Towards an Examination of the Sweet Spot Principle in Cr$_7$Mn, a Single Molecule Magnet Qubit

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Abstract

Quantum decoherence, the loss of phase information in a quantum system over time, is a major impediment to the real-world realization of qubits that can be used in large-scale applications such as quantum computing. Working in a quantum system’s “Sweet Spot” regime, the position in the system’s parameter space where its eigenstates are least affected by small changes in any given controllable parameter, represents one possible solution to the problem of decoherence. Prior studies have shown that working in a sweet spot, by reducing the dephasing effects of noise fluctuations in controllable parameters, improves coherence times. We examine the Single Molecule Magnet (SMM), Cr$_7$Mn, which has a sweet spot at zero magnetic field. Cr$_7$Mn is an S=1 SMM that has a large zero-field tunnel splitting and eigenenergies that stay roughly constant up to magnetic field values of several hundred Oe. In this thesis, I outline steps taken towards exploits these properties to extract coherence times from electron spin resonance (ESR) spectroscopy studies of Cr$_7$Mn near and away from its zero-field sweet spot. I describe the unexpected finding of temperature independent paramagnetism exhibited by our Cr$_7$Mn sample. Furthermore, I describe ESR spectroscopy studies on a separate Single Molecule Magnet, Mn$_3$, and present evidence for the observation of photon assisted tunneling in this molecule.
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Chapter 1

Introduction

Much of the effort of physicists over recent decades has gone into exploring the dynamics and functionality of qubits. Qubits, like classical computer bits, are systems with two discrete states. However, unlike classical computer bits, qubits exhibit quantum mechanical properties. Qubits adhere to the superposition principle, which allows a system with discrete states to be in a superposition of these discrete states, whereby the system isn’t in one of the discrete states but rather is in a state that incorporates the probability of being measured in either discrete state. Furthermore, unlike classical bits, qubits can have their quantum states entangled with one another, whereby it is impossible to say definitely what the state of a single entangled qubit is. The quantum mechanical properties that govern the possible states of qubits make these systems a potentially valuable tool in such applications as quantum information technologies, quantum computing, and cryptography. The potential values of these applications come largely from theoretical work developing algorithms
that rely on the quantum properties of qubits and are better suited to solve certain types of problems than classical computational algorithms [1].

However, the actual employment of real world qubits in these applications remains limited, largely due to decoherence. Stemming from interactions between quantum systems and the surrounding environment [2], noise fluctuations in controllable parameters in quantum systems make the coherence of quantum properties of these systems especially unstable [3]. Because of this, we, as of yet, can only examine and exploit the quantum mechanical properties of qubits over time scales that are too short to allow for the realization of large-scale applications.

The question remains then of how to significantly improve the time-scale of quantum coherence in real world qubits. In this thesis, I discuss experiments exploring possible answers to this question. Motivated by the results of studies in the past two decades touching on the “Sweet Spot” principle, and the use of single molecule magnet (SMM) qubits, these experiments examine coherence time-scales of the SMM, Cr$_7$Mn, for different sets of parameters.

I will begin, in this chapter, by first discussing decoherence in generalized two-state quantum systems. Following this discussion, I will give a description of SMMs and explain the mechanisms of decoherence for Cr$_7$Mn. Lastly, I will present the notion of a sweet spot and discuss how our own sweet spot experiments are designed to address the decoherence issue in our qubit.
1.1 Decoherence in Two-State Systems

Consider a two-state quantum system. We can use \(|0\rangle\) and \(|1\rangle\) to represent the two discrete basis states in which the system can be measured. As generally speaking as possible, the quantum state, \(|\Psi\rangle\), of such a system is given by

\[
|\Psi\rangle = a|0\rangle + b|1\rangle
\]  

(1.1)
a superposition of the two basis states, where \(a\) and \(b\) are complex coefficients. In this case, the probability of measuring the system to be in the \(|0\rangle\) state is \(|a|^2\) and likewise, the probability of measuring the system in the \(|1\rangle\) state is \(|b|^2\). To more fully capture how these coefficients affect the state, \(|\Psi\rangle\), we can rewrite this equation as

\[
|\Psi\rangle = a^\prime e^{i\delta_0}|0\rangle + b^\prime e^{i\delta_1}|1\rangle
\]  

(1.2)
indicating both the magnitude and the phase of the coefficients. In this case, \(a^\prime\) and \(b^\prime\) are the magnitude of \(a\) and \(b\) respectively. We can further rewrite this equation, bringing an overall phase factor to the front of the right side of the equation, such that

\[
|\Psi\rangle = e^{i\delta_0}(a^\prime|0\rangle + b^\prime e^{i\delta}|1\rangle).
\]  

(1.3)
The phase factor outside the parenthesis is a global phase factor, which has little meaning when considering the state \(|\Psi\rangle\). The relative phase factor, \(e^{i\delta}\), on the other hand gives us information about the probability of measuring the
state $|\Psi\rangle$ in some other superposition state $|\Psi_0\rangle$. It is thus from this relative phase factor that the properties of quantum mechanics emerge.

Contained within the $\delta$ in the above equation, among other things, is time. Therefore, the state $|\Psi\rangle$ evolves over time based on this relative phase. Ideally, the quantum system described by the state $|\Psi\rangle$ would be completely isolated and we could observe the time evolution of this quantum state as it’s changing phase causes oscillations between in phase and out of phase basis states, indefinitely. Realistically however, the system inevitably couples with its surrounding environment. From this coupling with the surrounding environment, we lose access to the information held in the relative phase factor in Eq. 1.3. This loss in information is what we call decoherence.

To illustrate decoherence more thoroughly, consider the time evolution of $|\Psi\rangle$ as dictated by the system’s Hamiltonian:

$$|\Psi(t)\rangle = e^{-i\hat{H}t/\hbar}(a'|0\rangle + b'e^{i\delta}|1\rangle).$$

The eigenstates of the Hamiltonian, $\hat{H}$, are the system’s energy eigenstates. The Hamiltonian is typically dependent on certain controllable parameters such as applied magnetic field. These parameters therefore determine the system’s energy eigenvalues, the energy in the system when it’s in a particular eigenstate. In the generalized two-state system example, if $|0\rangle$ and $|1\rangle$ are separate eigenstates with different energy eigenvalues, applying the Hamiltonian operator as in eq. 1.4 evolves the relative phase difference between these two states. This evolution is based on the makeup of the Hamiltonian, and in particular, on the Hamiltonian’s controllable parameters.
In an isolated system, this dependence on controllable parameters wouldn’t present an issue to the stability of the phase information. However, when the controllable parameters in the Hamiltonian, inevitably interacting with the surrounding environment, thus experience noise fluctuations, these noise fluctuations directly alter the time evolution of the relative phase. Over time, the effects of continuous small fluctuations in controllable parameters in the Hamiltonian add up to a substantial, irreversible altering of the time evolution of the phase. The information held in the phase is therefore lost.

To see this more fully, consider the basic Hamiltonian for magnetic resonance,

\[ \hat{H} = -\mu \cdot B - \frac{g\mu_B}{2mc} \hat{S} \cdot (B_1 \cos(\omega t)\hat{i} + B_0 \hat{k}) \]  

(1.5)

where \( B \) is the applied field, \( \hat{S} \) is the spin angular momentum operator, and \( \omega \) comes from the application of an oscillating field. Setting \( \hbar \) equal to 1, we can rewrite this as

\[ \hat{H} = \omega_0 \hat{S}_z + \omega_1 (\cos \omega t) \hat{S}_x \]  

(1.6)

where \( \omega_0 \) and \( \omega_1 \) depend directly on the strength of the applied field. For simplicity’s sake, let us assume that \( \omega_1 \) is 0 and therefore we are only considering a uniform field in the z-direction. If we use Eq 1.4 we get the following result:

\[ |\Psi(t)\rangle = a' e^{-i\omega_0 t/2} |0\rangle + b' e^{i\omega_0 t/2} e^{i\delta} |1\rangle \]  

(1.7)

assuming a spin-1/2 system where \( |0\rangle \) and \( |1\rangle \) are \( \hat{S}_z \) eigenstates. We can,
again taking out a global phase, rewrite this as

$$|\Psi(t)\rangle = a'|0\rangle + b'e^{i\omega_0 t} e^{i\delta}|1\rangle$$  

(1.8)

Now let’s consider the situation where $\omega_0' = \omega_0 + \Delta(t)$. In this situation, $\Delta(t)$ comes from some unknown and unaccounted for noise fluctuation. Taking this into account, the spin state now should now be written as

$$|\Psi(t)\rangle = a'|0\rangle + b'e^{i\omega_0 t} e^{i\delta} e^{i\int_0^t \Delta(t) \, dt} |1\rangle$$  

(1.9)

Now there’s a phase factor, $\int_0^t \Delta(t) \, dt$ that comes from unaccounted for fluctuations in the magnetic field. Because $\Delta(t)$ is a function of random fluctuations, we can consider it much like we would a random walk situation. Ultimately, we would expect the average value of $\int_0^t \Delta(t) \, dt$ to be 0, so it may seem like this unaccounted for phase factor shouldn’t have an effect on the state, $|\Psi(t)\rangle$. However, the standard deviation from this average of the phase factor, like the standard deviation from 0 in the random walk problem, increases with time. As the standard deviation of the phase factor approaches and ultimately grows larger than $2\pi$, we effectively lose all information regarding the relative phase of the state, $|\Psi(t)\rangle$. That loss of information is then, what we refer to as decoherence, and what causes serious issues in being able to maintain and control a quantum state.
1.2 Single Molecule Magnets

In the previous section, I describe a generalized two-state system to introduce some of the basic physics behind qubits. The specific qubit we examine in this thesis is a Single Molecule Magnet (SMM). SMMs are molecules with magnetic moments, thus acting as single nanomagnets. They have a number of unique properties that have made them a source of interest among many condensed matter physicists over the last couple decades.

SMMs fall into a crystalline structure, such that a single crystal of a particular SMM can contain on the order of $10^{15}$ individual nanomagnets. These individual nanomagnets are spaced apart enough within the crystalline structure as not to significantly interact, allowing for the behavior of the individual nanomagnets to be reflected in the observable total magnetization of a crystal [4]. SMMs, therefore, give us the opportunity to readily observe and characterize the behavior, through large-scale experiments, of microscopic objects.

Because of this crystalline makeup, SMMs offer the opportunity to observe spin tunneling on a macroscopic scale, as changes in the overall magnetization of a given SMM crystal. Such macroscopic quantum tunneling was first observed by Friedman et al. [5] in Mn12-ac, a molecule with an overall spin of $S=10$. Fig 1.1 shows the energy diagram of such a spin-10 system, illustrating the possibility of tunneling between opposing spin states. While this thesis doesn’t rely directly on the observation of tunneling between different sets of energy levels for large spin systems, which has been at the core of numerous studies of SMMs [6, 7], the tunneling effects exhibited by SMMs allow for transitions between energy eigenstates, which will be important when considering
the behavior and Hamiltonian of the SMM we use.

Figure 1.1: Energy as a function of spin orientation for an S=10 SMM. The energy acts as a double well potential, where inside of each well are the discrete spin states. This particular energy diagram shows the spin states lining up directly across from one another, the condition for which tunneling occurs as illustrated by the arrows going from spin states in one well to the opposite spin states in the other.

More importantly for this thesis is the applicability of SMMs to the role of qubits, as SMMs straddle the line between the quantum and classical worlds. SMMs, based on their large magnetic moments, are subject to macroscopic control and manipulation, yet exhibit quantum properties more in line with the microscopic world. As discussed in [4], this occupation of a middle ground between the quantum and classical world gives SMMs an advantage over other possible qubits in addressing both sets of needs for the use of qubits in large-scale applications. Large-scale applications of qubits rely on both the coherence of quantum properties such as superposition and entanglement over a long enough time-scale and the ability to easily control individual qubits.
The particular SMM I work with in this thesis is Cr$_7$Mn seen in Fig 1.2. The Cr$_7$Mn molecule has a ring structure identical to the spin-0 Cr$_8$ molecule but with one of the Cr atoms replaced by a Mn atom. This replacement gives Cr$_7$Mn a total spin of $S=1$. Cr$_7$Mn has already proven valuable in SMM experiments, and particularly in a study conducted by Ardavan et al. [8] in which these molecules were used to observe spin echo. From this study, Ardavan et al. measured long coherence times, as high as 0.55 $\mu$s for Cr$_7$Mn at $T=1.8$ K.

The molecule is described by the Hamiltonian

$$H = -DS_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B H \cdot S$$  \hspace{1cm} (1.10)$$

where $D = 21$ GHz, $E = 1.9$ GHz, and $H_z$ is the applied DC magnetic field [8]. The first two terms in this Hamiltonian describe the molecule’s anisotropy, the directional dependence of its eigenstates, while the last term gives the Zeeman splitting of the eigenstates as a function of field. With this Hamiltonian, we
can see that the Cr$_7$Mn molecule has one controllable parameter, the applied DC magnetic field, which itself has three directional components. From this Hamiltonian, we can discern a tunnel splitting between the molecule’s two lowest energy eigenstates of 3.8 GHz—large enough to be observable with an experimental setup using microwave radiation to drive transitions between these two lowest energy eigenstates.

While Cr$_7$Mn has proven useful in spin echo experiments and because of its large tunnel splitting would be interesting to examine with microwave radiation, it is subject to decoherence particularly due to small spacing between individual molecules leading to dipolar interactions between the free electron spins in one molecule and the nuclear magnetic moments of another [8, 9]. In particular, Ardavan et al.’s work suggests strong coupling between free electron spins and the protons in nearby nuclei. This coupling is theorized to be a particularly limiting decoherence mechanism [10].

