the Berry-
phase interference effect with pressure. This was the original objective of this thesis, and still remains a worthwhile experiment. I have already designed the resonator probe necessary to conduct this experiment, so it should take minimal effort to get the project running. Otherwise, the pressure will be applied unevenly. Furthermore, the sample must be prepared in the proper way, encased in epoxy and machined, so that it can fit inside the probe and the pressure apparatus can function. As Jim Atkinson has done a similar experiment, I point readers to [21] for a salient discussion on sample preparation.

Regardless of the direction this experiment may proceed, the result of this experiment was a success. By performing perpendicular-mode ESR, we were able to observe the Berry-phase interference in Ni$_4$. 
Appendix A

Acquiring Data

A.1 Data Acquisition Protocols

The data-taking process begins with mounting the sample onto the Loop-gap resonator, which was covered in the last section of Chapter III. Next, assemble the probe, making sure all of the screws are in and all the connections are secure. Place the probe holder into the sample space inside the PPMS. Clamp the probe holder to the sample space, sealing off the space inside. Before cooling down the system, it is imperative that the air inside the sample space be purged so that there is no condensation at low temperatures. In order to prevent any helium loss as this process occurs, close the helium tank and open the 3-junction valve that is attached to the tank. After the sample chamber is purged, reverse this step - close the valve and open the helium tank. Finally, cool down the sample to the desired temperature - in our case, either 10K or 2K. Make sure the PPMS readout display indicates that the temperature is at
[STABLE], meaning that it has thermalized fully.

At this point, we transition towards preparing other features of the experiment. Attach the motor to the G10' rod by fitting the rotator adapter to both the motor and the rod and tightening the screws with the proper micro-hex tool. After the system reaches the target temperature, it is important to check that the resonance peak still exists. Most likely, it has shifted to a slightly higher frequency - in some cases, it has jumped as much as .1 GHz. Find the peak and narrow the span until you have a Lorentzian peak as shown in Fig. 3.4. At this point, the data-taking process may begin. Pull up the proper LabView VI on the computer to set the limits for the number of rotations, the field range to sweep over, the power of the frequency output, etc. This is all saved to a cloud file that we can access from any computer in the lab. Ultimately, this data-taking process yields a spectrum like Fig. 4.1.
Appendix B

Simulation and Analysis Code

I used Matlab and the EasySpin software to design simulation programs for my Ni$_4$ ESR experiment.

B.1 Simulation Program

This first file is the one I used to run simulations. I have separated the code for simulations of a single orientation and simulations of a range of $\phi$.

% Hamiltonian parameters (2nd conformational state)
\begin{verbatim}
d = 15.551456;
c = 0.006446;
b = 0.137871;
h = 0;
\end{verbatim}
\begin{verbatim}
gx = 2.220401;
gy = gx;
gz = 2.157266;
\end{verbatim}
\begin{verbatim}
T = 2;
fmw = 3.78;  % uwave frequency
\end{verbatim}
\begin{verbatim}
%field range
Bmin = 0;
\end{verbatim}
\( B_{\text{max}} = 2800 \); \( \% \) in milli-Tesla

\% three Euler angles
\[ \theta = 90; \quad \phi = 24; \quad \psi = 0; \]

\( c_H = 1; \quad \% \) Hstrain strength. determine the width of the peak

\( B_{22} = 0; \quad \% \) Pressure \( B_{22} \) term

\[
\text{Sys} = \text{struct}('S', 4, 'g', [gx, gy, gz]);
\]
\[
\text{Sys}.B2 = [B_{22}, 0, -(d/3+575*b/105+1807*h/21)*10^3, 0, 0]; \quad \% \text{In MHz}
\]
\[
\text{Sys}.B4 = [2*10^3*c, 0, 0, 0, (-b/35-53*h/77)*10^3, 0, 0, 0, 0];
\]
\[
\text{Sys}.B6 = [0, 0, 0, 0, 0, -h/231*10^3, 0, 0, 0, 0, 0, 0];
\]
\[
\text{Sys}.\text{HStrain} = c_H*[100, 100, 100];
\]

\( \text{Exp.mwFreq} = \text{fmw}; \)
\( \text{Exp.Range} = [\text{Bmin} \ B_{\text{max}}]; \)
\( \text{Exp.Harmonic} = 0; \)

