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ROLE OF INTERNAL DEGREES OF FREEDOM IN THE QUANTUM TUNNELING OF THE MAGNETIZATION IN SINGLE-MOLECULE MAGNETS

by

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MS University of Central Florida, 2010

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics in the Department of Physics in the College of Sciences at the University of Central Florida Orlando, Florida

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Major Professor: Enrique del Barco
ABSTRACT

The prominent features of single molecule magnets (SMMs), such as the quantum tunneling of the magnetization (QTM), are conventionally understood through the giant spin approximation (GSA) which considers the molecule as a single rigid spin. This model often requires the inclusion of high order anisotropy terms in the Hamiltonian, a manifestation of admixing of low lying excited states that can be more naturally understood by employing a multi-spin (MS) description i.e. considering the individual spins and the interactions between ions within the molecule. However, solving the MS Hamiltonian for high nuclearity molecules is not feasible due to the enormous dimensions of the associated Hilbert space that put it beyond the capability of existing computational resources. In contrast, low nuclearity systems permit the complete diagonalization of the MS Hamiltonian required to sample the effect of internal degrees of freedom, such as exchange interactions and single ion anisotropies, on the QTM.

This dissertation focuses on the study of low nuclearity SMMs in view of understanding these subtle quantum effects. To accomplish this, we have developed a series of magnetic characterization techniques, such as integrated microchip sensors resulting from the combination of two dimensional electron gas (2DEG) Hall-Effect magnetometers and microstrip resonators, capable of performing measurements of magnetization and EPR spectroscopy simultaneously. The thesis bases on a comparative study of two low nuclearity SMMs with identical magnetic cores (Mn$_4$ dicubane) but differing ligands. Notably, one of these SMMs lacked solvent molecules for crystallization; a characteristic that gives rise to extremely sharp resonances in the magnetization loops and whose basic QTM behavior can be well explained with the GSA. On the contrary, the second SMM exhibited mixed energy levels, making a MS description necessary to explain the observations. We have also examined the role of internal degrees of freedom on more subtle QTM phenomena, leading to the explanation of asymmetric Berry-phase interference patterns observed in a Mn$_4$ SMM in terms of a competition between different intermolecular magnetic interactions, i.e. non-collinear zero-field splitting tensors and intramolecular dipolar...
interactions, resulting in astonishing manifestations of the structural molecular symmetry on the quantum
dynamics of the molecular spin.
To my Parents
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# LIST OF ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPI</td>
<td>Berry phase interference</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
</tr>
<tr>
<td>GSA</td>
<td>Giant spin approximation</td>
</tr>
<tr>
<td>HEM</td>
<td>Hall Effect magnetometer</td>
</tr>
<tr>
<td>JT</td>
<td>Jahn Teller</td>
</tr>
<tr>
<td>MS</td>
<td>Multi-spin</td>
</tr>
<tr>
<td>QTM</td>
<td>Quantum tunneling of magnetization</td>
</tr>
<tr>
<td>SMM</td>
<td>Single molecule magnet</td>
</tr>
<tr>
<td>ZFS</td>
<td>Zero field splitting</td>
</tr>
<tr>
<td>2DEG</td>
<td>Two dimensional electron gas</td>
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</tbody>
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CHAPTER 1: INTRODUCTION

This dissertation begins with discussion on the development of novel techniques to study quantum dynamics, relaxation mechanisms and decoherence in nanoscale magnetic systems. In particular, it focuses on the investigation of the quantum properties of spin in Single Molecule Magnets (called SMMs for short) [1-15] and, more specifically, on low nuclearity SMMs such as Mn$_3$ and Mn$_4$. Studying low nuclearity systems allows for the complete diagonalization of the multi-spin Hamiltonian and sampling of the effect of internal degrees of freedom (e.g., exchange interactions, dipolar interactions and single ion anisotropies etc.) on the quantum tunneling of magnetization (QTM) behavior. The giant-spin approximation (GSA) (which treats the molecule as a rigid spin $S$) works well to describe many effects like resonance quantum tunneling and berry phase interference. It also explains many quantum phenomena including relaxation behaviors, Rabi oscillations, and intermolecular interactions, such as dipolar or phonon. But it fails to justify many phenomena, including among others:

- Absence of spin selection rules in QTM
- Presence of low lying excited spin states
- Asymmetric berry phase interference

In an interesting recent example, it has been shown that non-collinearity between single-ion Jahn-Teller axes in a Mn$_3$ SMM lowers the molecular site symmetry (i.e. C$_{3v}$ versus C$_3$), breaking some tunneling degeneracies at zero transverse field and strongly affecting the transverse field dependence of forbidden resonances, bringing the tunnel relaxation rates to observable levels with the help of weak magnetic fields (readily achievable by intermolecular dipolar interactions and/or crystal disorder) [16]. This effect may explain the prevalent absence of spin selection rules in QTM of most SMMs studied to date. The detailed understanding of these and other similar effects has been facilitated by studies of
SMMs of low nuclearity [17, 18], where the exact diagonalization of the multi-spin Hamiltonian allows probing different degrees of freedom internal to the SMM.