1.3 “Sweet Spots”

In attempting to overcome the decoherence mechanisms in Cr$_7$Mn, we perform experiments testing the existence and viability of what have previously been called “Sweet Spots.” The sweet spot principle was put forth in a landmark study by Vion, et al. [3] This study describes an experiment in which the transition frequency between discrete quantum states of a Cooper pair box [11] was measured as a function of two of the system’s controllable parameters. Fig 1.3, taken from [3], shows the results of this experiment. As seen
in this figure, the transition frequency varies dramatically as a function of the system’s parameters, $N_g$, a dimensionless charge factor set by the gate capacitance in the Cooper pair box and the source voltage, and $\phi$, a phase set by the flux through the current loop in their system. This dramatic dependence of the transition frequency on the system’s parameters suggests that a small change in one parameter greatly alters the eigenvalues of the system’s energy eigenstates. The alterations caused by random fluctuations in a given parameter would then quickly lead to decoherence, as the standard deviation of the $\int_0^t \Delta(t) \, dt$ phase mentioned in the above discussion of decoherence would increase rapidly with time. However, the study identified the saddle point in part (A) of Fig. 1.3 as a sweet spot, a position where small alterations in the value of given parameters have only minimal effects on the overall system’s transition frequency. Working at this sweet spot would thus greatly increase the time over which the phase factor, $\int_0^t \Delta(t) \, dt$, found in Eq 1.9, has a standard deviation significantly less than $2\pi$. This sweet spot was therefore identified as ideal for performing various experiments such as examining Rabi oscillations and Ramsey Fringes [3]. From the Ramsey Fringes experiment, Vion et al were able to identify a precise decoherence time for the qubit in the sweet spot regime, which was shown to be larger than that elsewhere in the system’s parameter space.

While the transition frequency data and the sweet spot seen in Fig 1.3 are particular to the qubit system devised in this study, the sweet spot principle guiding the study is widely adaptable. The principle merely depends on the existence of regimes in the parameter space of a given system at which
Figure 1.3: (A) A graph of the transition frequency, $\nu_{10}$, as a function of $N_g$ and $\phi/2\pi$, two of the parameters dictating degrees of freedom in the study’s Cooper pair box. The blue and red intersecting lines indicate a saddle point taken to be the “Sweet Spot” in this parameter space. (B) zooms in on one slice of the data depicted in (A), closely showing how flat the sweet spot is in comparison to the rest of the curve. Reproduced from [3] with permission from Michel Devoret.
small changes in a given parameter have only miniscule effects on the energy eigenstates of the system.

Fig 1.4 shows the energy eigenstates of Cr$_7$Mn as a function of $H_z$, the applied magnetic field. This figure takes the z-axis, also known as the sample’s easy axis, to be the direction along which the magnetic field is applied, though we could likewise apply a magnetic field along the x-axis or the y-axis. For the purposes of our experiment, we are concerned with the two lowest energy eigenstates, which at $H_z = 0$ have a tunnel splitting of 3.8 GHz. The sweet spot in this figure is at and around the $H_z = 0$ condition, as the energies of the lowest energy eigenstates remain roughly constant in this regime.

By working in a regime where small changes in $H_z$ have minimal effects on the eigenstates of Cr$_7$Mn, we can minimize the effects of the dipolar interactions between the free electrons in our system and the protons in nearby nuclei. These dipolar interactions introduce fluctuations in the magnetic field seen by the free electron in the system, which at high field would greatly alter the eigenstates, affecting the splitting between the two lowest energy eigenstates. At low fields however, as we can see in Fig 1.4, these fluctuations don’t greatly change the energy of the eigenstates.

In this thesis, we set up and describe ESR experiments designed for performance both near and away from the $H_z$ sweet spot to measure coherence times in either position and compare these coherence times, expecting them to be much greater near the "Sweet Spot."
1.4 Forthcoming Chapters

In chapter 2, I will discuss the experimental apparatus used to perform ESR spectroscopy experiments, and in particular will delve into the use of resonators and the characterization of the resonator used in our own experiments. In the course of the work that went towards this thesis, I ran into difficulty deducing whether I was getting a proper signal from the Cr\textsubscript{7}Mn sample I used in my attempts at ESR spectroscopy. It therefore became necessary to do a thorough magnetic study of the Cr\textsubscript{7}Mn sample. This magnetic study produced
a number of unexpected results which provide interesting insight into Cr$_7$Mn crystal samples but at the same time complicate our understanding of what we expect to see in ESR experiments. Throughout chapter 3, I will present the results of this study, explaining why these results were unexpected and what complications this leads to, while also providing background information on paramagnetism and diamagnetism to motivate the interpretation of these results. I will then spend chapter 4 giving background information on ESR spectroscopy before presenting the results of our own efforts at performing ESR spectroscopy, both on Cr$_7$Mn and and on separate Mn$_3$ samples. Finally, I will present the conclusions of my research, as well as a look into how to carry out the work of this thesis further, throughout chapter 5.
Chapter 2

Experimental Design

The experiments described in this thesis are performed using a straightforward setup. I couple a crystal sample of the SMMs I am studying to a superconducting resonator. The superconducting resonator is situated at the end of a probe, designed both for functionality with the Physical Property Measurement System (PPMS) in which the experiments are conducted and to minimize any undesired effects seen by the resonator and the sample. In the experimental apparatus, a microwave source generates a current oscillating at a microwave frequency. This microwave radiation source is attached to one end of my probe, feeding a current through the superconducting resonator which induces an oscillating field where my sample is coupled to the resonator. A well coupled sample will absorb some of this microwave radiation from the resonant cavity, driving transitions between the sample’s two lowest energy eigenstates. The signal from the other end of my probe is then measured to analyze the behavior of the SMM upon absorbing microwave radiation from the resonant
I will flesh out this procedure in more detail throughout this chapter, first discussing resonators and the design and construction of the resonator I have used. I will then discuss the remaining pieces of the experimental apparatus and the considerations taken to ensure the experimental apparatus allows for a relatively high resonance quality factor. Finally, I will discuss the SMM crystal samples used and the necessary considerations for working with these crystal samples. Chapter 4 will describe the behavior we expect to see in our SMMs, upon absorbing radiation, and will give a more detailed picture of the ESR Spectroscopy experiments we run.

2.1 Resonators

Simply speaking, a resonator is a system designed to oscillate at very particular frequencies with a noticeably larger amplitude than any other frequencies. These particular frequencies are referred to as a resonator’s resonant frequencies. Resonators have widespread use in physics and can be characterized by analyzing the power transmitted from the resonator upon applying an oscillating radiation source.

The resonators used in this thesis are one-dimensional cavity resonators. Such a system is simply a basic one-dimensional wave resonator, as studied in introductory physics. The primary geometric property then of the resonator that dictates its resonant frequencies is the resonator’s length. The resonators we use act as open end harmonic oscillators when examining their resonant
modes. As illustrated in Fig 2.1, taken from www.physicsclassroom.com [12], the resonances for such harmonic oscillators occur when the length of the oscillator is equal to half the wavelength of the incoming radiation frequency and for integer multiples of this first resonant frequency. We call this first resonant frequency the fundamental mode and subsequent resonant frequencies the second, third, etc. harmonic mode respectively.

Figure 2.1: The first three harmonic modes for an open end one-dimensional resonator. The first harmonic mode fits half a wavelength, the second a full wavelength, and the third one and a half wavelengths of a standing wave between the oscillator’s two ends. Reproduced from [12]

2.1.1 Coplanar Waveguide Resonators

Even something as simple as a one-dimensional resonator can come in many different forms. For these experiments, we use a coplanar waveguide (CPW) resonator, the basic geometry of which can be seen in Fig 2.2, a modified version of a figure taken from a paper by Goppl, et al. [13] that has informed
much of our considerations and calculations in working with these resonators. As seen in this illustration, CPWs contain trenches etched out of a superconducting material on either side of a central conductor, all on top of a substrate material. CPWs act as LCR circuits where an oscillating current runs through the central conductor inducing an oscillating magnetic field that circles around the central conductor.

Figure 2.2: Side view of a coplanar waveguide resonator. The blue section in the picture is the superconducting material while the yellow section is the substrate material underneath this superconducting material. The picture includes field lines for the oscillating magnetic field and a simplified representation of how a Cr₇Mn ring sits relative to this magnetic field, though a representation that’s in no way to scale. Reproduced from [13] and modified with permission from Andreas Wallraff.

These resonators have become increasingly popular in quantum electrodynamics applications, as they can be designed for use at frequencies in the microwave regime and manufactured with high quality factors. For the purposes of our experiments, we look for resonators with resonant frequencies in the microwave regime; in particular, we aim for resonant frequencies around
4-5 GHz. Furthermore, the higher the quality factor of a resonator, the less power dissipation across the resonator, and thus the higher the transmitted power from the resonator, a characteristic important for our experiments, as much of what we hope to see requires observing small differences in transmitted power, differences that would be too small to notice on our digital multimeter without using a relatively high Q resonator.

The first harmonic mode of a CPW resonator can be calculated with the following equation

\[ f_0 = \frac{c}{\sqrt{\varepsilon_{eff}}} \frac{1}{2l} \]  

(2.1)

where \( c \) is the speed of light, \( l \) is the length of the resonator, and \( \varepsilon_{eff} \) is the effective dielectric constant of the system. This equation comes from the basic relation between frequency and wavelength and the relation between wavelength of the first harmonic mode and resonator length explained above, as well as the speed, \( c/\sqrt{\varepsilon_{eff}} \), of electromagnetic radiation traveling through the resonator.

The paper by Goppl, et al. [13] offers a detailed account of how to explicitly calculate the quality factor, \( Q \), for a given CPW at a given frequency. \( Q \) is a dimensionless parameter of resonators which dictates the lossiness of the resonator and is given by the resonant frequency divided by \( \delta f \), the width of a resonance peak at half the peak’s amplitude. I relate here just the following set of equations, which contain the most significant information I have used for estimating expected values of \( Q \). Refer to [13] for more in depth derivations of these equations. The capacitance per unit length of the resonator’s
transmission line, $C_t$, can be calculated by

$$C_t = 4\epsilon_0\epsilon_{eff} \frac{K(k_0)}{K(k'_0)} \quad (2.2)$$

where $K$ refers to the complete elliptic integral of the first kind, given by the equation

$$K(k) = \int_0^1 \frac{dt}{\sqrt{(1 - t^2)(1 - k^2t^2)}} \quad (2.3)$$

$k_0$ and $k'_0$ in Equation 2.2 are given by

$$k_0 = \frac{w}{w + 2s} \quad (2.4)$$

$$k'_0 = \sqrt{1 - k_0^2} \quad (2.5)$$

where $w$ and $s$ are the same as those given in Fig 2.2.

Figure 2.3: LCR circuit representation of a coplanar waveguide resonator. Reproduced from [13] with permission from Andreas Wallraff.

If we use the near-resonance approximation for comparing a CPW to an
LCR circuit (which is valid given that our actual Q characterization, described later in this chapter, comes from looking at the transmitted power of the resonator at and very near its resonant frequency), we can use the circuit diagram in Fig 2.3 to describe the CPW characteristics. In this case, the capacitance of the transmission line is given by

\[ C = \frac{C_l l}{2} \]  
(2.6)

The circuit diagram in Fig 2.3 can be transformed into the equivalent circuit diagram shown in Fig 2.4 through several parameter transformations.

![Circuit Diagram](image)

**Figure 2.4**: Circuit diagram of a coplanar waveguide resonator equivalent to that shown in Fig 2.3 but with capacitance and resistance transformations relevant for calculating Q values. Reproduced from [13] with permission from Andreas Wallraff.

The resulting, \( R^* \), which as will be seen, is the most important new parameter for my own calculations is given by

\[ R^* = \frac{1 + \omega_n^2 C_k^2 R_L^2}{\omega_n^2 C_k^2 R_L} \]  
(2.7)

In this equation, \( \omega_n \) is simply \( n\omega_0 \) where \( n \) is the resonance mode number.
(1 for the fundamental mode). $C_k$ is the coupling capacitance, which I will soon describe in more detail. And finally, $R_L$ is the load resistance which throughout our experiments is roughly 50 Ohms. With this information, I can now give the equation I used for calculating the $Q$ of my resonator,

$$Q = \frac{\omega_n R^* C}{2}$$

[13] Of the parameters considered in performing the calculations above, $C_k$ in particular can be altered significantly to control expected $Q$ values. Depending on both the size and the type of coupling capacitor used to connect the transmission line with input and output lines, you can make resonators with expected $Q$ values that range from just a few hundred to on the order of $10^5$. In the next subsection I will discuss the particular characteristics of the resonators I have used in my experiments, including the type and size of the coupling capacitors.

### 2.1.2 Design, Fabrication, and Characteristics of My Resonators

The resonators at my disposal, including the particular resonator on which I have performed my experiments, were manufactured in the summer and fall of 2012, using a very similar design to that used by Goppl, et al. [13] in their studies. The basic design can be seen in Fig 2.5. To make individual resonator chips as small as possible, the coplanar waveguide is designed to have a snake pattern. However, the resonator is still effectively a one-dimensional harmonic
oscillator.

![Image](image_url)

Figure 2.5: Overhead view of the basic design of the coplanar waveguide resonator including input and output signal lines, coupling capacitors, transmission line, and the ground planes. Image courtesy of Saiti Datta

Our resonators use niobium as the superconducting material and silicon as the substrate on which the niobium lies. The resonators were fabricated by Saiti Datta, with the help of Mustafa Bal throughout the summer and fall of 2012. Following fabrication, I diced the wafer of available resonators into individual chips, making sure to leave the resonators clean of any debris produced in the dicing process by spinning a resist material onto the wafer before dicing to catch debris and cleaning this resist material off individual resonators using Acetone followed by Isopropynol.

We have resonators of ten different lengths, varying from 5921 \( \mu m \) to 15976 \( \mu m \). A resonator with a length of 13976 \( \mu m \) was found to have a resonant frequency of \( \approx 4.8 \) GHz without any coupling to a sample, from which we calculate the effective dielectric constant for our resonators to be \( \approx 5 \). From
this we estimate that our resonators have first harmonic modes at frequencies ranging from $\approx 4.2$ GHz to $\approx 11.3$ GHZ. The gap widths for each of our resonators are 2 $\mu$m. The central conductor widths are either 4 $\mu$m or 2 $\mu$m. Finally, each of the resonators uses a gap coupling capacitor as shown in Fig 2.6 of either 50 $\mu$m or 10 $\mu$m in length. According to Goppl, et al., the 50 $\mu$m gap capacitor has a capacitance approximately half that of the 10 $\mu$m gap capacitor. Goppl, et al. calculated expected Q values for both of these types of coupling capacitors to be on the order of $10^5$. We have resonators with each combination of the parameters listed above.