\( \text{Exp.Mode} = '\text{perpendicular}'; \)
\( \text{Exp.CrystalOrientation} = [\phi/180*\pi, \theta/180*\pi, \psi/180*\pi]; \)
\( \text{Exp.Temperature} = T; \)
\( \text{Exp.nPoints} = B_{\text{max}}-B_{\text{min}}+1; \)

\% Opt. Transitions = [5 6];
\( \text{Opt.Transitions} = '\text{all}'; \)
\( [\text{B, spec, trans}] = \text{pepper(Sys, Exp, Opt); \% B = 1:1000} \)
\( [\text{Pos}] = \text{resfields(Sys, Exp, Opt);} \)

\% Hamiltonian parameters (2nd conformational state)
\( d = 15.551456; \)
\( c = 0.006446; \)
\( b = 0.137871; \)
\( h = 0; \)

\( gx = 2.220401; \)
\( gy = gx; \)
\( gz = 2.157266; \)
Sys1 = struct ( 'S' , 4 , 'g' , [gx , gy , gz] ) ;
Sys1.B2 = [B22,0,−(d/3+575*b/105+1807*h/21)*10^3,0,0] ; %In MHz
Sys1.B4 = [2*10^3*c,0,0,0,−(b/35−53*h/77)*10^3,0,0,0,0] ;
Sys1.B6 = [0,0,0,0,0,−h/231*10^3,0,0,0,0,0,0] ;
Sys1.HStrain = cH *[100 100 100] ;

Exp.mwFreq = fmw ;
Exp.Range = [Bmin Bmax] ;
Exp.Harmonic = 0 ;
Exp.Mode = 'perpendicular' ;
Exp.CrystalOrientation = [phi/180*pi theta/180*pi psi/180*pi] ;
Exp.Temperature = T ;
Exp.nPoints = Bmax−Bmin+1 ;

%Opt.Transitions = 'all' ;
[B1 , spec1 , trans1] = pepper (Sys1 , Exp , Opt) ; % B = 1:1000
[Pos] = resfields (Sys , Exp , Opt) ;
[Pos1] = resfields (Sys1 , Exp , Opt) ;

% clf (figure(1))
% figure(1)
figure
subplot (2 , 1 , 2)
plot (B1 , spec1) ;
% hold on
% plot (B , spec1) ;
title ([num2str (fmw) ' GHz, T=2K Spectrum: Theta=' num2str (theta) ' Phi=' num2str (phi) ' '])
xlabel ('B Field (mT) ')
ylabel ('Power Density ')xlim ([0 , 800])% hold on
% legend ('1st State', '2nd State ')

subplot (2 , 1 , 1)
levelsplot (Sys1 , [phi , theta , psi]/180*pi , [Bmin , Bmax] , fmw)
xlabel ('B Field (T) ')

97
% Now we have to make a plot for res field as a function of phi for ALL
% resonances
% last_phi = phi
phi_list = 0:1:phi;
dummy_phi_matrix = [];
Pos_matrix = [];
Amp_matrix = [];
close(figure(4))
for i = phi_list
    Exp.CrystalOrientation = [i/180*pi theta/180*pi psi/180*pi];
    Opt.Transitions = [5 6];
    %Opt.Transitions = 'all';
    [Pos, Amp] = resfields(Sys, Exp, Opt);
    dummy_phi = ones(length(Pos),1)*i
    dummy_phi_matrix = [dummy_phi_matrix, dummy_phi];
    Pos_matrix = [Pos_matrix, Pos];
    Amp_matrix = [Amp_matrix, Amp];
end

dummy_phi_vector = dummy_phi_matrix(:)
Pos_vector = Pos_matrix(:)
Amp_vector = Amp_matrix(:)*50

figure(4)
fig4 = figure(4);
scatter(Pos_vector, dummy_phi_vector, Amp_vector)
% hold on;
% plot(phi_vec, res_center2 , '.b');
% hold on;
% plot(phi_vec, res_center3 , '-g');
title([num2str(fmw) ' GHz, T=' num2str(T) ', Res Field v. Phi: Theta=' num2str(theta) ])
xlabel('Resonance Peak Center (B Field)');
B.2 Fitting Programs and Data