The primary goal of my dissertation research has been to study low nuclearity SMMs and understand how individual-ion anisotropies determine the molecular spin ground state in otherwise identical low and high-spin molecules, thus providing unique insights into the key factors that control QTM in SMMs, factors such as

- Exchange interactions (interaction between single-ion’s spins) – With intent to understand low-lying excited spin states and the QTM properties of non-rigid total spin states.
- Dipolar interactions between single-ions - To understand the effect of the dipolar coupling between the molecular magnetic ions on the anisotropy of the molecule.
- Single-ion anisotropies - To understand the effect of tilts of the zero field splitting (ZFS) tensors of different ions on the overall QTM behavior of the SMM.

We are also interested in studying the effects of different symmetries on the QTM, including parity & time reversal and rotational & mirror symmetry. We have hoped that this research could provide a means for mapping the properties found in multi-spin (MS) description onto the giant spin approximation Hamiltonian.

There is quite a variety of transition metals available to be used in the synthesis of SMMs (Mn$^{II}$, III, IV, Ni$^{II}$, Fe$^{II}$, or Co$^{II}$), but Mn has stood out as a contestant in this field due to its characteristic of producing a well assorted collection of SMMs in terms of topology, spin and anisotropy. Availability in multiple oxidation states (Mn$^{II}$, Mn$^{III}$, Mn$^{IV}$ etc.), and its ability to exist in various stable coordination geometries has led to the birth of many zero- and multi-dimensional SMMs of different topologies such as cubanes, dicubanes and wheels etc [19-41]. In this dissertation we have used low nuclearity Mn-based SMMs (dicubane Mn$_4$ and trigonal symmetric Mn$_3$) to fulfill our research goals of exploring the effects of internal degrees of freedom on the QTM.
The second chapter presents the design, fabrication and implementation of novel magnetic characterization techniques such as microstrip cross resonators [42], integrated EPR/magnetometry sensors based on microstrip line resonators and Hall Effect magnetometers (HEM) [43]. These devices have high sensitivity and offer high ac magnetic field at the sample position and also allow absolute control of the microwaves polarization degree at frequencies up to 30 GHz.

The third chapter gives further introduction to SMMs and numerical techniques, detailing the spin Hamiltonian (and comparing the GSA and MS Hamiltonian) used to analyze and understand the spin dynamics of these molecules. It discusses the QTM and EPR studies of mixed valent Mn₄ SMM and indicates the lead of a MS Hamiltonian approach over GSA in understanding and describing the related quantum phenomena.

The fourth chapter begins with a brief introduction of Berry phase interference (BPI) in SMMs and then elaborates on the asymmetric BPI patterns that we have observed in Mn₄ based SMMs for the first time. We show that this remarkable behavior of the BPI patterns is due to the competition of the single-ion ZFS tensors, which can only be explained by employing a MS description of the molecule. We also show that the BPI symmetry follows the time reversal symmetry expected from spin-orbit coupling.

The final chapter discusses the exploration of BPI patterns in Mn₃ SMM. The work in this chapter is motivated by previous studies on the molecule and some theoretical predictions. The experimental work presented in this chapter is still in progress, although it does indicate a possible direction to conduct further research.
CHAPTER 2: NOVEL TECHNIQUES TO STUDY SPIN DYNAMICS AND DECOHERENCE IN NANOSCALE MAGNETIC SYSTEMS

The work presented in this chapter can be found in the following articles;


Nanoscience has emerged during the last three decades and has become a center of immense interest. At the nanoscale, quantum mechanics plays the key role in describing the thermal, mechanical, optical, electric and magnetic behavior of a system, providing high potential for applications in emerging technologies, such as quantum information, nano-optoelectronics and molecular spintronics. Therefore, understanding the quantum mechanical principles governing nanoscale systems [44-46] is of vital importance for applications. Almost two decades of active research all around the world have established single-molecule magnets (SMMs) [9, 15, 47-55] as prototype systems for the understanding of fundamental quantum mechanical phenomena associated with nanoscale magnetism. Significant efforts have been devoted to investigate the quantum dynamics of molecular magnets in view of their possible use in quantum information technologies [56-68] and as a means of enhancing our knowledge of decoherence in nanoscale systems [69-74]. Recent experimental work [48, 75-78] has established that, in order to study intrinsic decoherence mechanisms of the electron spin in molecular magnets, dephasing caused by fluctuating dipolar interactions needs to be eliminated. The latter can be achieved by sample dilution (separating the molecules in solution [48, 75, 76]), or by polarization of the spin bath by means of
a large magnetic field [77-79]. Unfortunately, the dilution of molecule magnets in solution creates a dispersion of the molecular spin orientation and anisotropy axes (among other effects), significantly influencing the energy landscape of the magnetic levels and causing the molecule within the sample to respond differently upon application of an external perturbation. A recent alternative approach is to study crystals in where dipolar dephasing is eliminated by magnetic dilution [80], but this can only be achieved efficiently in mono-order SMMs, where each molecule only contains a single magnetic center [81]. Spin bath polarization restricts the experimental conditions to large magnetic fields and high frequencies ($f$). Pulse EPR setups working at $f < 20$GHz and $T < 0.1$K are needed, where the intrinsic energy separation between spin levels (due to the anisotropy) is enough to polarize the spin bath. Therefore, the development of novel techniques of measurement to identify the relaxation mechanisms in molecular magnets is important toward understanding decoherence in nanoscale magnetic systems and to explore the potential of molecular magnets in quantum technologies.