The resonator used throughout this thesis has length 13976 $\mu$m, conductor width 4 $\mu$m, and uses 50 $\mu$m gap capacitors. Based on these characteristics and the effective dielectric constant calculated we estimate an expected Q value of $\approx 1.08 \times 10^5$. In the following subsection, I will go through the process of characterizing this resonator and give the actual Q values we have found.
2.1.3 Resonator Characterization

To characterize our resonator, we seek out the resonance peak, first taking a transmitted power spectrum across a wide range of microwave frequencies. Fig 2.7 shows what such a power spectrum looks like. As can be seen, numerous peaks appear. Most of these peaks are, however, parasitic resonances that result from a number of different factors, discussed in more detail later in the chapter. We can determine which of these peaks are actually the resonant frequencies of our superconducting resonator by observing the response of the resonant peaks to changing temperatures and magnetic fields. Niobium has a critical temperature of roughly 9 K, above which it isn’t superconducting. We therefore see only the resonance peaks associated with our superconducting resonator diminish with increasing temperature. Furthermore, the superconductivity of niobium diminishes with increasing magnetic field. If we apply a high magnetic field, we therefore see only the superconducting resonances disappear.

Based on these initial characterization efforts, we find the first harmonic mode of our resonator to have a resonant frequency of 4.8 GHz. We perform a higher resolution frequency sweep around this approximate resonant frequency, looking at the transmitted power spectrum to get a more careful characterization of this resonance. Fig 2.8 shows the shape of the resonant peak as well as a lorentzian function fitted to this peak, of the form

\[ P(f) = A \frac{(\Delta f/2)^2}{(f - f_0)^2 + (\Delta f/2)^2} + P_0 \]  

\[ (2.9) \]
where $P$ is the transmitted power, $A$ is the amplitude of the peak, $\gamma$ is the width at half the amplitude, $f_0$ is the resonant frequency, and $P_0$ is the baseline transmitted power.

The Q value of our resonator is then $f_0/\Delta f$. The Q value for the resonator used in these experiments depends on microwave source power, temperature, and applied magnetic field. The resonant peak shown in Fig 2.8 is calculated, by fitting to a lorentzian, to have a resonant frequency equal to 4.7949 GHz and a Q equal to $6.38(3) \times 10^3$ (the reason I don’t report error for the resonant frequency in my data is that the calculated error is always smaller than the furthest decimal place calculated for the resonant frequency). This Q value

Figure 2.7: Transmission spectrum at T=2K and microwave source power equal to -10 dBm after creating new packaging, as will be discussed in the next section, which helped eliminate much of the interfering parasitic resonances.
Figure 2.8: Transmission spectrum for a microwave source power of -34 dBm at temperature T=1.8 K with no applied field, showing a resonant peak. The fit line comes from fitting the curve with Eq. 2.9.

is the highest calculated Q found in any of the resonator characterization measurements I have done. It should be noted that this Q is significantly smaller than expected from our calculations. At this point, we don’t know what is causing this discrepancy but have seen, as will be described in the next section, how significantly the design and construction of our apparatus affects the Q value of our resonators.

At microwave source powers of around -31 dBm and above, the transmission spectrum begins to show bifurcation, as seen in Fig 2.9, where the resonant peak splits.

Fig 2.10 shows the dependence of the resonant peak on microwave source
Figure 2.9: Transmission spectrum at T=1.8 K for a -31 dBm microwave source power and no applied field, showing bifurcation of the resonance peak.

power for powers between -43 dBm and -34 dBm. Lowering the microwave source power causes the resonant peak amplitude to decrease and a slight broadening of the peak, though it doesn’t cause any shifting in the resonant frequency. The Q values for microwave source powers of -37 dBm, -40 dBm, and -43 dBm were calculated to be, respectively, $6.17(5) \times 10^3$, $5.51(13) \times 10^3$, and $5.4(2) \times 10^3$.

The resonance peaks show significant dependence on temperature, both diminishing and shifting when increasing temperature from 1.8 K. This temperature dependence comes from the diminishing of the superconducting resonance as temperature approaches 9 K, the critical temperature for Niobium.
Figure 2.10: Transmission spectrum at T=1.8 K, with no applied field, for a range of microwave source powers.

Fig 2.11 shows transmission spectrum for temperatures up to 4 K, at which the resonant frequency of the peak has shifted to 4.7846 GHz and the measured Q value has dropped to $2.64(7) \times 10^3$.

The original transmission spectrum shown in Fig 2.7 shows, along with the first harmonic mode described above, a superconducting resonance taken to be the second harmonic mode. At incoming power equal to -31 dBm, as high as I can go without seeing bifurcation, and temperature equal to 1.8 K, I perform a characterization study of the resonant peak, like those above, shown in Fig 2.12. Fitting the resonance curve to a lorentzian, I measure the resonant frequency to be 9.581 GHz and the Q to be $2.60(4) \times 10^3$. As expected, the
resonant frequency of the second harmonic mode is almost twice that of the first. The diminishing Q is likewise expected but may be exacerbated by increased structure in the baseline transmission spectrum (that measured above the superconducting critical temperature) interfering with the superconducting resonance.

After the transmission spectra seen in the figures above were taken, I removed the probe from the PPMS and added a Cr$_7$Mn sample before reinstalling the probe in the PPMS. It was then after removing the probe again, removing the sample from the resonator, and reinstalling the probe again that I took the following data measuring characteristics of the resonant peaks as a func-
Figure 2.12: Transmission spectrum at $T=1.8$ K for microwave source power equal to -31 dBm and no applied field, showing the resonance peak of the resonator’s second harmonic mode.

The resonance peaks show significant dependence on the applied field, presumably stemming from applied fields diminishing the superconductivity of the Niobium. Fig 2.13 shows how resonant frequency depends on field. As can be seen, the data in this figure follows a smooth, seemingly parabolic curve, decreasing with increasing rapidity as field increases. The data goes up to $H = 2000$ Oe which was near the highest fields we were able to reach and still
see a resonance peak. We would expect to be able to go to much higher fields without such a substantially diminished resonant peak but suspect that either there’s some small angle between the surface of the resonator and the applied magnetic field that is causing the resonator to see a small transverse field, or that the magnetism of the SMA connectors used in our probe are resulting in bending of the magnetic field lines, again causing the resonator to see a small transverse field.

Figure 2.13: Resonant Frequency as a function of Applied Field for the resonator without coupling to a sample.

Fig 2.14 shows the width at half maximum of the resonance peaks as a function of applied field. The width increases only slightly up to fields of 1500 Oe before rapidly increasing.
2.2 Circuit Board and Probe Considerations

The resonator and the SMMs are the core of the physics of my thesis. Ostensibly, the remaining pieces of my apparatus, the circuit board to which the resonator is attached, the probe, and the connectors that bring all these pieces together, are merely the support that allow me to study the behavior of the resonator-SMM system. That being said, there are many important considerations taken into account when designing, constructing, and putting together these remaining pieces, to insure the absolute best possible functioning of the resonator and to insure that the magnetic fields and temperatures in which the resonator-SMM system are situated are what I expect them to be.
Most notably, the circuit board is designed to roughly match the resonator’s 50 Ohm impedance and to minimize any parasitic resonances, mentioned above, as much as possible. The circuit board was constructed on a CNC machine from the design seen in Fig 2.15. The circuit board itself is a coplanar waveguide with a central conducting strip and gaps on either side of this strip. The ratio of the central conducting strip to the gaps, throughout the design is calculated to have 50 Ohm impedance. The dimensions of the wider portion of the coplanar waveguide, on either side of the design, are designed to allow for our SMA launch connectors to fit on the ends of the circuit board. The thin central portion of the coplanar waveguide is designed to have dimensions close to those of the coplanar waveguide on either end of the resonator chip (the portion on either side of, rather than in between, the two coupling capacitors). Refer to Appendix A for more information on the impedance calculations and the specific dimensions of the circuit board. The design is cut into a PCB board with copper plating on both sides, as the coplanar waveguide dimensions for 50 Ohm impedance matching are much more workable in the case of a second ground plane.

Furthermore, the central square seen in the design is cut out to allow for placement of the resonator so as to make the top of the resonator roughly even with the top of the circuit board. Along with having a relatively simple design, with little going on besides the coplanar waveguide, this central pit in which we place the resonator was crucial for minimizing parasitic resonances. The simple design allowed for few possibilities of parasitic resonances spawning from undesired current paths in the ground plane and allowed for easy bonding
from the resonator to the ground plane. The central pit, which allows the resonator to lie level with the circuit board, makes for effective bonding from the resonator to the circuit board. The resonator is bonded to the circuit board using an aluminum wire bonder. While bonding, I make as many bonds as possible, several from between the central conductors of board and resonator on either end and then dozens between the resonator’s and the board’s ground planes all around each side of the resonator. I attempt to make these bonds as short as they can be made while still being functional. The goal is to approximate, through bonding, having a uniform connection from board to resonator all around the resonator, on either side of both the ground plane and the central conductors. Fig 2.16 shows an overhead view of the bonded chip seen under a microscope. I cannot stress enough how important the efforts for both impedance matching and reducing parasitic resonances wherever possible have been for seeing superconducting resonances with workable Qs. With less effective equipment, we would routinely see resonances with Qs of, at best, a few hundred. Now, we are consistently seeing Qs of several thousand. There
are still sources of parasitic resonances, including the second ground plane (though the tradeoff of not having it is the inability to make a rough 50 Ohm impedance coplanar waveguide on the circuit board). The parasitic resonances from this second ground plane could be removed with vias that connect the ground planes on either side of the circuit board, though we don’t have the capabilities to easily make those in our own machine shop.

Figure 2.16: Microscope view of a bonded resonator chip with a Cr$_7$Mn crystal sample lying on it.

The circuit board is connected to the remainder of the probe, which can be seen in Fig 2.17, on either end by SMA launch connectors. The SMA connectors used here and those used elsewhere in the probe, we have discovered recently, are magnetic and thus may be a source of some of the issues we have had related to magnetic field control. We therefore look to possibly replace these in the future with non-magnetic connectors. Most of the probe is constructed from stainless steel coaxial cables. The stainless steel is important
in not conducting heat, so that we can get the sample chamber where measurements take place down to temperatures as low as 1.8 K without much difficulty. The probe uses two coaxial cables and two G10 rods all held snugly in place along the length of the probe. The two G10 rods allow the probe to be relatively stable while transported to and from the PPMS.

Figure 2.17: Overhead view of probe consisting of stainless steel coax cables and G10 support rods.

Figure 2.18: Circuit board holder which fits snugly both around the circuit board and inside the PPMS chamber.

As mentioned in the previous section, the superconducting resonances diminish with increased applied magnetic field. To maximize the field in which we continue to see these resonances, we would like to line the resonator up to be precisely parallel to the applied magnetic field. The piece shown in Fig 2.18 was designed and constructed to fit snugly in the PPMS while holding the circuit board tightly in place in an orientation that minimizes the angle between
the resonator and the applied field, which is oriented vertically in the sample chamber, as much as possible.

2.3 Cr\textsubscript{7}Mn and Mn\textsubscript{3} Sample

This thesis covers experiments with two SMMs, Cr\textsubscript{7}Mn and Mn\textsubscript{3}. I will expand greatly on the properties of the Cr\textsubscript{7}Mn sample in the next chapter, but for now will cover some of the basic practical issues with working with the crystal SMM samples at our disposal.

![Image of Cr\textsubscript{7}Mn crystal](image)

Figure 2.19: Close up view of an individual crystal sample of Cr\textsubscript{7}Mn. The numbers indicate the axial direction of each of the crystal’s faces. Image courtesy of Dr. Jonathan Baugh.

The Cr\textsubscript{7}Mn crystals we have were created by Dr. Jonathan Baugh. The molecule’s full name is [Cr\textsubscript{7}MnF\textsubscript{8}(O\textsubscript{2}CCMe\textsubscript{3})\textsubscript{16}]\textsuperscript{−} [14]. The crystals are green in color and range in size, but mostly have width and length dimensions on the order of tens to hundreds of \(\mu m\). A closeup of an individual crystal of Cr\textsubscript{7}Mn
can be seen in Fig 2.19. As opposed to many other SMMs, these crystals don’t have a uniform shape with an easily identifiable easy axis. This complicates working with these crystals, though in our attempts to perform spectroscopy on the molecule by coupling a crystal to a resonator, we felt we could make the assumption that some portion of the easy axis would be lying parallel to the resonator.

The Cr$_7$Mn crystal sample has a pyramidal shape with easy axis running through the apex of the pyramid. This structure necessitates some angle, which will be described in more detail in Chapter 4, between the easy axis and the resonator, if we are to lay the sample flat on one of its sides on the resonator.
Chapter 3

A Magnetic Study of Cr$_7$Mn

In the process of preparing the experiments I perform in this thesis, I decided to study the magnetic properties of the Cr$_7$Mn crystal samples that I have. These studies were performed to determine first, if the samples were indeed magnetic, and second, whether they behave like crystals of individual, non-interacting S=1 molecules. Furthermore, the existing literature on Cr$_7$Mn goes into very little depth when describing the magnetic characterization of the molecule. I therefore took data looking at both the DC magnetization and the AC susceptibility of my sample as a function of applied field strength and temperature.

The data was taken in the PPMS, using the PPMS’s AC Measurement System setup for analyzing magnetic samples. The AC Susceptibility measurements are performed by applying a small alternating magnetic field in addition to whatever the constant applied magnetic field is. The system measures the magnetic response of the sample, using the same method described below for
measuring DC magnetization, and by dividing by the amplitude of the alternating field, we can get the AC Susceptibility. AC Susceptibility is thus given by

\[ \chi = \frac{dM}{dH} \]  

(3.1)

where \( dM \) is the small change in magnetization from the alternating field and \( dH \) is the amplitude of the alternating field. The DC Magnetization of the sample is measured by looking at the signal induced by moving the sample through copper coils. These tests were performed on a group of 10 crystals, packed together.