These next two scripts were used to fit the $m = \pm 4$ data. The first file contains the function script, while the second file is the master fitting file. The second file also contains all of the central data for the 2K and the 10K experiments. Here is the 1st file:

```matlab
function [Pos1]=Euler_tester(phi, psi, offset, ksi_list_fix)
% Hamiltonian parameters (2nd conformational state)
d = 15.551456;
c = 0.006446;
b = 0.137871;
h = 0;

gx = 2.220401;
gy = gx;
gz = 2.157266;

T = 10;
fmw = 3.78; % uwave frequency

%field range
Bmin = 0;
Bmax = 2800; %In milli-Tesla

% phi = -14.7954;
% psi = 0;

cent_freq=[];
cent_freq1=[];
ksi_vec=[];
Euler_Array=[];
theta=90;

for i=ksi_list_fix
```

```matlab
```

```matlab
```
%three Euler angles + ksi and theta1 rod correction
theta1 = 0*pi/180; %accounts for misalignment of gear crystal holder
ksi = (i)*pi/180–offset*pi/180 %amp–offset; % real time lab frame rotation
%i–phase is used to shift the phi values to match the data

%Crystal transformation steps
Euler_knot = [phi/180*pi theta/180*pi psi/180*pi];
Euler_matrix=erot(Euler_knot);
x_rot_matrix=[1 0 0;0 cos(ksi) −sin(ksi);0 sin(ksi) cos(ksi)];
y_rot_matrix=[cos(theta1) 0 sin(theta1);0 1;−sin(theta1) 0 cos(theta1)];
transformed_matrix=x_rot_matrix*Euler_matrix;
transformed_matrix=y_rot_matrix*transformed_matrix;
Euler_prime=eulang(transformed_matrix);
Euler_Array=[Euler_Array; Euler_prime];
end

cH = 1; % Hstrain strength. determine the width of the peak

%%%%%%%%%%%%%%%%%%%%%%%%%%%%

B22=0; %Pressure B22 term
Sys = struct ('S',4,'g',[gx,gy,gz]);
Sys.B2 = [B22,0,−(d/3+575*b/105+1807*h/21)*10^3,0,0]; %In MHz
Sys.B4 = [2*10^3*c,0,0,0,(-b/35−53*h/77)*10^3,0,0,0,0];
Sys.B6 = [0,0,0,0,0,−h/231*10^3,0,0,0,0,0,0];
Sys.HStrain = cH *[100 100 100];
Exp.mwFreq = fmw;
Exp.Range = [Bmin Bmax];
Exp.Harmonic = 0;