In this chapter we present design, fabrication and implementation of novel microstrip cross resonators [42] and integrated EPR/magnetometry sensors based on microstrip line resonators and Hall Effect magnetometers HEM [43]. These devices with their high sensitivity provide a high ac magnetic field at the sample position and allow absolute control of the microwaves polarization degree at frequencies up to 30 GHz. A novel high-frequency microstrip resonator integrated with a high-sensitivity HEM allows real-time measurements of the magnetization of micron scale samples in response to microwave excitation, while the microwave power absorbed by the sample can be obtained simultaneously through electron paramagnetic resonance (EPR) spectroscopy. The high efficiency in the conversion of microwave power into ac magnetic field at the sample position and the large filling factors of these resonators together with the fast response of the HEM make these sensors ideal for time-resolved studies of quantum dynamics of molecular nanomagnets at low frequencies and very low temperature.
2.1 Planar Transmission Lines

Transmission lines are configurations designed to transmit electromagnetic waves at radio frequencies (300 kHz -300 GHz). They can be realized in many forms with various geometries and characteristics [82]. The particular shape and physical dimensions of the transmission line define the frequency range and greatly influence the natural propagation mode of the line. One popular type is the planar transmission lines [83] which are typically compact, economical and can be easily integrated with circuits. This archetype includes stripline, micro-strip, slotlines, and co-planar waveguides, among others, each having its distinctive modal distribution, phase velocity, characteristic impedance and attenuation [84-87]. This chapter mainly focuses on the microstrip transmission lines which are used as the basic building block in various microwave integrated circuits [88-92] and can be easily fabricated using photolithographic techniques. Microstrip line constitutes a conducting flat strip of width \( w \) and a ground plane separated by a low loss dielectric material of thickness \( h \) as shown in Figure 1 (a). The conducting strip does not have a homogeneous dielectric region around it, and therefore the microstrip line cannot support pure transverse electromagnetic (TEM) waves. Most of the electromagnetic field lines are concentrated in the dielectric between the conducting strip and ground plane, while a portion of them travel through air, as indicated in Figure 1 (b), thus giving rise to a quasi-TEM wave.

With the specified dimensions of the microstrip line, the characteristic impedance can be calculated as [86];

\[
Z_0 = \begin{cases} 
\frac{60}{\sqrt{\varepsilon_e}} \ln \left( \frac{8h}{w} + \frac{w}{4h} \right) & \text{for } \frac{w}{h} \leq 1 \\
\frac{120\pi}{\sqrt{\varepsilon_e}} \left[ \frac{w}{h} + 1.393 + 0.667 \ln \left( \frac{w}{h} + 1.444 \right) \right] & \text{for } \frac{w}{h} \geq 1
\end{cases}
\] (1)
For a specific characteristic impedance and dielectric constant, the ratio of width and thickness $w/d$ can be established as [86];

$$
\frac{w}{h} = \begin{cases} 
\frac{8\epsilon^A}{\epsilon^{2A} - 2} & \text{for } \frac{w}{h} < 2 \\
\frac{2}{\pi} \left[ B - 1 - \ln(2B - 1) + \frac{\epsilon_r - 1}{2\epsilon_r} \left\{ \ln(B - 1) + 0.39 - \frac{0.61}{\epsilon_r} \right\} \right] & \text{for } \frac{w}{h} > 2
\end{cases}
$$  \hspace{1cm} (2)

where

$$A = \frac{Z_0}{60} \sqrt{\frac{\epsilon_r + 1}{2} + \frac{\epsilon_r - 1}{\epsilon_r + 1} \left( 0.23 + \frac{0.11}{\epsilon_r} \right)}$$

$$B = \frac{377\pi}{2Z_0\sqrt{\epsilon_r}}$$

The attenuation due to dielectric loss for a quasi-TEM microstrip line can be found as [86];

$$\alpha_d = \frac{k_0\epsilon_r(\epsilon_r - 1) \tan \delta}{2\sqrt{\epsilon_r}(\epsilon_r - 1)} \text{ Np/m}$$  \hspace{1cm} (3)

where $\tan \delta$ is the loss tangent of the dielectric.
2.2 Microstrip Line Resonators

The microstrip resonator is a scheme that confines oscillating electromagnetic modes. It has numerous variants including, line, ring, constricted and patch resonators. In this section we are focusing on microstrip line resonators defined by an isolated microstrip line of length $L$, for which resonance occurs if the following condition holds [93]:

$$\beta L = n\pi$$

with $n = 1, 2, 3, \ldots \ldots$ and ‘$\beta$’ is the phase constant along the microstrip, i.e., $\beta = \frac{2\pi f}{c} (\varepsilon_r)^{1/2}$