These tests produced a number of unexpected results, suggesting magnetic properties that don’t line up with the predictions we can make by considering the Hamiltonian for \( \text{Cr}_7\text{Mn} \) presented in Eq 1.10. While certain results of these magnetic characterization studies can be explained, others remain a mystery and require further tests. In this chapter, I will first cover some of the results and conclusions from the background literature discussing the synthesis and characterization of \( \text{Cr}_7\text{Mn} \) rings. I will then present theoretical simulations based on the published Hamiltonian for the molecule. I will follow this up with our data and in the process give an overview of diamagnetism and paramagnetism. And finally, I will discuss how our results diverge from our expectations, and how we plan to test possible explanations for this divergence.
3.1 Cr$_7$Mn Background

Heterometallic rings that are structurally identical to Cr$_8$ but have one Cr atom in the ring replaced by a different atom date back to 2003, when Larsen, et al. [14] reported on the basic synthesis and magnetic study of such rings. The paper describes a number of species of these heterometallic rings, including Cr$_7$Mn. The researchers present $\chi T$ a function of $T$, where $\chi$ is magnetic susceptibility, measured at a field of 1 T, and $T$ is temperature, for these molecules. For Cr$_7$Mn, $\chi T$ increases roughly linearly as a function of $T$ before beginning to plateau at around $T=50$ K (though it continues to increase more and more gradually all the way up to $T=300$ K). The paper claims that the low temperature $\chi T$ values suggest a $S=1$ system though it gives little explanation for how the researchers came to this conclusion.

Ardavan, et al. [8] present ESR spectroscopy results and data for measured $T_1$ and $T_2$ relaxation times as a function of temperature, as mentioned in Chapter 1. The paper also offers a discussion of the spin relaxation mechanisms in Cr$_7$Mn and gives the Hamiltonian that can be found in Eq 1.10.

The Hamiltonian given by Ardavan, et al. looks at a Cr$_7$Mn molecule as a single spin. Caciuffo, et al. [15] alternatively present the following Hamiltonian, considering the spins of each of the individuals atoms in the molecule and the individual interactions between these spins.

$$ H = \sum_{i=1}^{6} J_{Cr-Cr} s_i \cdot s_{i+1} + J_{Cr-Mn}(s_7 \cdot s_8 + s_8 \cdot s_1) + \sum_{i=1}^{8} s_i \cdot D_i \cdot s_i + \sum_{i<j=1}^{8} s_i \cdot D_{ij} \cdot s_j \quad (3.2) $$
In this Hamiltonian, $i$ indicates the atom site within the molecule, $i = 1 - 7$ referring to sites occupied by Cr and $i = 8$ referring to the site occupied by Mn. The Hamiltonian is divided into three parts, the first, consisting of the first two terms, describes the interactions between neighboring atoms within the molecule. The third term of the Hamiltonian describes the anisotropy of the individual ion in each individual atom within the ring, while the fourth term describes anisotropic coupling between these ions [15]. While I largely rely on the Hamiltonian presented in Eq 1.10, that looks at each Cr$_7$Mn molecule as a single spin, throughout the simulations given in this thesis, I will address our plans to further study the Hamiltonian in Eq 3.2, in the final section of this chapter.

3.2 DC Magnetization Simulation

The Hamiltonian we use to model the eigenstates and eigenenergies of Cr$_7$Mn is as follows

$$H = g\mu B \cdot S - DS_z^2 + E(S_x^2 - S_y^2)$$

(3.3)

where $S$, $S_x$, $S_y$, and $S_z$ are the spin angular momentum operators for a spin-$\frac{1}{2}$ system, $g = 1.9$, $D = 21$ GHz, and $E = 1.9$ GHz [8] (Note: this is the same Hamiltonian presented in the introduction. It is replicated here for the sake of convenience). Based on this model, we calculate the expected DC magnetization as a function of applied magnetic field for a crystal sample of Cr$_7$Mn given a particular orientation of the applied field relative to the
sample's easy axis. Along with $S_x$, $S_y$, and $S_z$, we define a spin angular momentum operator in the direction of the field, $S_n$, given by

$$S_n = S_z \cos(\theta) + S_x \sin(\theta) \cos(\phi) + S_y \sin(\theta) \sin(\phi)$$ \hspace{1cm} (3.4)

We diagonalize the Hamiltonian to find the eigenstates and eigenenergies of the molecule in a given applied field. From these eigenstates, we can calculate $<S_n>$ the expectation value of the spin angular momentum in the direction of the applied field with the equation

$$<S_{n,i}> = <\Psi_i | S_n | \Psi_i >$$ \hspace{1cm} (3.5)

where $\Psi_i$ is the ith eigenstate of the Hamiltonian. We then use Boltzmann’s statistics to determine the probability of a molecule being found in a given eigenstate, as below:

$$P_i = \frac{e^{-E_i/kT}}{Z}$$ \hspace{1cm} (3.6)

where $Z$ is the partition function given by

$$Z = \sum_{i=0}^{2} e^{-E_i/kT}$$ \hspace{1cm} (3.7)

summing over all eigenstates, where $E_i$ is the eigenenergy of the ith eigenstate. With the probabilities of being in each given eigenstate, we can calculate the overall magnetization using the following formula:
\[ M = \sum_{i=0}^{2} <S_{n,i}> P_i \] (3.8)

which is merely the sum of the product of the expectation value of the spin angular momentum in the direction of the applied field for a given eigenstate and the probability of being found in that eigenstate. We’re ignoring conventional units of magnetization for now.

Once we calculate magnetization as a function of applied magnetic field for a crystal lattice of Cr\textsubscript{7}Mn molecules with a given direction of easy axis relative to the direction of the applied field, we make the approximation that the grouping of crystals we study covers the full range of possible easy axis directions relative to the applied field because, to be able to study a sample of these crystals that will produce a relatively large signal, we pack together 10 individual crystals. The individual crystals face in an array of directions and furthermore have no easily identifiable easy axis in and of themselves. We therefore integrate the magnetization found in Eq 3.8 over possible values of \( \theta \) and \( \phi \) as defined in Eq 3.4.

The calculations described above were done using a Mathematica notebook that can be found in Appendix C. From these calculations, we produced the simulation curves shown in Fig 3.1. These simulations can be explained by considering the Cr\textsubscript{7}Mn molecules to be paramagnets. The following section fleshes out paramagnetism and uses it to describe the shapes of the simulation curves.
Figure 3.1: Calculated DC Magnetization as a function of applied magnetic field at temperatures between 1.8 K and 10 K.

### 3.3 Paramagnetism

Paramagnetism is one type of magnetic response to an applied magnetic field, where magnetic moments tend toward lining up with the applied field. The molecules that make up paramagnetic materials have individual magnetic moments. In the case of our Cr$_7$Mn sample, each individual molecule has a total spin of 1 and thus has a magnetic moment with three basis states, the $s=1$, $s=0$, and $s=-1$ states, which describe the orientation of the molecule’s magnetic moment. Without an applied magnetic field, paramagnetic materials tend to have no net magnetic moment, as thermal activity creates a situation in which individual magnetic moments are randomly oriented throughout the material.
Paramagnetic materials are distinguished by their positive susceptibility to applied magnetic fields. When a field is applied, the magnetic moments tend toward attraction to the magnetic field, such that the magnetization of the material is in the direction of the field.

For a mathematical explanation of the paramagnetic response to an applied magnetic field, consider an ideal paramagnet, a system of non-interacting ions with equal non-zero total spins and no anisotropy. While paramagnetism, in reality, is governed by quantum mechanical principles, let us start by considering paramagnetism from a classical viewpoint. We can calculate the energy of the magnetic moment of an ion in the system situated in a magnetic field using the equation

\[ E = -\mu \cdot \vec{B} = -\mu B \cos(\theta) \]  

(3.9)

where \( \theta \) is the angle between the magnetic moment and the direction of the magnetic field. Using Boltzmann statistics, we can express the probability that a given magnetic moment is at an angle between \( \theta \) and \( \theta + d\theta \) relative to the magnetic field as

\[ p(\theta) = \frac{e^{-E_\theta/kT} \sin(\theta)d\theta}{\int_0^\pi e^{-E_\theta/kT} \sin(\theta)d\theta} = \frac{e^{-\mu B \cos(\theta)/kT} \sin(\theta)d\theta}{\int_0^\pi e^{-\mu B \cos(\theta)/kT} \sin(\theta)d\theta} \]  

(3.10)

With this probability, we can calculate the magnetization of the paramagnet by adding up the individual contributions of each individual magnetic moment. The equation that gives magnetization then is
where $N$ is the total number of spins within the system. Plugging the result in Eq 3.10 into Eq 3.11, we get the following for magnetization:

\[ M = N \mu \int_0^\pi e^{-\frac{\mu B \cos(\theta)}{kT} \sin(\theta) \cos(\theta)} d\theta \] (3.12)

Solving the integrals, we come to the resulting magnetism, given in the following form:

\[ M = N \mu [\coth(\frac{\mu B}{kT} - \frac{kT}{\mu B})] \] (3.13)

So far, I have shown how to reach the functional form seen in Eq 3.13 using a classical consideration of the magnetic moments in a paramagnet. In fact, these magnetic moments can’t take on any direction relative to the applied magnetic field and instead can only take on $2J+1$ discrete states where $J$ is the total angular momentum quantum number [16]. The fundamental difference here then comes in Eq 3.12 where the integrals in the numerator and denominator that give the magnetism in the classical treatment should be replaced by discrete sums over all states. These discrete forms can be reformulated, giving the following result which is very similar in form to that in Eq 3.13:

\[ M = NgJ\mu_B[\frac{2J+1}{2J} \coth(\frac{2J+1}{2J} x) - \frac{1}{2J} \coth(\frac{x}{2J})] = NgJ\mu_B B(x) \] (3.14)
where $B(x)$ is known as the Brillouin function. $x$ is given by

$$x = \frac{J g \mu_B B}{kT}$$

The Brillouin function has the following Taylor Series expansion:

$$B(x) = \frac{J + 1}{3J} x - \frac{(J + 1)^2 + J^2}{90J^3} (J + 1) x^3 + ...$$

Consider the $x \ll 1$ case. In this case, each of the subsequent terms after the first rapidly fall off so we can make the approximation,

$$M = NgJ \mu_B B(x) = \frac{Ng^2 J(J + 1) \mu_B^2 B}{3kT} = \frac{CB}{T}$$

where $C$ is called Curie’s constant and the linear dependence between $M$ and $\frac{B}{T}$ is known as Curie’s law. The derivation of Curie’s Law presented throughout this section is adapted from the derivation found in [17]. Before feeling comfortable making this approximation, we should consider the condition, $x \ll 1$, more closely. This means $\frac{J g \mu_B B}{kT} \ll 1$ which, no matter the temperature, will be the case at low enough fields.

Let's consider this picture of paramagnetism in the context of Cr$_7$Mn and the simulations presented in Fig 3.1. The anisotropy in Cr$_7$Mn makes it not an ideal paramagnet. Looking at the Hamiltonian in Eq 3.3, there are two anisotropic terms. The energy scale of the $DS_z^2$ term is set by $D$ which is 21 GHz and the energy scale of the $E(S_x^2 - S_y^2)$ term is set by $E$ which is 1.9 GHz. 21 GHz is just about equivalent to 1 K when using Boltzmann’s and Planck’s constants to convert temperature into energy. The anisotropic terms
are on a lower energy scale than the temperature energy scale for the entire range of temperatures at which we make our measurements. Though for the lowest temperatures at which we take measurements (ie 1.8 K), the energy scales are on the same order of magnitude, we can still roughly approximate our system as one in which the anisotropy can be ignored in the temperature regime we study.

So we can describe the simulations shown in Fig 3.1, in terms of the equations for magnetism presented in the above discussion of paramagnetism. For each curve in the simulations, there’s a positive dependence of magnetization on \( H \), the applied magnetic field, that, at low enough fields, can be approximated as a linear dependence. For each curve, \( M=0 \) when \( H=0 \), reflecting the zero-field behavior of paramagnets. The magnetization also shows a very clear temperature dependence, increasing more gradually with field at higher temperatures. Not only does the magnetization increase more gradually with field at higher temperatures; it also maintains a roughly linear dependence on the field up to higher fields as temperature increases, similar to what would be expected given the relationship between field and temperature offered by Curie’s Law. For each curve, the linear dependence starts to break at high enough field and ultimately the magnetization plateaus, which is likewise the case in the Brillouin function relationship between field and magnetization presented in Eq 3.14. Given the simulations in Fig 3.1 and a qualitative description of how they compare to the ideal paramagnet, I will now delve into the actual magnetization and AC Susceptibility data found for our sample of Cr\(_7\)Mn.
3.4 Diamagnetic Effects

The raw measurements for DC magnetization as a function of applied magnetic field are shown in Fig 3.2. As should be evident, at fields beyond 1 T the magnetization appears to decrease roughly linearly with a relatively large slope as magnetic field is increased. This result runs counter to the magnetization simulations discussed previously. We interpret this dramatic decrease in magnetization as a function of field to be the result of diamagnetic effects, which are negligible at low fields compared to the sample’s paramagnetic effects, but begin to appear dramatically as the magnetization would otherwise plateau.

![Magnetization vs. Field](image.png)

Figure 3.2: DC Magnetization measured as a function of applied magnetic field for a range of temperatures.
Diamagnetic effects in non-metallic materials are the result of the electrons in the material acting to oppose a change in magnetic field. Again, in deriving these effects, I am going to begin with a classical consideration of the behavior of these electrons. Diamagnetism can be thought of in terms of Lenz’s law. Lenz’s law can be stated as such: a current loop acts to oppose changes in magnetic flux through that current loop. Diamagnetism then comes from this opposition to changing magnetic flux [17]. To consider this explanation in more detail, let’s consider an electron moving in a circular path with angular velocity $\omega$. This circular path then can be thought of as a current loop where the current, the amount of charge passing a point in a given time, can be written as

$$ I = -\frac{e\omega}{2\pi} $$

(3.18)

The relationship between magnetic moment and a current loop is given by

$$ \mu = IA $$

(3.19)

so we can write the magnetic moment as

$$ \mu = -\frac{e\omega A}{2\pi} $$

(3.20)

where $A$ is the area of the loop. An applied magnetic field will induce a change in the angular frequency, $\Delta\omega$, which will in turn induce a change in the magnetic moment of the electron. To determine this change in angular frequency, consider an electron initially in circular motion with angular frequency, $\omega_0$.  