Exp.Mode = 'perpendicular';
Exp.CrystalOrientation=Euler_Array;
Exp.Temperature = T;
Exp.nPoints = Bmax–Bmin+1;
Opt.Transitions = [1 2];%3 4];%5 6];
%Opt.Transitions = 'all';
[Pos1] = resfields(Sys,Exp,Opt); return
Here is the 2nd file:

```matlab
%Input Data (2K)
fieldoffset = 186
phi_list = 0:5:410;

phi0_field = [2291, 8650, 20478]
phi5_field = [];
phi10_field = [2037, 3572, 9046, 20993] % 2nd number NOT VERY CLEAR, BROAD CURVE
phi15_field = []
phi20_field = [1859, 4016, 9688, 21751]
phi25_field = [1832, 4169, 10223, 22420] % small dip before the 3rd min? prob not
phi30_field = [1935, 4235, 10672, 22908]
phi35_field = [1947, 4259, 10873, 23175]
phi40_field = [1995, 4267, 10874, 23261]
% phi45star_field = [2012, 4244, 10866, 23264] % bookkeeping error with phi40s.

phi45_field = [2030, 4159, 10679, 23156]
phi50_field = [2121, 3999, 10205, 22625]
phi55_field = [2220, 3706, 9742, 21689] % 2nd value NOT VERY CLEAR, BROAD CURVE
phi60_field = [2387, 3375, 9371, 21245] % 2nd value NOT VERY CLEAR, BROAD CURVE
phi65_field = [2639, 9042, 20905]
phi70_field = [2718, 8831, 20679]
phi75_field = [8689, 20683]
phi80_field = [8628, 20874]
phi85_field = [8585, 20900]
phi90_field = [8599, 20743]
phi95_field = [8714, 20746]
phi100_field = [2573, 8856, 20942]
phi105_field = [2191, 3446, 9145, 21264]
phi110star_field = [1928, 3635, 9471, 21549] % 2nd value NOT AS CLEAR
phi110_field = [1928, 3635, 9471, 21549] % 2nd value NOT AS CLEAR
phi115_field = [1920, 3826, 9927, 21683, 22221]
phi120_field = [1932, 4005, 10275, 22040, 22698]
phi125_field = [1861, 4154, 10590, 22491, 23080]
phi130_field = [1853, 4254, 10794, 22760, 23351]
phi135_field = [1883, 4264, 10910, 23057]
phi140_field = [1948, 4235, 10846, 22900]
phi145_field = [2033, 4180, 10596, 22823]
phi150_field = [2100, 3978, 10150, 22634]
```
phi155_field = [2219, 3789, 9636, 22289]
phi160_field = [2385, 3327, 9241, 21876]
phi165_field = [2583, 8916, 21267]
phi170_field = [2629, 8727, 20905]
phi175_field = [2460, 8565, 20611]
phi180_field = [2497, 8727, 20905]
phi185_field = [2325, 8448, 20321]
phi190_field = [2320, 8460, 20293]
phi195_field = [2455, 8572, 20392]
phi200_field = [2432, 8722, 20562]
phi205_field = [2118, 3094, 8995, 20820]
phi210_field = [1947, 3604, 9195, 21134]
phi215_field = [1911, 3879, 9556, 21697]
phi220_field = [1865, 3982, 9824, 22135]
phi225_field = [1894, 4138, 10309, 22462]
phi230_field = [1922, 4239, 10708, 22661]
phi235_field = []
phi240_field = [1969, 4253, 10843, 22778]
phi245_field = []
phi250_field = [2132, 3984, 10183, 22100]
phi255_field = [2238, 3613, 9750, 21652]
phi260_field = [2375, 3413, 9348, 21210]
phi265_field = [2626, 9029, 20944]
phi270_field = [2833, 8824, 21030]
phi275_field = [2639, 3385, 8685, 21105]
phi280_field = [2518, 3347, 8605, 21003]
phi285_field = [2462, 3321, 8558, 20606]
phi290_field = [2444, 8595, 20541]
phi295_field = [2472, 8701, 20675]
phi300_field = [2427, 3439, 8897, 20947]
phi305_field = [2056, 3616, 9178, 21266]
phi310_field = [2004, 3653, 9506, 21409]
phi315_field = [1862, 3817, 9943, 22051]
phi320_field = [1879, 3984, 10288, 22438]
phi325_field = [1894, 4156, 10603, 22892]
phi330_field = [1943, 4225, 10836, 23170]
phi335_field = []
phi340_field = [2012, 10999, 23487]
phi345_field = []
phi350_field = [2130, 4239, 10132, 22549]
phi355_field = [2211, 3801, 9717, 22092] % 2nd value unclear
phi360_field = [2361, 9197, 21003] % ENTIRE DATA SET IS FUNKY
phi365_field = [2448, 8961, 20634]
phi370_field = [2622, 8736, 20567] % Data set is funky, last point might be 2
phi375_field = []
phi380_field = [2297, 8450, 20403]
phi385_field = []
phi390_field = [2435, 8439, 20483]
phi395_field = []
phi400_field = [2248, 8672, 20581]
phi405_field = [1963, 8860, 20763]
phi410_field = [2065, 3263, 8985, 21213]

% Input Data (10K)