Figure 2: Schematic of reflection line resonator

Figure 2 shows the schematic of reflection resonator of length $L$ and width $w$ fabricated on dielectric substrate of thickness $h$. The resonator can be $\lambda/2$ or $\lambda/4$ depending on the wavelength of the ground mode confined by its length. As indicated by the above relations, the length ‘$L$’ of the resonator defines the frequency and can have infinite frequencies given that the “$n$” is equal or greater than 1. But increasing the operating frequency increases the radiation effects in the microstrip thus decreasing the so-called “quality factor” of the resonator. Therefore, microstrip resonators with frequencies of 40GHz or more are rarely used. The quality factor is a crucial parameter characterizing resonator and is associated with the geometry and losses in the device. It is defined by [94]:

$$Q = \frac{f (\text{energy stored in the resonator})}{\text{(power dissipated)}}$$

The energy losses in microstrip resonator mainly come from the conductor resistance, charge impurities in the dielectric, radiative or fringing effects. Conductor loss (also known as ohmic or resistive
loss) is the most significant power loss and occurs due to the high current density in the conducting strip of the resonator, and varies with the particular resistance of the device. It also depends on the skin effect, surface roughness and thickness of the conducting strip. The expression for the quality factor of the conductor is given by [95];

$$Q_c = \frac{t}{\delta}$$  \hspace{1cm} (6)

$t$ is the thickness of the metallic line and $\delta$ is the skin depth. A detailed analysis of the conductor loss in a microstrip structure can be found elsewhere [87]. Dielectric loss comes from the dielectric substrate used for the fabrication of the resonator. This power loss is very minimal at microwave frequencies and can typically be neglected. The expression for dielectric quality factor is [95];

$$Q_d = \frac{\epsilon f}{\sigma}$$  \hspace{1cm} (7)

$\epsilon$ is the dielectric constant, $f$ is frequency and $\sigma$ is tan loss.

Radiation losses are due to the characteristic of the resonator to act as an antenna. This causes the resonator to radiate some of its energy, contributing to power loss. Radiation loss can be comparable to the conductor loss and dominates at higher frequencies. It can be reduced by shielding the resonator with a metallic cap.

Fringing fields arise due to the interaction of the field lines with the material outside the perimeter of the resonator line. The quality factor due to these fields is given by;

$$Q_f = fA/\sigma_{2D}M$$  \hspace{1cm} (8)

$A$ is area and $M$ is the perimeter of the resonator, where, $\sigma_{2D}$ is the conductivity of the external layer. The total unloaded $Q$ (the quality factor of a device in the absence of external circuitry) for the resonator is sum of all the above losses and is given by;

$$\frac{1}{Q} = \frac{1}{Q_c} + \frac{1}{Q_d} + \frac{1}{Q_{mw}} + \frac{1}{Q_f}$$  \hspace{1cm} (9)
To facilitate measurements, the resonator is coupled to the external circuitry via various techniques like gap coupling or aperture coupling. In case of gap coupling, a microstrip feed line is added at a calculated distance from the resonator. Figure 2 shows the schematic of the reflection resonator of length \( L \) and width \( w \). The width of the gap \( g_c \) is adjusted in a way that the resonator and feedline are critically coupled (matched at the resonant frequency) to each other, ensuring a critical equilibrium between power transferred into the resonator and power lost out of the resonator. The coupling coefficient ‘\( g \)’ is given by [86]:

\[
g = \frac{Q}{Q_e}
\]  \hspace{1cm} (10)

where, \( Q_e \) is the external quality factor due to added external circuitry, which in result lowers the overall or loaded quality factor. The loaded \( Q \) can be expressed as;

\[
\frac{1}{Q_L} = \frac{1}{Q_e} + \frac{1}{Q}
\]  \hspace{1cm} (11)

If,

1. \( g < 1 \) The resonator is said to be undercoupled to the feedline.
2. \( g = 1 \) The resonator is said to be critically coupled to the feedline.
3. \( g > 1 \) The resonator is said to be overcoupled to the feedline.

### 2.3 Design and Characterization of Microstrip Line Resonators

Half-wavelength microstrip line resonators have been employed for EPR spectroscopy measurements since 1974 [95, 96]. In this section we illustrate the \( \lambda/2 \) microstrip resonators designed and fabricated to perform EPR spectroscopic studies on micron scale single crystals of SMM. While designing a microstrip resonator, there are various parameters which are taken into consideration. These include choice of substrate, impedance matching, power handling, critical coupling and losses. The ultimate device is the one with low loss, high power capability and high quality factor. We used 99.95%
pure undoped high dielectric constant GaAs as a substrate. The choice of GaAs is also based on the prospect of integrating these devices with Hall Effect magnetometers based on GaAs/AlGaAs heterostructures. This significantly reduces the dielectric loss, thus improving the quality factor of the device. The width of the microstrip line, \( w \), and thickness of the dielectric substrate, \( h \), have been carefully calculated using equations 1 and 2 to match the impedance of the microwave coaxial lines (50 \( \Omega \)) in order to avoid reflections at the connections between the device (resonator) and external circuitry.