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There’s a centrifugal force, $F$, associated with this motion, equal to $m\omega_0^2r$ where $r$ is the radius of the electron’s circular path and $m$ is the electron’s mass. Once a field is applied, we can appeal to Lorentz’s law for charged particles in an electromagnetic field, given by

$$F_L = q[E + (v \times B)]$$

(3.21)

where $q$ is the charge of the charged particle, $E$ is the electric field, $v$ is the particle’s velocity, and $B$ is the magnetic field. Now we can write the following equation of motion for an electron after a field is applied:

$$m\omega^2r = F + F_L = m\omega_0^2r - e\omega r B$$

(3.22)

where $\omega$ is the electron’s angular frequency after a field is applied. With some algebra, this becomes

$$\omega^2 - \omega_0^2 = -e\omega B/m$$

(3.23)

$\Delta\omega$ then is $\omega - \omega_0$. With some more algebraic manipulation, and the assumption that $\Delta\omega$ is much less than $\omega$ or $\omega_0$, we can see that the change in angular frequency induced by a magnetic field is given by

$$\Delta\omega = eB/2m$$

(3.24)

This expression for the change in angular frequency of an electron after applying a magnetic field is called the Larmor Frequency, the prior derivation.
of which was adapted from [16]. We thus get the following for the change in magnetic moment due to the applied field:

\[ \mu = -\frac{e^2 BA}{4\pi m} \]  

(3.25)

We can extend our consideration from a single electron in an atom to the change of magnetic moment of an entire atom, with \( Z \) electrons. Then for a system of \( N \) atoms, the magnetic response to an applied field is given by,

\[ M = N\mu = -N\frac{Ze^2 BA}{4\pi m} \]  

(3.26)

Taking \( e, A, m, \) and \( N \) to be constant then, we find that the diamagnetic response to an applied field has a negative linear dependence on the field, which is what we see to be the case looking at the high field data shown in Fig 3.2. Furthermore, unlike paramagnetism, diamagnetism is entirely independent of temperature, which will be important to note when considering how we subtract off the diamagnetic effects in Fig 3.2.

### 3.5 DC Magnetization Measurements

Given that diamagnetic effects create a negative linear relationship between magnetization and applied field, we can subtract off these effects in our measurements by just subtracting a fixed slope, independent of temperature, from all the measurements. This fixed slope is found by fitting the \( T=1.8 \) K DC Magnetization measurements, between \( H=6 \) T and \( H=9 \) T, to a line. We
choose only the highest field measurements to do the fitting so as to ensure we’re in the regime, in our data, of only diamagnetic effects. Subtracting this slope from each set of DC Magnetization measurements results in the data shown in Fig 3.3.

![Graph showing DC Magnetization measurements as a function of applied magnetic field. A fixed slope, calculated by fitting the high field portion of the T=1.8 K measurements, is subtracted from each of the raw magnetization curves to subtract out the diamagnetic effects seen in Fig 3.2.](image)

Figure 3.3: DC Magnetization measurements as a function of applied magnetic field. A fixed slope, calculated by fitting the high field portion of the T=1.8 K measurements, is subtracted from each of the raw magnetization curves to subtract out the diamagnetic effects seen in Fig 3.2.

Even subtracting out the diamagnetic effects, the DC Magnetization measurements don’t conform qualitatively to the predicted response to increasing field seen in Fig 3.1. While what we see is a paramagnetic response to magnetic field, showing increasing magnetization in the direction of increasing field, the measurements are temperature independent in the low-field regime. This runs
completely contrary to the results expected given how magnetization is calculated from the Hamiltonian. Temperature comes up repeatedly throughout the calculations that went into producing the simulations in Fig 3.1. And furthermore, with Curie’s Law we see an inverse relationship between magnetization and temperature. For there to be no temperature dependence at all at low fields doesn’t seem to make any sense and represents a particularly unexpected finding in performing these magnetic studies. For another view of this puzzling result refer to Fig 3.4, which plots DC Magnetization as a function of H/T. As a note, I have subtracted diamagnetic effects out of all of the following figures, including Fig 3.4.

![Figure 3.4: DC Magnetization measurements as a function of applied magnetic field divided by temperature with diamagnetic effects subtracted out of the measurements](image)

Figure 3.4: DC Magnetization measurements as a function of applied magnetic field divided by temperature with diamagnetic effects subtracted out of the measurements
Based on Eq 3.17, we would expect magnetization measurements at different temperatures to map onto a single curve when plotted as a function of H/T. We can even see such a thing happening in our system when replotting the simulations in Fig 3.1 as a function of H/T instead of H as can be seen in Fig 3.5.

![DC Magnetization calculated as a function of H/T for a range of temperatures.](image)

Figure 3.5: DC Magnetization calculated as a function of H/T for a range of temperatures.

As the measurements in Fig 3.4 show, at high fields, as the curves plateau, this scaling to a single curve does appear to be the case, with each curve mapping onto a single curve at fields above 15000-20000 Oe/K. However, in the regime where H/T is less than around 15000-20000 Oe/K, the magnetization measurements don’t precisely scale onto the same curve when plotted against
H/T. This represents the same unexpected result as shown in Fig 3.3, though presented differently. I should stress again that this result is extremely unusual and has been, and to a large extent still is, a source of major confusion and speculation. In the final section of this chapter, I will present some of the possible explanations developed to potentially explain this result.

### 3.6 AC Susceptibility Measurements

Throughout this section, I will describe the AC Susceptibility measurements made on our sample, discussing both expected and actual results of these measurements. AC Susceptibility describes the response of the magnetization of a given material to a magnetic field. By definition, it is a constant of proportionality relating magnetization and applied field as seen in Eq 3.1.

In Fig 3.6, we see measurements of $\chi T$ as a function of $T$ for temperatures up to 50 K. The relationship between $\chi T$ and $T$, for ideal paramagnetic materials, is given by

$$\chi T = (M/H)T = C$$  \hspace{1cm} (3.27)

where $C$ once again is Curie’s constant. Again, I should note that Cr$_7$Mn isn’t an ideal paramagnet, given its anisotropy. That being said, I will continue to rely on Curie’s Law as, in our temperature regime, it has proven to be an effective approximation of the magnetization behavior we expect to see, based on our simulations. Because the only applied field, in this case, is the small alternating field (at most 10 Oe) used to make the AC Susceptibility
measurement, the linear approximation for magnetization in a paramagnetic material is expected to hold. We would thus expect the measurements in Fig 3.6 to be constant across all temperatures. Instead, we see a roughly linear dependence of $\chi T$ on $T$, again conflicting dramatically with our expectations. As with the measurements of DC Magnetization, which are independent of temperature, it would seem that our expectations diverge from what we find in the following manner:

$$M_{\text{exp}} = \frac{CH}{T}, \chi_{\text{exp}}T = (M_{\text{exp}}/H)T = C$$  \hspace{1cm} (3.28)

$$M_{\text{act}} = CH, \chi_{\text{act}}T = (M_{\text{act}}/H)T = CT$$  \hspace{1cm} (3.29)

where $M_{\text{exp}}$ and $\chi_{\text{exp}}$ are the expected magnetization and susceptibility and $M_{\text{act}}$ and $\chi_{\text{act}}$ are what we actually measure. There is then a factor of $T$ that we don’t expect that comes into the relationship between magnetization and $H/T$ across all of our measurements.

We further examine the relationship between $\chi$ and temperature in Fig 3.7, which shows measurements for $\chi$ as a function of temperature all the way out to 300 K.

Given the results seen in Fig 3.6, a roughly linear dependence of $\chi T$ on temperature, it’s not surprising that $\chi$ quickly levels off after rapidly decreasing at low temperatures, remaining roughly constant between 10 K and 90 K. However, we don’t have an explanation for the behavior seen out from around 90 K all the way to 300 K. Between around 90 K and around 120 K, $\chi$ seems to increase with temperature before decreasing steadily. This behavior
Figure 3.6: Measurements of AC Susceptibility multiplied by temperature as a function of temperature at H=0 Oe between 1.8 K and 50 K.

looks to be reproducible, as the higher resolution second temperature scan plotted in Fig 3.7 qualitatively follows the first temperature scan taken out to 300 K. However, at around 175-200 K, the measurements of $\chi$ begin to have irreproducible fluctuations that carry on all the way out to 300 K.

Sudden fluctuations in $\chi$ as a function of temperature can likewise be seen at relatively low temperature and with a constant applied field. Fig 3.8 shows $\chi$ measurements for three subsequent temperature sweeps, each taken at H=300 Oe.

As can be seen in these measurements, a seemingly random jump is made in the first temperature sweep upwards. For the remaining measurements the
Figure 3.7: Measurements of AC Susceptibility as a function of temperature at \( H=0 \) Oe between 1.8 K and 300 K. The measurements shown in blue were taken following the first measurements, shown in red, to attempt to reproduce and fill in the gaps in the first measurements.

dependence of \( \chi \) on temperature follows the dependence set out after the random jump rather than the dependence established before this jump. This includes the rest of the first temperature sweep and the entirety of the second and third temperature sweep. You can most obviously see this by the looking at the discrepancy between \( \chi \) values in the second and third sweep and the \( \chi \) values in the first sweep, between 1.8 K and around 3 K. We are unsure if this jump is the result of some artifact related to the apparatus used to make the measurements or involves some other mechanism, though we suspect that we are maintaining fairly precise control of temperature and field throughout the
measurements, and don’t see similar fluctuations when studying $\chi$ by sweeping the magnetic field at fixed temperatures. Perhaps though, the same mechanism, whether it be intrinsic to the sample or some experimental artifact, that induces this mysterious low temperature behavior causes the irreproducible fluctuations in $\chi$ at much higher temperatures as well.

As well as studying the dependence of $\chi$ on temperature, we measure $\chi$ as a function of magnetic field. The initial results of these measurements can be seen in Fig 3.9, which includes measurements at temperatures between 1.8 K and 2.94 K. We have similar measurements between 3.16 K and 10 K but each
of the curves looks qualitatively the same. A constant was subtracted from all of these measurements so that the curves level off at $\chi = 0$. This was done to subtract off diamagnetic effects.

Figure 3.9: Measurements of AC Susceptibility as a function of magnetic field for temperatures between 1.8 K and 2.94 K. All data are corrected, by subtracting off a fixed constant, to not include diamagnetic effects.

Across all temperatures, the AC Susceptibility of the sample increases at very low fields (up to around 300 Oe) before dropping off rapidly. One possible explanation for the initial increase in AC Susceptibility at low fields is tunneling between the two lowest energy eigenstates at low fields. This low field tunneling, in the regime where the two lowest energy eigenstates don’t change much with field, may cause a particularly sharp low-field increase in the magnetization reflected in Fig 3.9 by the initial jump in the derivative
of the magnetization as a function of field. This is because both tunneling and the effects described by the mechanism of paramagnetism laid out earlier in this chapter are resulting in spins changing their orientation to be in the direction of the magnetic field. At higher fields though there's an increasing unlikeness of tunneling at the avoided level crossing (refer back to Fig 1.4 to see the lowest energy eigenstates increasingly move apart from each other as field increases), removing this effect.

![AC Susceptibility graph](image)

**Figure 3.10:** AC Susceptibility calculated as a function of applied magnetic field.

We can see simulations of AC Susceptibility for our sample as a function of magnetic field, as a point of comparison, in Fig 3.10. These simulations take the same calculations seen in Fig 3.1 and differentiate them using Kalei-
dagraph’s derivate function. Again, we see a temperature dependence in the simulations that doesn’t show up in the actual measurements. I will ignore that for now, considering it reflects the same result that I discussed earlier when talking about Fig 3.3. Qualitatively, the simulations don’t resemble the actual measurements and very clearly don’t include an initial increase in susceptibility at low fields before dropping off, ruling out the possibility that low field tunneling causes the initial increase in AC susceptibility seen in Fig 3.9. The low field susceptibility in the simulations doesn’t increase but rather only decreases relatively gradually up to 1 T. The drastic difference here between simulations and actual data likely ties back as well to the unexpected temperature independent paramagnetism described above.

Given the relationship, \( \chi = \frac{dM}{dH} \), we expect to reproduce the DC Magnetization vs. magnetic field curves seen in the previous section, if we integrate the curves in Fig 3.9. Integrating the AC Susceptibility data, using Kaleidagraph’s integrate function, we get the curves seen in Fig 3.11, matched to the corresponding DC Magnetization curve. The DC Magnetization measurements had to be uniformly multiplied by 10. This factor of 10 comes from the fact that \( \chi \) is in fact a magnetization measurement divided by the \( dH \) in Eq 3.1 which in this case is 10 Oe across all measurements.

The DC Magnetization curves seem to roughly follow the corresponding integrated AC Susceptibility curves for temperatures of 3.04 K, 4.67 K, and 10 K. However there’s a large qualitative discrepancy between the corresponding 1.8 K curves. Because a fixed slope is subtracted from the integrated AC Susceptibility measurements to account for diamagnetic effects (the integration
Figure 3.11: Integrated AC Susceptibility measurements as well as DC Magnetization measurements as a function of magnetic field. The DC Magnetization measurements are uniformly multiplied by 10.

was done without subtracting a constant from the original AC Susceptibility measurements), it could be argued that the discrepancy may be alleviated by subtracting a different fixed slope. However, this would undoubtedly change the 3.04, 4.67 K, and 10 K integrated AC Susceptibility measurements as substantially as it did the 1.8 K measurements, greatly misaligning these curves from the corresponding DC Magnetization curves. While we don’t have a proper explanation for the discrepancy found here, we don’t believe this discrepancy is at the core of the differences between simulation and actual measurements discussed previously in this chapter, because the integrated AC Susceptibility measurements still show the same sort of temperature independent
paramagnetic behavior that has be seen throughout the DC Magnetization measurements.

3.7 Considering the Discrepancies between Theory and Experiment

As discussed above, the major discrepancy we have discovered in this magnetic study between our expectations and our results is the seemingly temperature independent paramagnetic response of the sample’s susceptibility at low fields. We expect the magnetization to be inversely proportional to temperature but in our measurements we see effectively no relationship between temperature and magnetization at low fields. We have considered multiple possibilities for what causes this phenomenon.