% field offset = 204; % in Oe
% phi_list = 0:5:410;
%
%
% phi0_field = [1770, 3984, 9720, 21640];
% phi5_field = [1751, 4170, 9501, 10224, 21978];
% phi10_field = [1815, 4263, 10591, 22338];
% phi15_field = [1851, 4280, 10850, 22535];
% phi20_field = [1933, 4273, 10894, 22658];
% phi25_field = [1997, 4188, 10587, 22664]; % 3rd peak is odd
% phi30_field = [2076, 4049, 10222]; % Too noisy for 4, -4 peak
% phi35_field = [2211, 3468, 3926, 9713, 21569];
% phi40_field = [2396, 9369, 21279];
% phi45_field = [2567, 9093, 20861];
% phi50_field = [2615, 8890, 20717];
% phi55_field = [2550, 8718, 20632];
% phi60_field = [2469, 8654, 20591];
% phi65_field = [2417, 8624, 20549];
% phi70_field = [2365, 8643, 20526];
% phi75_field = [2394, 8741, 20683];
% phi80_field = [2207, 8882, 20889];
% phi85_field = [1977, 9131, 21238];
% phi90_field = [1824, 3453, 9428, 21647];
% phi95_field = [1769, 3829, 9848, 22131];
% phi100_field = [1799, 4046, 10290]; %4,-4 peak lost in noise
% phi105_field = [1755, 4206, 10629]; %4,-4 peak lost in noise
% phi110_field = [1719, 4280, 10814, 22618];
% phi115_field = [1810, 4322, 10912, 22626];
% phi120_field = [1895, 4312, 10913, 22552];
% phi125_field = [1875, 4141, 10624, 22191];
% phi130_field = [2018, 3983, 10261, 22187];
% phi135_field = [2160, 3658, 9683, 21798];
% phi140_field = [2287, 9256, 21078];
% phi145_field = [2350, 8834, 20784];
% phi150_field = [2525, 8704, 20349, 20793]; %odd 4,-4 split
% phi155_field = [2341, 8442, 18939, 19671]; %odd 4,-4 split
% phi160_field = [2167, 8439, 20137]; %Resonance shifted off screen
% phi165_field = [2164, 8397, 19320, 20178]; %odd 4,-4 split
% phi170_field = [2079, 8408, 18777];
% phi175_field = [2066, 8475, 20046];
% phi180_field = [1980, 8669, 20350];
% phi185_field = [1861] %Data is COMPLETELY WONKY
% phi190_field = [1847, 3182, 9161, 20882];
% phi195_field = [1778, 3718, 9420, 21252];
% phi200_field = [1763, 4019, 9852, 21628];
%
% phi205_field = [1819, 4176, 10404, 21945];
% phi210_field = [1824, 4273, 10690, 22315];
% phi215_field = [1666, 4270, 10851, 22533]; %1st peak is not clear
% phi220_field = [1919, 4296, 10878, 22647];
% phi225_field = [1952, 4224, 10650, 22434]; %4th peak unclear
% phi230_field = [2047, 4076, 10284, 22231];
% phi235_field = [ ];
% phi235_field = [2186, 3756, 9750, 22236] %DATA REALLY ODD/NOISY
% phi240_field = [2289, 3708, 9653, 21381];
% phi245_field = [2516, 9202, 21028]; %3,-3 and 4,-4 peaks are HUGE
% phi250_field = [2715, 9078, 20939];
% phi255_field = [2597, 8810, 20767];
% phi260_field = [2512, 8812, 20778];
% phi265_field = [2459, 8737, 20620];
% phi270_field = [2467, 8769, 20623];
% phi275_field = [2285, 8876, 20778]; %1st peak not clear, omitted
% phi280_field = [2090, 8899, 20896];
% phi285_field = [1946, 9128, 21045];
% phi290_field = [1814, 3394, 9478]; % 4th peak unclear
% phi295_field = [1786, 3822, 9847]; % 4th peak completely unclear
% phi300_field = [1774, 4042, 10237, 21678]; % 4th peak still kind of unclear
% phi305_field = [1767, 4222, 10617, 22212];
% phi310_field = [1731, 4263, 10840, 22472];
% phi315_field = [1802, 4284, 11122, 22514];
% phi320_field = [1866, 4277, 10856, 22625]; % 3,4 transitions not clear
% phi325_field = [1961, 4172, 10811, 22731]; % 3,4 transitions not clear
% phi330_field = [1976, 3968, 10251, 22289];
% phi335_field = [2141, 3567, 9493, 21118];
% phi340_field = [2148, 9314, 20965];
% phi345_field = [2278]; % middle peaks all lost to noise
% phi350_field = [2383, 8953]; % 4 peak not visible
% phi355_field = [2410, 8619]; % 4 peak not visible
% phi360_field = [2294, 3835, 19347]; % 4 peak not clear
% phi365_field = [2261, 8345]; % 4 peak not visible
% phi370_field = [2075, 8314]; % 4 peak not visible
% phi375_field = []; % data too noisy
% phi380_field = [1908, 8620]; % 4 peak not visible
% phi385_field = [1828, 3058, 8810]; % 4 peak not visible
% phi390_field = [1719, 3275, 8967, 20756]; % 4 peak not too clear
% phi395_field = []; % data too noisy
% phi400_field = [1744, 3979, 9739, 21747];
% phi405_field = [1729, 4171, 10239, 22416];
% phi410_field = [1734, 4264, 10522, 22273];

% Looks at phi_tot_new and picks out the proper transition; in this case, % the m=\pm 4 states.

phitot_new = [];
phi_list_fix = [];
for i = phi_list;
    j = i / 5; % Indexed phi_list values
    k = 90/100; % Creates a phi-to-proberotation ratio
    phi_tot{j+1} = eval(['phi' num2str(i) '_field']);
    phi_tot{j+1} = phi_tot{j+1} - fieldoffset;
end