Our goal is to engineer microstrip resonators which can be employed for the study of quantum dynamics of micron scale solid state magnetic samples. In order to fulfill this requirement, the microstrip resonators should produce a homogeneous ac magnetic field at their center and allow an efficient conversion of microwave power into ac field at the sample position. These strong electromagnetic fields can be achieved by critical coupling of the feedline with the resonator. We have used Advanced Design System (ADS) Software from Agilent Technologies to optimize the coupling gap for reflection resonators with fundamental modes at various frequencies. In this section we will discuss the design of microstrip resonators with the fundamental mode at \(~10\), \(~15\) and \(~25\) GHz.

### 2.3.1 \(~15\) GHz Microstrip Line Resonators

We performed the simulations using ADS software for the resonator with the fundamental mode at \(~15\) GHz. Figure 3 shows the simulated frequency dependence of the reflection parameter \( S_{11} \) for different coupling gaps ranging from 120-160 \( \mu \text{m} \) with an interval of 10 \( \mu \text{m} \).
As indicated in the above figure, different coupling gaps introduce different resonance width, but the critical coupling occurs when the gap is 140 µm (sharpest resonance) between the feedline and the central line of microstrip resonator. The geometrical parameters used to calculate this optimal coupling gap include; length of feed line $L_f = 8.45$ mm, length of resonator $L = 3$ mm, width $w = 500$ µm and coupling gap $g_c = 140$ µm and are shown in Figure 4.
Figure 4: Design of ~15GHz reflection resonator illustrating optimum geometrical parameters for critical coupling

Figure 5 shows the ac current density and its distribution within the resonator at resonance. Selection of coupling gap as 140µm maximizes the strength of ac field at the center of the resonator (red shows the strength of current density as maximum) thus maximizing the microwave magnetic field at the sample position.

Figure 5: Magnitude of current density (in A/m) in the ~ 15 GHz reflection resonators at resonance

Reflection resonators are not convenient to work with at low temperatures because long coaxial lines with necessary sectioning/joints for thermal anchoring are required to transfer the microwave radiation to the sample. Reflections and standing waves generate oscillations in the reflected power ($S_{11}$), masking the response of the resonator. To solve this problem we have developed transmission resonators
by adding a second feedline on the other side of the resonator separated by a transmission gap \( g_t \), as shown in Figure 6.

![Figure 6: Schematic of transmission microstrip line resonator](image)

The second feedline may perturb the response of the resonator, increasing the losses and substantially decreasing the quality factor. The black lines in Figure 7 show the reflection \( S_{11} \) (solid) and the transmission \( S_{21} \) (dashed) parameters of a transmission resonator designed to work at \( \sim 15 \) GHz with a transmission gap, \( g_t = g_c = 140 \) µm. Note that almost 30% of the microwave amplitude (9% of the power) is reflected back (\( S_{11} = 0.3 \) at resonance). In addition, the resonance width is substantially larger (i.e., lower \( Q \)) than that of the corresponding reflection resonator.

In order to minimize this distortion of the resonator response we have increased the transmission gap. Figure 7 also shows the \( S_{ij} \)-parameters of two resonators with different transmission gap sizes (red and blue lines). Both the transmission and the reflection at resonance decrease (\( Q \) increases) upon increasing the transmission gap sizes. Beyond a certain gap size the reflected signal is almost indistinguishable from that of a reflection resonator (\( g_r = \infty \)), as is the ac density (in Figure 8), while the transmitted signal continues to be sufficient for measurements.
Figure 7: Reflection and transmission parameters of ~15 GHz transmission resonators with several transmission gaps.

Figure 8: Color-coded sketches representing the magnitude in A/m of the current density in the device at resonance.
Using the aforementioned design and calculated parameters we fabricated our resonators on 600 µm thick GaAs substrate with a 300 nm thick Au conductor using photolithographic techniques. The detailed fabrication recipe can be found in appendix A. We measured the response of our transmission resonators with an Agilent PNA vector network analyzer as shown in Figure 9. The measured transmitted signal is in excellent agreement with the calculated one (<10% signal reflected), giving quality factor ~100 and fulfilling the technical requirements necessary to study the magnetic samples.

![Figure 9: Measured reflection and transmission parameters of a ~15GHz resonator fabricated on GaAs with transmission gap of 400µm](image)

**2.3.2 ~10GHz Microstrip Line Resonators**

The reflection parameter was simulated (using ADS) with respect to frequency for the microstrip resonator with fundamental mode at 10 GHz using various coupling gaps as shown in Figure 10. These
simulations specify the optimal coupling gap for critical coupling between feedline and resonator central line as 40 µm.

![Figure 10](image1.png)

**Figure 10:** S11 as a function of frequency for different coupling gaps between feed line and the central line of a ~10 GHz microstrip resonator.

The geometrical parameters used to calculate this optimal coupling gap ($g_c = 40$ µm) include; length of feed line $L_f = 7.5$ mm, length of resonator $L = 4.8$ mm, and width $w = 480$ µm and are shown in Figure 11.