First, we plan to examine Eq 3.2 further, performing simulations for DC Magnetization based on this Hamiltonian rather than the one presented in Eq 3.3. We justify this further exploration of Caciuffo, et al.’s Hamiltonian based on results presented in their paper. They offer a plot of the lowest eigenenergies for Cr$_7$Mn, seen in Fig 3.12. They argue that the S=1-4 lowest eigenenergies can be fit to a parabola when plotted as a function of total spin. These energy levels exist at increasingly high energy (and thus temperature on an analogous temperature scale) with increasing total spin. It’s possible that this relationship can account for the extra factor of T seemingly dictating the relationship between magnetization and applied field, in our sample [15].

The discrepancy could also come from the interactions between nearby
Cr$_7$Mn molecules within the crystals. To either provide evidence for or rule out this possibility, we are asking Dr. Baugh to produce new Cr$_7$Mn samples, using a method that would space out the individual molecules within the sample substantially more than in our current sample.

It’s possible that there’s some other explanation as well, relating to the ring structure of the individual molecules. Determining what the explanation is, through testing of new samples and a careful exploration of Caciuffo, et al.’s Hamiltonian will be the first step in determining how to move the experiment forward.

At this point, we have still made efforts at performing low-field spectroscopy on the sample, as will be discussed in the next chapter. The behavior of the sample only begins to conform with our expectations regarding its magnetic properties at fields above around 1 T. This is a significantly higher field than that at which we could reasonably expect any transitions between the two lowest eigenstates. Attempting to peform ESR spectroscopy at and around 1
T would require a much higher frequency resonance than we could possibly expect to see in any of our resonators. We start running into major problems, at this point, even just applying fields greater than .2 T. The idea of doing low-field spectroscopy relates largely to the fact that the low-field regime is, based on our simulations of the lowest energy eigenstates for Cr₇Mn, the sweet spot in our experiment so only working at much higher fields would push off the testing of the sweet spot principle that’s at the heart of these experiments. Furthermore, our resonators, at this point, appear to be unable to go above, at most, .2 T before their superconducting resonance peaks completely disappear, though we believe we should be able to go higher and are currently testing reasons for the issues we’re having at higher fields.
Chapter 4

ESR Spectroscopy

In this chapter, I will describe the efforts we’ve taken to perform Electron Spin Resonance (ESR) spectroscopy on two SMM crystal samples. ESR is a procedure for studying paramagnetic materials that’s similar to Nuclear Magnetic Resonance (NMR), though it exploits the magnetic properties of electrons rather than those of atomic nuclei [18].

I will begin this chapter by offering some background on ESR spectroscopy and comparing the basic setup of ESR spectroscopy to that of our own experiment. I will follow that by presenting ESR spectroscopy simulations and going through the calculations used to develop these simulations. I will then discuss our efforts at performing ESR spectroscopy on Cr$_7$Mn and how our expectations as to what we would find compare to our actual results. Finally, I will discuss similar experiments performed on a Mn$_3$ crystal sample and the results found in those experiments.
4.1 Background on ESR Spectroscopy

ESR spectroscopy is a procedure used to study paramagnetic materials, such as our $Cr_7Mn$ sample. The unpaired electrons in paramagnetic materials, because of their spin angular momentum, act as magnetic dipoles. When a constant magnetic field is applied, there will be an energy splitting between the spin states of the unpaired electrons. If an rf (radio frequency) radiation field is then applied, it can cause transitions between these spin states, depending on the frequency of the rf field.

![Energy splitting of spin states](image)

Figure 4.1: Energy splitting of the spin states of unpaired electrons due to a constant magnetic field

Traditionally, ESR is described using a picture of the energy splitting for
unpaired electrons like that seen in Fig 4.1. I will describe this picture in terms of the simple case of a system of one unpaired electron, where $s=1/2$. The system splits into two levels upon application of a magnetic field, with energies given by

$$E = g\mu_B B m_s$$  \hspace{1cm} (4.1)$$

where $m_s = \pm 1/2$ is the unpaired electron’s spin quantum number. The energy difference between the two states is then given by

$$\Delta E = g\mu_B B$$  \hspace{1cm} (4.2)$$

Furthermore, in traditional ESR, the rf field is then applied perpendicularly to the constant magnetic field, as seen in Fig 4.2. In this figure, $\omega_0$ is the precession frequency of the electron spin around the constant magnetic field and is given by Eq 4.2, transformed into units of frequency. $\omega$ is the rf field frequency. In the rotating frame, where the frame’s rotation is equal to $\omega$, the precession frequency of the electron spin, $\omega'$, is simply $\omega - \omega_0$.

Transitions between the electron’s two spin states occur when $\omega' = 0$ which we call the resonance condition. This resonance condition is thus given by the equation

$$\Delta E = g\mu_B B = \hbar \omega$$  \hspace{1cm} (4.3)$$

Because of the transitions between spin states, one expects to see an absorption of the power from the incoming rf field, into the system of unpaired
electrons, at the resonance condition, as I will flesh out further for our specific case later in this section. ESR spectroscopy then consists of varying the magnetic field to see the increased power absorption on resonance.

The above description of traditional ESR spectroscopy provides a basic understanding of how ESR works and is similar in principle to the ESR spectroscopy performed in this thesis. However there are a number of important differences between what I do in this thesis and what I’ve described above. One difference that should be evident is that Cr₇Mn is a molecule with two unpaired electrons whose collective spins add up to a total spin, s=1. I am thus looking at the splitting between energy levels in a three-state system, and in this case between the two lowest energy levels. The transitions are between an avoided level crossing, like the one seen in Fig 4.3. An avoided level cross-
ing is a case where the energy levels of a given system would cross at some value of a given parameter within that system. However, a perturbation to that system causes the energy levels to couple. The result of this coupling is the situation seen in Fig 4.3, where the energy levels repel one another [19].

Figure 4.3: Eigenenergies as a function of DC field transformed into units of energy, showing avoided level crossing. The line snaking back in forth along the $\epsilon$ axis represents the rf field used to drive transitions between the energy levels.

In this picture of the avoided level crossing, we see the two energy levels that form an avoided crossing as a function of the parameter $\epsilon$. The picture shows $\epsilon_0$, the transition energy between the two energy levels, $\Delta$, the tunnel splitting at the avoided level crossing, and an illustration of the rf field. As opposed to conventional ESR, we apply an rf field along the same direction as the constant magnetic field. This is because the important matrix elements that allow for transitions between the two lowest eigenstates in Cr$_7$Mn are the $\hat{S}_z$ matrix elements rather than the $\hat{S}_y$ or $\hat{S}_x$ matrix elements. The parameter

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\[ \epsilon = \epsilon_0 + \epsilon_1 \sin(\omega t) \] (4.4)

where \( \epsilon_1 \) is proportional to the magnitude of the rf field. The resonance condition, as before though, is the condition where \( \epsilon_0 \), the transition energy between the energy levels, is equal to \( \hbar \omega \). As with conventional ESR spectroscopy, we vary the constant magnetic field to examine the resonance.

### 4.2 ESR Spectroscopy Simulations

In this section I will describe the simulations we develop for our ESR spectroscopy experiments using Cr\(_7\)Mn, calculating the expected absorbed power, as a function of magnetic field. This section appeals to density matrix theory, a specific discussion of which can be found in Appendix B. To perform these calculations, we begin by diagonalizing the Hamiltonian found in Eq 3.3, setting the constant applied field to a particular value and direction, to attain the eigenstates and eigenvalues. After attaining the eigenstates, we calculate the \( \hat{S}_z \) matrix elements which are given by

\[ S_{z,i,k}^2 = | < \Psi_i | \hat{S}_z | \Psi_k > |^2 \] (4.5)

where \( \Psi_n \) is the nth eigenstate of the Hamiltonian and i and k are integer values between 1 and \( 2s + 1 \) (so 3 for this s=1 system).

We then set up the Bloch equations for our system. The Bloch equations
are a set of equations, first published by Felix Bloch [20], that describe the magnetization of a system in magnetic resonance procedures. Here, we use the “optical” Bloch equations, a formulation of the Bloch equations that can be generalized to any two level system. While we are working with a molecule with three energy eigenstates, we only see transitions in our system between the two lowest energy eigenstates and thus are only concerned with these states. We can therefore consider our system analogously to a spin-1/2 system with a “spin up” state and a “spin down” state. Realistically though for our system, at low fields, the two eigenstates we’re concerned with are superpositions, of the $|+1\rangle$ and $|-1\rangle$ basis states, which allows for the non-zero $\hat{S}_z$ matrix elements that make transitions between the eigenstates possible. At much higher fields, the lower and higher eigenstates can be approximated as the $|+1\rangle$ and $|-1\rangle$ basis states respectively. Here, any $\hat{S}_z$ matrix elements disappear because the eigenstates are merely the orthonormal ”spin-up” and ”spin-down” basis states. The consideration of our two-level system analogously to a spin-1/2 system allows for the generalized set of Bloch equations given by

\[
\frac{dv_1}{dt} = [\omega_v \times v]_1 - \frac{v_1}{T_2} \tag{4.6}
\]

\[
\frac{dv_2}{dt} = [\omega_v \times v]_2 - \frac{v_2}{T_2} \tag{4.7}
\]

\[
\frac{dv_3}{dt} = [\omega_v \times v]_3 - \frac{v_3}{T_1} \tag{4.8}
\]

[21]. Here, $T_1$ and $T_2$ are the two characteristic relaxation times for the system,
the first describing the relaxation of the magnetization into thermal equilibrium and the second describing relaxation due to quantum decoherence. \( \omega_v \) and \( \mathbf{v} \) are vectors, describing the applied field and the density matrix elements of the two-level system, respectively. The components, \( \omega_1, \omega_2, \) and \( \omega_3, \) of the \( \omega_v \) vector are given by

\[
\begin{align*}
\omega_1 &= V_{12} + V_{21}, \\
\omega_2 &= V_{12} - V_{21}, \\
\omega_3 &= \epsilon_0 / \hbar = \omega_0
\end{align*}
\] (4.9)

where \( \epsilon_0 \) is the transition energy between eigenstates as described in the previous section. \( V_{12} \) and \( V_{21} \) are matrix elements of the \( V(t) \) operator. For our system, with a driving rf field, the \( V(t) \) operator is given by

\[
V(t) = g \mu_B B_1 \cos(\omega t) \hat{S}_z
\] (4.10)

where \( B_1 \) is the amplitude of the rf field and \( \omega \) is the driving frequency. [21] gives the following relationship which can help us in finding the matrix elements for this operator:

\[
<2|V(t)|1> = (1/2) <2|V|1> e^{-i\omega t}, <1|V(t)|2> = (1/2) <1|V|2> e^{i\omega t}
\] (4.11)

where \( V \) is the magnitude of \( V(t) \). The matrix element, \( <1|V|2> \) is given by \( g \mu_B B_1 S_{z,1,2} \), and likewise \( <2|V|1> \) is given by \( g \mu_B B_1 S_{z,2,1}^2 \). Looking back at Eq 4.5, knowing that \( <2|\hat{S}_z|1> \) is merely the complex conjugate of \( <1|\hat{S}_z|2> \), and recognizing that the absolute values of complex conjugates are
equal, we can see that $<\text{1}|\text{V}|\text{2}>=<\text{2}|\text{V}|\text{1}>$, as long as the matrix elements of $\hat{S}_z$ are real. From Eq 4.11 and Eq 4.9 then, we get the following for $\omega_1$ and $\omega_2$:

$$\omega_1 = \omega_R \cos(\omega t), \omega_2 = \omega_R \sin(\omega t)$$ (4.12)

where $\omega_R$ is equal to $g\mu_B B_1 \sqrt{S_{z,1,2}^2}$. $\omega_R$ is known as the Rabi frequency and describes the frequency at which magnetization oscillates due to transitions back and forth between the two eigenstates, before reaching a steady-state equilibrium where the magnetization remains constant.

The components of the $\mathbf{v}$ vector in the “optical” Bloch equations contain terms from the density matrix for our two level system. These components are given by

$$v_1 = tr[\rho(t)\sigma_x] = \rho_{12} + \rho_{21}$$ (4.13)

$$v_2 = tr[\rho(t)\sigma_y] = i[\rho_{12} - \rho_{21}]$$ (4.14)

$$v_3 = tr[\rho(t)\sigma_z] = \rho_{11} - \rho_{22}$$ (4.15)

where $\rho(t)$ is the density matrix and $\sigma_x$, $\sigma_y$, and $\sigma_z$ are the Pauli matrices [21]. Because density matrices are Hermitian, $\rho_{12}$ is equal to the complex conjugate of $\rho_{21}$. Furthermore, $\rho_{11}$ and $\rho_{22}$, which are the probabilities of being found in the ground state and the excited energy state respectively in the two-level system, add up to 1. We can therefore rewrite the components of the $\mathbf{v}$ vector as follows:
$$v_1 = 2Re[\rho_{12}], \quad v_2 = -2Im[\rho_{12}], \quad v_3 = 1 - 2\rho_{22} \quad (4.16)$$

If we plug in the components of the $\mathbf{v}$ and $\omega_v$ vectors to the Bloch equations given in Eq 4.6, Eq 4.7, and Eq 4.8, the result is a set of differential equations each with cosine and sine terms, that would be very difficult to solve directly. We can simplify these equations though taking a couple considerations into account. We can first simplify these equations by considering the magnetization’s steady state. After initial oscillations in the magnetization of our sample, the magnetization will reach a constant value, which reflects the balance between the excitation that comes from continuously driving the sample with an rf field and the tendency towards relaxation back to thermal equilibrium. In this steady state, the magnetization doesn’t change, and likewise the density matrix elements for the system, on which the magnetization depends, aren’t changing. We can therefore set each of the differential terms to 0. Furthermore, considering the system within the rotating frame of the driving field, we can apply the following set of transformations for the components of the $\mathbf{v}$ vector:

$$v'_1 = v_1 \cos(\omega t) - v_2 \sin(\omega t) \quad (4.17)$$
$$v'_2 = v_1 \sin(\omega t) + v_2 \cos(\omega t) \quad (4.18)$$
$$v'_3 = v_3 \quad (4.19)$$

Given the equivalence of the primed components of the $\mathbf{v}$ vector in the rotating
frame to the unprimed components in the non-rotating frame, and taking the result, given by [22], of applying these transformations to the Bloch equations, we get the following formulation of the Bloch equations:

\[(\omega - \omega_0)(-2\text{Im}[\rho_{12}]) - \frac{2\text{Re}[\rho_{12}]}{T_2} = 0\] (4.20)

\[-(\omega - \omega_0)(2\text{Re}[\rho_{12}]) + \omega_T(1 - 2\rho_{22}) - \frac{-2\text{Im}[\rho_{12}]}{T_2} = 0\] (4.21)

\[-\omega_T(-2\text{Im}[\rho_{12}]) - \frac{1 - 2\rho_{22}}{T_1}\] (4.22)

Taking \(\text{Im}[\rho_{12}], \text{Re}[\rho_{12}],\) and \(\rho_{22}\) to be the three variables in these equations, we now have a set of three linear equations with three variables. We can therefore solve this set of equations to extract values for each of the three variables. Of course, this requires that we plug in a number of values for constants that show up throughout these equations. \(T_1\) and \(T_2\) are estimated to be 10^6 and 50 ns respectively while we estimate \(B_1\) to be 2 Gauss. The value for \(\omega_0\) is given by subtracting the energy of the ground state from the energy of the excited state. We get these energies from diagonalizing the Cr_7Mn Hamiltonian given in Eq 3.3 for a particular applied constant magnetic field. Our simulations then perform calculations for a range of fields. Finally, we set a particular driving frequency each time we run the calculations (as will be seen later, we run our simulations at several different driving frequencies).