105
for l = 1:length(phi_tot{j+1})
    if ~isempty(phi_tot{j+1});
        if phi_tot{j+1}(l)>16000; & phi_tot{j+1}(l)<14000;
            phi_tot{new}=phi_tot{new} phi_tot{j+1}(l)/10; %converts to mT and changes
            phi_list_fix=[phi_list_fix i*k]; %Adds the proper phi to the list (adjusted %phi/rotator ratio)
        end
    end
end

i=1;
len=length(phi_tot{new});
len1=length(phi_list_fix);

y=phi_tot{new}
x=phi_list_fix
fit = @(fitinfo ,x) Euler_tester(fitinfo(1),fitinfo(2),fitinfo(3),x)% ,fit info (4), x ) % Function to fit
%fitinfo(1,2,3) correlate to phi, psi, offset
fcn = @(fitinfo ) sum((fit(fitinfo ,x) − y).^2); % Least−Squares cost function
s = fminsearch(fcn , [0,0,0]) % Minimise Least−Squares

%s(1): best fit phi
%s(2): best fit psi
%s(3): best fit offset

xtot=0:3:380;
figure
plot(phi_tot{new},x,'.−−',fit(s,xtot),xtot, '.−−r ')
ylabel(' Ksi ')
xlabel('Central Field (mT) ')
title('100% Ni4 m=\pm4 Data: 2K ')
grid
B.3 Plotting all Fittings

The last file contains a script that plots the fit for all the $m = \pm 3, \pm 4, \pm 4$ states and overlays it on top of the data.

```matlab
% Hamiltonian parameters (2nd conformational state)
d = 15.551456;
c = 0.006446;
b = 0.137871;
h = 0;

gx = 2.220401;
gy = gx;
gz = 2.157266;

T = 2;
fmw = 3.78; % uwave frequency

% field range
Bmin = 0;
Bmax = 2800; % In milli-Tesla

% misc parameters
cent_freq = []
cent_freq1 = []
ksi = 0:3:360 % Measured in turns
ksi_vec = []
Euler_Array = []
offset = (17.5439)
ratio = 90/100;

B22 = 0; % Pressure B22 term
Sys = struct('S', 4, 'g', [gx, gy, gz]);
Sys.B2 = [B22, 0, -(d/3+575*b/105+1807*h/21) * 10^3, 0, 0, 0]; % In MHz
Sys.B4 = [2*10^3*c, 0, 0, 0, (-b/35-53*h/77) * 10^3, 0, 0, 0, 0, 0];
Sys.B6 = [0, 0, 0, 0, 0, -h/231 * 10^3, 0, 0, 0, 0, 0];
Sys.HStrain = cH *[100 100 100];
Exp.mwFreq = fmw;
Exp.Range = [Bmin Bmax];
Exp.Harmonic = 0;
```
Exp.Mode = 'perpendicular';
Exp.CrystalOrientation=Euler_Array
Exp.Temperature = T;
Exp.nPoints = B_{\text{max}} - B_{\text{min}} + 1;
Opt.Transitions = [1 2; 3 4; 5 6];
%Opt.Transitions = 'all';
[B1,spec1,trans1] = pepper(Sys,Exp,Opt);  % B = 1:1000
[Pos1] = resfields(Sys,Exp,Opt);

figure

%MUST define data before running

for i = phi_list
    j=i/5; %Indexed phi_list values
    phi_tot{j+1}=eval(['phi' num2str(i) 'field ']);
    phi_tot{j+1}=(phi_tot{j+1}-field_offset)/10  %Makes it into mT
end

for i = phi_list
    j=i/5;
    k=i*ratio %Creates a phi-to-probe rotation ratio
    plot(phi_tot{j+1},ones([1,length(phi_tot{j+1})])*k,'.')
    hold on
end

title('100% Ni4, Phi v. Central Field, 10K')
xlabel('Central Field (Oe)')
ylabel('phi')

plot(Pos1(1:4:end),ksi_vec);
hold on
plot(Pos1(2:4:end),ksi_vec);
hold on
plot(Pos1(3:4:end),ksi_vec);
hold on
plot(Pos1(4:4:end),ksi_vec);

title([num2str(fmw) ' GHz, T=' num2str(T) 'K \theta=' num2str(theta) ' psi=' num2str(psi) ' offset=' num2str(offset)])
xlabel('B Field (mT)')
ylabel('ksi')
Bibliography