![Figure 11](image2.png)

**Figure 11:** Design of ~10GHz reflection resonator illustrating optimum geometrical parameters for critical coupling
Due to the limitations of reflection resonator at low temperature we add a transmission line at a certain distance from the central line. For the case of ~10GHz resonator we optimized the transmission gap via plotting transmission and reflection parameters versus frequency for various transmission gaps as shown in Figure 12.

![Graph showing reflection and transmission parameters](image)

**Figure 12:** Reflection and transmission parameters of ~10 GHz transmission resonators with several transmission gaps.

As can be seen in the figure, a transmission gap of 40 µm corresponds to a 32 % reflection of the microwave amplitude. Also, the width of the resonance is broader, thus decreasing the quality factor and indicating 250 µm as the best suited transmission gap for this resonator. The measured transmission and reflection parameters for the resonator fabricated on GaAs for the optimal transmitted coupling gap ($g_t = 250 \mu m$) include; length of feed line $L_f = 7.5$ mm, length of resonator $L = 4.8$ mm, and width $w = 480$ µm, which are shown in Figure 13.
2.3.3 ~20 GHz Microstrip Line Resonators

The microstrip resonator with fundamental frequency mode at ~20GHz was also designed and simulated using ADS. The software was used to calculate the optimal coupling gap between the resonator and feedline to achieve critical coupling. Figure 14 shows the simulated plot between reflection parameter and frequency for different coupling gaps. The optimal coupling gap for the ~ 20 GHz resonators is 330µm with the width of 520µm. The geometrical parameters used to calculate this optimal coupling gap (g_c = 330 µm) include; length of feed line L_f = 8.67 mm, length of resonator L = 2 mm, and are shown in Figure 15.

The transmission is optimized by plotting transmission and reflection parameters versus frequency for various transmission gaps as shown in Figure 16. The transmission gap of 330 µm corresponds to a 30% reflection of the microwave amplitude. Also, the width of the resonance is broader, thus decreasing the quality factor and indicating 650 µm as the best suited transmission gap for this resonator.
Figure 14: $S_{11}$ as a function of frequency for different coupling gaps between the feed line and the central line of a ~20 GHz microstrip resonator.

Figure 15: Design of ~20GHz transmission resonator illustrating optimal geometrical parameters required for critical coupling
The measured transmission and reflection parameters for the resonator fabricated on GaAs for the optimal transmitted coupling gap \( g_t = 650 \text{ µm} \) include; length of feed line \( L_f = 8.67 \text{ mm} \), length of resonator \( L = 2 \text{ mm} \), and width \( w = 520 \text{ µm} \) and are shown in the Figure 17.
2.4 Strength and Homogeneity of the AC Field in Microstrip Line Resonators

From saturation measurements of the standard EPR marker 2,2-diphenyl-1-picrylhydrazyl (DPPH) \( S = 1/2 \), we have estimated that a power of \( \sim 10 \) mW at the input port of a 10 GHz microstrip resonator \( Q_L = Q_0/2 = 85 \) produces an AC magnetic field of \( h_{ac} \sim 1 \) Oe. The field right above the center of the resonator can be written in terms of the input power, \( P_{in} \), as follows:

\[
    h = \frac{\mu_0}{w} \sqrt{\frac{P_{in} Q_0}{2Z}}
\]

(12)

where, \( Z \) is the impedance of the resonator \( (Z=R \text{ at resonance}) \). An estimate of the AC field using Eq. 12 for this resonator gives \( h = 1.75 \) Oe, in good agreement with the value extracted from saturation. Note that large AC fields are necessary to induce fast Rabi oscillations to overcome decoherence. For a spin \( S = 1/2 \) system, an AC field of 10 Oe (easily attainable with our resonators) would generate Rabi oscillations with a period below 100 ns, fulfilling a requirement to perform spin echo experiments.

The magnetic field is very strong and homogeneous at the center of these microstrip resonators (10% variation within 50 \( \mu \)m from the surface), thus succeeding a necessary requirements to study the quantum dynamics of magnetic samples. The input impedance is also designed to maximize the power arriving at the resonator. These devices typically have moderate quality factors \( (Q \sim 100) \), which provide a fast dissipation of the energy stored in the resonator, allowing the use of fast microwave pulses \( (> 1 \) ns) without cavity ringing. Crucially, these microstrip resonators offer very high sensitivity for susceptibility studies, comparable or even larger than high-quality factor resonant cavities \( (Q \sim 10^4) \). This is due to the formulation of sensitivity as the product of the quality factor and the filling factor, \( \eta \). The latter is the ratio of the microwave energy in the sample volume over the total energy stored in the cavity. In microstrip resonators, almost all the energy is concentrated in the proximity of the resonator (at the center of the line) and the sample is within a large fraction of this volume, leading to the filling factors on the order of 0.1 (as opposed to \( \eta \sim 10^{-3} \) in resonant cavities).
2.5 Design and Characterization of Microstrip Cross Resonators

In this section we present the design, characterization and implementation of a novel polarizable EPR transmission microstrip cross resonator, composed of two \( \lambda/2 \) microstrip line resonators. It allows an \textit{in situ} and all-electronic arbitrary control of the polarization of microwaves for frequencies up to 30 GHz. Figure 18 shows the assembly of our polarizable resonator.