From solving the Bloch equations, we extract a value for \(\rho_{22}\) which we take to be the probability that a given molecule is in the excited state. To get the absorbed power from this, consider the dependence of the energy of the sample
on $\rho_{22}$. Given the energy difference, $\hbar\omega_0$, between the ground state and the first excited state, we can express the energy of the system as

$$E = (1 - \rho_{22})E_0 + \rho_{22}(E_0 + \hbar\omega_0) \quad (4.23)$$

Now let’s consider what happens if we turn the driving field off. Many of the excited spins will relax down to the ground state over time such that we can define a new time dependent value for the population of spins in the excited state (normalized to have a maximum value of 1), which here I will call $\rho(t)$. The population of spins in the excited state relaxes down to a thermal equilibrium level, such that $\rho(t)$ is given by

$$\rho(t) = (\rho_{t=0} - \rho_T)e^{-t/T_1} + \rho_T \quad (4.24)$$

where $\rho_T$ is the population of spins in the excited state at thermal equilibrium and $\rho_{t=0}$ is the initial increase, from thermal equilibrium, of the population of spins in the excited state, such that $\rho(0) = \rho_{22}$. Now we can write down the following time-dependent equation for the energy of the system:

$$E = (\rho_{t=0} - \rho_T)\hbar\omega_0 e^{-t/T_1} + \rho_T\hbar\omega_0 + E_0 \quad (4.25)$$

Differentiating this equation with respect to time, we get

$$\frac{dE}{dt} = P = \frac{-(\rho_{t=0} - \rho_T)\hbar\omega_0}{T_1}e^{-t/T_1} \quad (4.26)$$

In actuality, we continuously apply the driving field which, upon the system
reaching a steady state, exactly opposes the relaxation mechanism described
in the prior time-dependent equations for spin population in the excited state,
energy, and power. We therefore extract the \( t=0 \) value for power in Eq 4.26 as
that’s the power that must be balanced by the driving field in order to main-
tain the steady state. For our simulations then, we perform these calculations
for \( T=1.8 \) K, and over a range of fields, converting the value attained for the
absorbed power into dimensionless units, by dividing the results of calculating
power by the constant ratio, \( \frac{\hbar \omega}{T_1} \), seen in Eq 4.26. For each of the simulations
shown in this section, we perform these calculations considering a constant
field applied in the z direction. We run these calculations first for several dif-
ferent values of \( f \), the driving frequency (equal to \( \omega/2\pi \)). The values chosen
are 4.8 GHz, the approximate resonant frequency of the resonator employed
throughout this thesis, 4.2 GHz, the expected approximate resonant frequency
of the lowest frequency resonator we have available, and 3.8 GHz, the approx-
imate tunnel splitting of the lowest energy eigenstates for Cr\(_7\)Mn. The results
of these simulations can be seen in Fig 4.4.

As observed from Fig 4.4, the resonance in the power spectrum for \( f=4.8 \)
GHz occurs at \( H \approx 550 \) Oe, for \( f=4.2 \) GHz occurs at \( H \approx 400 \) Oe, and for \( f=3.8 \)
GHz occurs at 0 field. Looking back at Fig 1.4, the field value at which the
resonance occurs for both the \( f=4.2 \) GHz and the \( f=4.8 \) GHz resonators falls
within the regime where the eigenvalues of the two lowest energy eigenstates
for Cr\(_7\)Mn stay roughly constant as a function of field (ie the sweet spot). We
expect the result seen in Fig 4.4 that the resonance in the power spectrum
for \( f=\Delta \), the tunnel splitting, occurs at 0 field. One might ask then why our
resonators were not designed to have such a resonant frequency, which would allow us to examine a resonance at the true zero-field sweet spot. The reason for this is that our value for \( \Delta \) comes from the Hamiltonian found in Eq 3.3. As was made evident in Chapter 3, this Hamiltonian may not give the whole picture of the behavior of Cr\(_7\)Mn, and if in fact \( \Delta \), in our case, were even larger than 3.8 GHz, we would miss it entirely by employing a resonator with a 3.8 GHz resonant frequency.

We can also run the simulations for both the fundamental mode of our resonator and the second harmonic mode, as shown in Fig 4.5.

The resonant peak for the second harmonic mode occurs at around 1600-
Figure 4.5: Absorbed power spectrum, varying the magnetic field for the fundamental harmonic mode, $f=4.8$ GHz, and the second harmonic mode, $f=9.6$ GHz, of our resonator.

1650 Oe. Again looking back at Fig 1.4, it’s clear that the resonance thus occurs far enough away from the zero-field sweet spot that eigenvalues for the two lowest eigenstates change fairly significantly with changing field. Thus, the idea of performing ESR spectroscopy at the fundamental mode and the second harmonic mode of a resonator comparable to or the same as the one used throughout this thesis should allow for a stark comparison between spectroscopy in the sweet spot regime and spectroscopy away from the sweet spot. The depiction of second harmonic mode peak in Fig 4.5 is somewhat faulty as constant values are set as estimates for the relaxation times, $T_1$ and $T_2$, in the calculations performed for these simulations. In principle, as discussed be-
fore, $T_2$ in particular should be smaller further away from the sweet spot. The value for $T_2$ dictates the width of the resonance peak in the power spectrum. Therefore, we would hope that in performing ESR spectroscopy comparable to these simulations, the second harmonic mode resonance would be wider, relative to the fundamental harmonic mode resonance, than what we see here. However, these simulations should offer a good indication of the field at which we expect to see the resonance for the second harmonic mode. As a note, all calculations and simulations described in this section were done using a mathematica notebook given in Appendix C.

### 4.3 Cr\textsubscript{7}Mn spectroscopic data

The simulations presented in the previous section reflect what we ultimately strive to achieve in our studies of Cr\textsubscript{7}Mn. At this point, we have only attempted, for our current samples of Cr\textsubscript{7}Mn, basic spectroscopic experiments, intended to determine whether we are seeing a discernable signal from the sample.

These experiments resemble those presented in subsection 2.1.3, done to characterize our resonator’s response to a magnetic field. For a range of fields, we look at the transmitted power spectrum over a sweep of the rf field frequency, to determine how the resonant frequency and width of the resonant peaks found in these power spectra depend on field. The motivation for these experiments can be gleaned by understanding Fig 4.6, which gives a qualitative picture of the way both the energy of the excited eigenstate and the resonant
frequency of our resonator (without a sample) changes as a function of applied field. We expect the resonant frequency of the resonator and sample system to approximately follow the shape of the resonant frequency vs. field curve shown in Fig 4.6. However, approximately where the energy of the sample and the resonant frequency of the resonator are the same, we expect some step structure in the measurements of the resonant frequency of the coupled system, indicating the presence of the sample.

Figure 4.6: Rough sketch of the resonant frequency as a function of field for both the resonator, represented by the blue curve, and the sample, represented by the orange curve. The dashed black curve where the resonator curve and the sample curve cross, reflects qualitatively how we expect the resonant frequency vs. field measurements we take to differ, with a sample coupled to the resonator, from those without a sample.

With this basic picture of what a signal, from coupling of a sample to the resonator, should look like, we examine our own results from measuring the resonant frequency of our resonator, with a crystal sample of Cr$_7$Mn placed
on top, which are presented in Fig 4.7.

Figure 4.7: Resonant frequency measured as a function of magnetic field. The red data points come from taking measurements a smaller field increments than those used when making the measurements shown in blue.

While the measurements shown in Fig 4.7 shows some structure, especially in comparison to the analogous measurements shown in Fig 2.2 taken without a sample, we have little basis for knowing whether any of this structure reflects the presence of the sample. The structure doesn’t noticeably resemble the expected structure shown in Fig 4.6. Most, if not all of this structure, is likely to be a result of the undesired effects of not having our board lie completely vertically in the PPMS and of having magnetic materials, such as magnetic SMA connectors, used throughout our probe. While the same structure doesn’t show up in the measurements of only the resonator without
a sample shown in Chapter 2, the discrepancy may be due to the inability to precisely control either the effects of stray magnetic materials or how our board is oriented within the PPMS. Furthermore, the expected structure shown in Fig 4.6 is based on our determination of the eigenstates and eigenenergies for the Hamiltonian presented in Eq 3.3. As was described throughout Chapter 3, this Hamiltonian may not fully describe the crystal samples of $\text{Cr}_7\text{Mn}$ that we have. As we have yet to conclusively understand the magnetic properties of our sample, we likewise have yet to determine how the eigenstates and eigenenergies of our particular sample differ from those found by diagonalizing the Hamiltonian in Eq 3.3. With all of these considerations in mind, we can’t draw any conclusions from the efforts we’ve taken so far to spectroscopically analyze a $\text{Cr}_7\text{Mn}$ sample.

4.4 $\text{Mn}_3$ spectroscopic data

In attempting to gauge whether, with our current apparatus and resonator, we could definitively see a signal from a SMM coupled to our resonator, and in preparation for potential future experiments, examining dynamic effects of transitions at avoided level crossings, we perform the same spectroscopic experiments on a crystal sample of $\text{Mn}_3$.

$\text{Mn}_3$, chemically known as $[\text{NE}_4]_3[\text{Mn}_3\text{Zn}_2(\text{salox})_3\text{O}(\text{N}_3)_6\text{Cl}_2]$, is a molecule composed of three $\text{ Mn}^{III}$ ions, each with spin, $s=2$ [23], a crystal of which can be seen in Fig 4.8. The $\text{Mn}_3$ molecule then has a large total spin, $S=6$, and its behavior can be approximately described by the following Giant Spin
Hamiltonian

\[ \hat{H} = D \hat{S}_z^2 + B_4^0 \hat{O}_4^0 + B_4^3 \hat{O}_4^3 + B_6^6 \hat{O}_6^6 + g \mu_B \mathbf{B} \cdot \hat{S} \]  

(4.27)

where the last term in the Hamiltonian is the Zeeman term, and all the other terms reflect the molecule’s anisotropy [23]. The \( \hat{O} \) operators are defined operators, composed of the \( \hat{S}_z \), \( \hat{S}_x \), and \( \hat{S}_y \) operators and the \( B_q^p \) reflects the energy scale at which its corresponding operator effects the system’s anisotropy. As will be seen later on, I am only focusing on the Zeeman term throughout this section, when attempting to explore resonances within this system. I will therefore leave off further description of these anisotropic terms. It should be noted that the Giant Spin Hamiltonian doesn’t explicitly reflect the intramolecular interactions in Mn\(_3\) and that, like Cr\(_7\)Mn as seen in Eq 3.2, Mn\(_3\) can be described by a Multi Spin Hamiltonian [23, 24]. However, for the purposes of my current study of Mn\(_3\), I will only treat the Giant Spin Hamiltonian, focusing on the Zeeman term.

Fig 4.9 shows the energy levels for Mn\(_3\) as a function of applied magnetic field along the molecule’s easy axis. This figure was created by diagonalizing
Figure 4.9: Calculated eigenenergies for the $m_s = \pm 2 - 6$ energy levels of Mn$_3$ as a function of magnetic field.

As can be seen in Fig 4.9, the zero-field value for any given values of $\pm m_s$ are equivalent but the two levels corresponding to positive and negative $m_s$ values, of the same integer, split as a function of field due to the Zeeman term. The anisotropy effects the zero-field energy value of a given $\pm m_s$ set of levels. This anisotropy results in the $m_s = \pm 6$ pair of levels being the molecule’s ground state and each subsequently lower integer value of $m_s$ having a higher zero-field energy value. However, the splitting of these levels relative to each other, which is what we’re concerned with when considering resonances within the system, only depends on the Zeeman term and so we can ignore the specifics
of the anisotropy terms.

Based on the expression for energy given in Eq 4.1, the energy levels depicted in Fig 4.9, and the way the pyramidal Mn$_3$ is mounted on the resonator, we expect the resonance condition in our spectroscopic experiments for this sample to be given by

$$g\mu_B B\cos(\theta)\Delta m_s = hf$$  \hspace{1cm} (4.28)

where $\Delta m_s$ reflects the splitting between spin states (ie $\Delta m_s = 12$ for $m_s = \pm 6$). Thus the $\Delta m_s$ term in Eq 4.28 can be replaced by even integers between 2 and 12 to determine the fields at which we may expect to see resonances. The cosine term comes from the fact that the easy axis runs through the apex of the pyramidal sample. Given this geometry, laying the sample flat on the resonator, which we must do to expect any sort of coupling, necessarily causes the easy axis of the sample to be at some angle, which here we call $\theta$, to the constant applied magnetic field in the PPMS.

Our measurements of resonant frequency as a function of field can be seen in Fig 4.10. The reason each of these measurements begins at zero for zero field is that, to line up the temperature data for the purpose of comparison, I subtract off the zero-field frequency at that temperature from each set of measurements. One sees a small difference in the curves as we change temperature.