![Figure 18: Sketch of polarizable microstrip cross resonator. Two half wavelength microstrip line resonators are assembled together to form a cross resonator. The coupling, \( g_c \), and transmission, \( g_t \), gaps are engineered differently to optimize device performance. The relative magnitude and phase between ports P1 and P2 allow control of the polarization of microwaves at the center of the cross.](image)

We designed this polarizer by placing two half-wavelength microstrip reflection line resonators (discussed in previous section) in an orthogonal arrangement, forming a square cross. Note that in our case, where \( h<\lambda/2 \), the signal transmission corresponds to a quasi-transverse electromagnetic mode in each of the resonator lines. At their fundamental resonant mode, the microwave magnetic field components, \( h_1^{ac} \) and \( h_2^{ac} \), are maximum and perpendicular to each other at the center of the resonator (see red and blue arrows in Fig. 13). The cross resonator in the figure is connected to ports P1 and P2 through feedlines separated by a \textit{coupling gap}, \( g_c \), designed to critically couple the resonator to the feedlines. The transmission line, connected to port P3, is coupled to an opposite resonator arm through a \textit{transmission gap}, \( g_t (>g_c) \), which is designed to allow measurements in transmission mode (i.e., \( S_{31} \)).
parameter) as explained in the previous section. The observed response of the resonator upon the excitation of each of the input ports provides the principle of operation of our polarizable resonator. For this, microwave stimuli are applied to both ports $P_1$ and $P_2$. The microstrip cross resonator with the fundamental mode at 10 GHz is designed using the parameters shown in Figure 19.

![Figure 19: Design of ~10GHz cross polarizer illustrating the optimal parameters required for critical coupling](image)

We simulated the response of this cross resonator using ADS software and then measured the response using a 50 GHz Agilent Technologies PNA vector network analyzer. A power splitter, phase shifter and variable attenuators were used to control the magnitude and phase of the input signals at ports $P_1$ and $P_2$. Figure 20 shows the reflection ($S_{11}$) and transmission ($S_{31}$) parameters measured at room temperature (RT) when the microwave excitation is sent only via port $P_1$. 

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As can be seen in the Figure 20, we observed two sharp resonances ($Q\sim100$) at $f_d=9.7$ GHz and $f_q=11.5$ GHz for this resonator. The simulated response of the resonator is also presented in Fig. 15 for comparison (dotted lines) exhibiting excellent agreement with the experimental data.

The current density at each of the resonances for the applied stimulus via port P1 (white arrow), is shown in Figure 21. At the first resonant frequency, $f_d=9.7$ GHz (RT), a dipolar resonant excitation develops along one of the arms of the cross resonator. This excitation corresponds to the fundamental resonant excitation mode of an individual microstrip line resonator, which can be estimated as;

$$f_0 \sim nc/(2(L + \Delta L)\sqrt{\varepsilon_r}) \quad (13)$$
where \( n \) is the resonant mode, \( c \) is the speed of light in vacuum, \( L \) is the resonator length, \( \varepsilon_r \) is the effective dielectric constant of the device, and \( \Delta L \) is a correction factor to take into account the effect of the gap.

The same excitation occurs along the other arm of the cross resonator when feeding with microwaves of the same frequency using port P 2. The second resonance, \( f_q = 11.5 \text{ GHz} \), corresponds to a quadrupole resonant excitation of the whole cross resonator, which develops equally when feeding P 2 with microwaves. The relative magnitude and phase between the two microwave signals modulate the response of the resonator. As discussed in the previous section, the transmission lines are added to the resonators in order to avoid potentially obscuring signals at low temperature. The long coaxial lines wiring the cryostats strongly affect the microwave power by masking the response of the resonator. Figure 22 shows a contour plot of the transmission parameter \( S_{31} \) as a function of the frequency and the phase delay between both signals. Both resonances show a \( 2\pi \) period modulation.

Figure 21: Current density at resonance in cross polarizer (left) Dipolar resonant excitation (right) Quadropolar resonant excitation
Figure 22: Contour plot of the transmission parameter $S_{31}$ measured on a 10 GHz microstrip cross resonator at $T=4$ K. The data show the onefold two modulation of the resonances as a function of the relative phase between microwave signals of equal magnitude applied to ports $P_1$ and $P_2$. Dashed lines are used to relate the constructive $0^\circ$ and destructive $180^\circ$ interferences of the quadrupole resonance 11.5 GHz with the modulation observed in the dipolar resonance 10 GHz. The slope of the lines is due to the linear frequency dependence of the phase supplied by the phase shifter employed.