To examine this more closely, I subtract off the T=1.8 K measurements from each of the measurements, at corresponding field, at other temperatures. The subsequent results can be seen in Fig 4.11. We see then what perhaps could be the sign of a signal associated with one of the resonances for Mn$_3$
Figure 4.10: Resonant frequency measured as a function of magnetic field subtracting off the zero-field resonant frequency for each temperature.

described above. We would expect if we were to see a signal that it would show up more strongly as we raise temperature, because, as I will shortly explain, we are considering a resonance that would, based on our calculations, be associated with an excited state. Therefore, the higher the temperature we are working at, the higher probability a molecule within our sample has of being in this excited state and thus the more signal we would see from this excited-state resonance.

The negative peak at around $H=700$ Oe that seems to get larger with increasing temperature then could be a result of the Mn$_3$ sample. (Before going further, I would like to note that there are some erratic measurements
Figure 4.11: Resonant frequency measured as a function of magnetic field subtracting off first the zero-field resonant frequency for each temperature and then the T=1.8 K measurements that show up in the T=2.5 K data. These are believed to be spurious as they correspond to sharp changes in the baseline transmitted power at seemingly random fields, suggesting a possible loss of temperature control.) Liu et al.’s findings suggest that tunneling should only occur between the $m_s = \pm 6$ states and the $m_s = \pm 3$ states. Plugging in some numbers for Eq 4.28, we find that a resonance at $H=700$ Oe couldn’t possibly reflect tunneling between $m_s = \pm 6$ states but could reflect tunneling between the $m_s = \pm 3$ states depending on the angle, $\theta$, in our apparatus, defined above. Solving Eq 4.28 for $\theta$ based on a resonance at $H \approx 700$ Oe and a $\Delta m_s$ value of 6, we find $\theta$ to be approximately $66^\circ$. 

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We examine Fig 4.12 and Fig 4.8, both pictures of the same crystal taken from different view points, to attempt to get a rough estimate of the angle between the easy axis of the of the pyramidal crystal and the direction of the applied magnetic field. Based on these pictures, I would estimate an angle, $\theta$, that’s less than 66°, as was calculated to be the expected value of $\theta$. While it’s difficult to make any really precise estimate based on these pictures, my estimate of $\theta$ based on this crystal would be around 45°.

If what we see in Fig 4.11 does indeed reflect a small signal from the Mn$_3$ sample, then the discrepancy between its location and what we would expect, given an estimate of the angle a Mn$_3$ crystal would make relative to the applied magnetic field, could come from an error in estimating this angle or from differences in shape for different Mn$_3$ crystals. The crystal shown in Fig 4.12 and Fig 4.8 may be taller from its apex to the flat side opposite its apex than the crystal we have coupled to our resonator. The discrepancy could also be due to the crystal not being placed perfectly flatly on the resonator.
which would affect the angle, $\theta$.

![Figure 4.13: Double well potential giving energy as a function of a spin orientation. Each line within the wells represents a possible energy level for the molecule to be in. We see in this illustration a depiction of photon-assisted tunneling from the $m_s = -3$ energy level to the $m_s = 3$ energy level.](image)

It’s also possible that we aren’t seeing a true signal from the Mn$_3$ sample. Further tests of the resonator and further attempts to reproduce the data seen in Fig 4.11 could help us clarify whether what we’re seeing now is a signal or just an artifact. However, if what we are seeing is truly a signal, it would be an indication of photon-assisted tunneling, depicted in Fig 4.13. In the presence of a magnetic field, the splitting of energy levels is reflected in the off-resonance condition shown in the double-well potential, where corresponding energy levels don’t precisely line up on either side of the double well. This off-resonance condition makes tunneling between corresponding energy levels (ie from the $m_s = -3$ to the $m_s = 3$ level) unlikely, except when the presence of a photon increases the energy of a molecule in the lower energy level, allowing
the molecule to make the transition to the higher energy level. We may then be seeing photon-assisted tunneling from the $m_s = -3$ level to the $m_s = 3$ level.

![Graph showing width at half maximum as a function of magnetic field for several temperatures.](image)

Figure 4.14: Width at half maximum measured as a function of magnetic field for several temperatures.

Fig 4.14 and Fig 4.15 show $\Delta f$, the width at half maximum, and the amplitude of the resonant peak respectively as a function of magnetic field. While these measurements show structure and differ by temperature, we likewise have no more basis for concluding that what we see in these graphs reflects a signal than we do for Fig 4.11.
Figure 4.15: Resonant peak amplitude measured as a function of magnetic field for several temperatures.
Chapter 5

Conclusions

To harken back to the motivation for these experiments, we aim to perform spectroscopic studies on Cr$_7$Mn that will allow us to extract coherence times both near the zero-field sweet spot and away from this sweet spot. In comparing these coherence times, we hope to validate the sweet spot principle set out in the Introduction for an SMM. As of yet, these things have yet to be achieved, as even our initial spectroscopic studies offer little in the way of definitive results from which we know we are observing a signal from the Cr$_7$Mn sample.

However, what originally seemed to us to be a small digression for the sake of ensuring certain behaviors in our sample has given us unusual results that perhaps could shed light on very interesting physics. We, as of yet, don’t have a definitive interpretation of the unusual, temperature independent, paramagnetism we were seeing in our Cr$_7$Mn sample. One potential interpretation though perhaps could be obtained by considering the claim that Caciuffo et
al. make that the respective lowest energy levels for $S=1$, $S=2$, $S=3$, and $S=4$ can be fit to a parabola [15]. This interpretation would suggest an unusual set of physical mechanisms combining to seemingly perfectly cancel out the temperature dependence in Curie’s Law, which itself would beg for further probing and a more precise theoretical understanding of these opposing physical mechanisms.

It remains to be seen though whether we believe this interpretation to be the most likely one to describe our data. Future experiments with new samples should help us to determine whether the phenomena we’re seeing comes from interactions between individual molecules or from interactions within individual molecules. Furthermore, future work into performing simulations, like those seen in Chapter 3, using the Hamiltonian presented in Eq 3.2, may also shed light on what we might expect to see when running magnetic studies of Cr$_7$Mn.

A number of steps need to be taken before we can realistically get our spectroscopic studies of either Cr$_7$Mn or Mn$_3$ further off the ground. Significant work this year, as detailed in Chapter 2 of this thesis has already been put into improving the packaging for our superconducting resonator. Strengthening the probe, redesigning the circuit board, improving the wire bonds between the circuit and the probe, and stabilizing the circuit board within the PPMS have all helped in improving the quality factors of our resonator and improving our control of the magnetic field in which the resonator is situated. However, there are number of further improvements in the works. We are currently in the process of adapting our apparatus to work with the non-magnetic SMA
connectors that we have just recently attained and will soon see what sort of improvements come from this. Hopefully in the near future, we can make sure that the effects of stray magnetic materials don’t impinge upon our experiments and furthermore, that our resonator is truly set vertically to within a miniscule angle so that it’s orientation lines up nearly exactly with the magnetic field within the PPMS. When these improvements come together further thorough characterizations of the resonator’s response to magnetic fields, both at the fundamental mode and the second harmonic mode, will need to be conducted. Ideally, we will be able to uninstall and reinstall the probe and still be able to reproduce very closely the results of these characterization studies so that we have a true, reproducible set of background data to which we can compare our spectroscopic studies of the resonator once a sample is mounted.

Once we have the resonator and its packaging working as ideally as possible, we should be able to discern any signal, using similar techniques to those described in Chapter 4, that would be coming from a sample. We will hopefully be receiving new Cr$_7$Mn crystal samples from Dr. Baugh synthesized using the procedures used in [8] which may allow us to more accurately describe the molecules in these samples using the Hamiltonian in Eq. 3.3. If this is the case and we can then successfully perform spectroscopic studies on these samples akin to the simulations in Chapter 4, we will hopefully be able to deduce from these studies, coherence times both in the sweet spot regime and away from it. The next steps after that then would perhaps be to explore, if possible, the dynamical effects of the transitions between eigenstates in our sample, such as Rabi oscillations and spin echo. At this point though, it’s difficult to forecast
how far off these sorts of experiments are at this point, and it is quite possible that these experiments will run into further unforeseen complications.

For now however, we can take consolation in what quite possibly could be the observation of photon assisted tunneling in Mn$_3$. While future studies, with an improved apparatus, will need to be conducted to verify the results presented at the end of Chapter 4, the measurements presented so far reflect the stark possibility of an interesting observation of a unique physical phenomenon and could be an excellent starting point for a more thorough study of tunneling in Mn$_3$. 
Appendix A

Circuit Board Specifications

In Chapter 2, I offer a brief account of how I designed the circuit board used in our experiments. Here, I will give, in more detail, the specifications of the circuit board and the considerations that went into developing these specifications. Refer to Fig 2.15 for a picture of the layout of the circuit board.

The trenches of the circuit board are cut into one side of a circuit board materials with copper plating on both sides. The overall width of the circuit board is 1.008” while the overall height is .597”. The width measurement was taken from measuring our previous circuit board, though ultimately we change the connectors on either end of the circuit board, which required us to alter the probe to compensate for these changes. The height measurement was also taken from measuring our previous circuit board and is crucial for ensure that the circuit board fits, along with the rest of the probe, in the PPMS chamber.

In designing the coplanar waveguide on the circuit board, I first take into consideration the specifications of the resonator chip and the connectors we
use. The measurement, at either end of the circuit board, from the outer edge of one cavity in the coplanar waveguide to the outer edge of the cavity on the opposite side of the central conductor is .181”, so as to match the measurement between the legs of our launch SMA connecters. This allows the legs of these conductors to sit on the ground plane, while coming right up to the edge of the coplanar waveguide cavities. To determine the gap widths and the central conductor width for this section of the coplanar waveguide I use the follow set of equations.

\[ z_0 = \frac{60\pi}{\sqrt{\epsilon_{\text{eff}}}} \frac{1}{K(k) + \frac{K(kl)}{K(k'l')}} \]  

(A.1)

where \( k \) is given by the ratio of the central conductor width to the overall width of the central conductor plus both cavities. \( k', kl, \) and \( kl' \), are then given by

\[ k' = \sqrt{1 - k^2} \]  

(A.2)

\[ kl = \frac{\tanh\left(\frac{a}{4h}\right)}{\tanh\left(\frac{b}{4h}\right)} \]  

(A.3)

\[ kl' = \sqrt{1 - kl'^2} \]  

(A.4)

where \( a \) is the central conductor width, \( b \) is the width of central conductor and both gaps added together, and \( h \) is the circuit board’s thickness. Finally, to find the effective dielectric constant, \( \epsilon_{\text{eff}} \), we plug the dielectric constant of the circuit board material, \( \epsilon_r \) into the equation,
This entire set of equations is taken from [26]. Using these equations, I specify the central conductor width for the coplanar waveguide on either end of the circuit board to be .098" and the width of the cavities to be .042". The coplanar waveguide narrows towards the center so that the central conductor width approximately matches that on either end of the resonator chip. Again using the equations from above, I specify the central conductor width in this section of the circuit board to be .057" and the width of the cavities to be .008". The central conductor width is in fact a little larger than that on either end of the resonator chip. The reason for this is that I couldn’t make it any smaller without having to make the cavity widths smaller than can could be precisely cut using our CNC machine in the machine shop.

The length of the wider section of the waveguide and the narrower section are given by .415”, and .156” respectively. These specifications were made fairly arbitrarily. They take into account the width of the resonator chip and are made to ensure that the resonator chip can be bonded to the narrow section of the coplanar waveguide. The wider section is specified to be slightly longer than the legs of the SMA connectors so that the SMA connectors’ legs can lie entirely along the coplanar waveguide.

The square trench in the center of the circuit board is designed to fit our resonator. It measures .228” by .228” and .017” deep. These specifications were made to ensure that all resonators (which vary slightly by width and
length due to the imprecision of our dicing mechanism) can fit within the trench but that, for the most part, there isn’t much space between the ends of the resonator and the walls of the trench. The depth is specified so that the top of our resonators lie even with top of the copper material on the circuit board.
Appendix B

Density Matrix Theory

In this appendix, I will give a very basic overview of general density matrix theory as it is laid out in [21]. To begin with, I offer this basic definition of the density matrix, $\rho$, of a quantum system,

$$\rho = \sum_n W_n |\Psi_n> <\Psi_n|$$  \hfill (B.1)

where $|\Psi_n>$ are the independent states within a mixture, composed of spins with different, independent spin states. $W_n$ gives the percentage out of all the spins in the mixture of spins in the state of $|\Psi_n>$. The density matrix then is a sum that goes over all the independent states within the mixture.

Each of the states, $|\Psi_n>$, is a superposition of orthonormal basis states which we will call, $|\phi_1>$, $|\phi_2>$, etc. $|\Psi_n>$ can therefore be expressed in the following way:

$$|\Psi_n> = \sum_m a_m^{(n)} |\phi_m>$$  \hfill (B.2)
Plugging this back into Eq B.1, we get the density matrix equation,

$$\rho = \sum_{n,m',m} W_n a_m^{(n)} a_{m'}^{(n)*} |\phi_{m'}><\phi_m|$$

(B.3)

Given that we chose orthonormal basis states, we can calculate individual elements of the matrix given in Eq B.3 as follows:

$$\rho_{i,j} = <\phi_i|\rho|\phi_j> = \sum_n W_n a_i^{(n)} a_j^{(n)*}$$

(B.4)

From this equation, we can determine that $\rho$ is a Hermitian matrix meaning that the matrix element, $\rho_{i,j}$ is necessarily equal to the complex conjugate of the matrix element, $\rho_{j,i}$. We can also deduce that the matrix element along the diagonal, $\rho_{i,i}$, gives the probability of finding a spin in the mixture in the basis state $|\phi_i>$ and that this probability is given by

$$\rho_{i,i} = \sum_n W_n |a_i^{(n)}|^2$$

(B.5)

While plenty more can be said about density matrix theory, I won’t go into any further depth in this appendix, as this discussion lays out the basic principles that are appealed to in Chapter 4. As a note, this whole discussion of density matrix theory comes directly from [21] which goes into much greater depth on the subject than I do here.
Appendix C

Mathematica Notebooks
Bibliography