For the case of second resonance ($f_q=11.5$ GHz), interference between the two microwave signals modulates the quadrupole resonant excitation of the whole cross. By adjusting the magnitudes of the signals, one can completely eliminate the quadrupole resonance when the two microwave signals are $180^\circ$ out of phase (destructive interference). On the contrary, in-phase microwave signals add together (constructive interference) to develop a maximum in the transmission parameter ($S_{31}$). Thus, quadrupole resonance can be employed to adjust the relative magnitude and phase between both input signals. Our results also indicate that the input signals can be tuned in order to control the microwave polarization at the center of the cross resonator in the first resonance, $f_d=9.9$ GHz at $T=4$ K. For signals of equal magnitude at ports $P_1$ and $P_2$, the relative phase, $\Delta\phi$, between them will determine the type of polarization obtained. For $\Delta\phi=m\times180^\circ$ (with $m=0, \pm1, \pm2, \ldots$), the microwaves at the center of the resonator will be
linearly polarized (coinciding with the destructive and constructive interferences of the quadrupole resonance), with the microwave magnetic field aligned 45° with respect to the resonator arms. For $\Delta \phi = n \times 90^\circ$ (with $n = \pm 1, \pm 3, \pm 5, \ldots$), the microwaves will be circularly polarized. $\Delta \phi = 90^\circ$ and 270° give rise to left ($\sigma^-$) and right ($\sigma^+$) circular polarizations, respectively, as indicated in Figure 22. The sensitivity of our resonator obtained with a lower concentrated sample at low temperature (300 mK) is $N_{\text{min}} \sim 10^6$ spins/Hz$^{1/2}$, when estimated as the number of spins detected for a frequency bandwidth, $f$, of 1 Hz according to:

$$N_{\text{min}} = N_{\text{spins}}/\left[(S/N)\sqrt{f}\right]$$  \hspace{1cm} (14)

We used a ~10GHz polarizable microstrip cross resonator to study the EPR spectra of a single crystal (~0.3 $\times$ 0.3$\times$0.3 mm$^3$) of Fe$_{17}$Ga molecular wheels ($S=5/2$), shown in Figure 23, diluted within a sea of antiferromagnetic Fe$_{18}$ wheels ($S=0$), with a dilution factor 0.09:1 (Fe$_{17}$Ga:Fe$_{18}$).

Figure 23: Sketch of the Fe$_{17}$Ga molecular wheel, in which one Fe ($S=5/2$) ion has been supplanted by a Ga ($S=0$), resulting in a frustrated molecular spin $S=5/2$ at low temperatures.

The Fe$_{17}$Ga molecules present a positive zero-field splitting, $D S_z^2$ ($D=0.5$ K), making the $S_z=1/2$ spin projections the lowest energy states of the system. Experiments were carried out at 300 mK, where
only the $S_z = 1/2$ spin states are populated. Figure 24 shows the EPR spectra of the sample obtained at 9.9 GHz for two different phase delays, $\Delta \phi = -90^\circ$ ($\sigma^-$) and $90^\circ$ ($\sigma^+$) between the microwave signals at ports $P_1$ and $P_2$.

![EPR spectra graph](image)

**Figure 24:** EPR spectra obtained at 300 mK on a magnetically dilute single crystal of Fe$_{17}$Ga molecular magnets. The two curves correspond to two different phase delays, $\Delta \phi = -90^\circ$ ($\sigma^-$) and $90^\circ$ ($\sigma^+$), between the microwave signals at ports $P_1$ and $P_2$ of the cross resonator.

The observed EPR absorption peak at 0.32 T corresponds to a transition between the ground spin projection states ($S_z = 1/2$) of the molecule ($g=2$) [61]. The difference in the peak magnitude is associated with the selection rule imposed by spin transitions ($\Delta S = \pm 1$). In our case, the positive magnetic field makes the negative spin projection the ground state ($\Delta S = +1$), therefore, only right circular polarized microwaves ($\sigma^+$) are capable to induce transitions. Figure 25 shows the modulation of the normalized height of the EPR peak as a function of the relative phase between the two microwave signals.
Figure 25: Modulation of the normalized EPR peak height as a function of the phase delay between the signals. An 82% degree of circular polarization is achieved over the central area of the resonator.

Note that the EPR absorption peak corresponding to $\Delta S = +1$ transition is proportional to the right polarized component of the microwave field. The continuous line in Figure 20 represents the normalized magnitude of the $\sigma^+$-component of the microwave field, $(H_x H_x^*)^{1/2} = (1 + \sin \phi)^{1/2}$, with ideal control of the polarization angle. We calculated the degree of polarization by using $P_+ = (A_{+90} - A_{-90})/(A_{+90} + A_{-90})$, where $A_{\Delta \phi}$ are the marginal values of the normalized heights of the EPR peaks, as shown in Figure 20) and for the region within the sample found it to be 82%. Note that complete circular polarization is only achieved at the exact center of the cross, which has a total area of $\sim 0.4 \times 0.4$ mm$^2$. Taking into account that the measured crystal covered more than 50% of the resonator area, the obtained degree of polarization is remarkable.

Our designed and implemented polarizable microstrip cross resonator allows an arbitrary control of the polarization of high frequency micro waves. The electronic control of the polarization by this cross resonator makes it an ideal device for pulsed EPR and to investigate spin transition selection rules. The
idea of our microstrip cross resonator can also be extended to *microstrip cross lines* or *coplanar cross waveguides* to generate circular polarized microwaves in a broad range of frequencies.

### 2.6 Hall-Effect

The Hall Effect is a transverse isothermal galvanomagnetic phenomenon in which transverse electromotive force is generated in an electrical conductor carrying an electric current and exposed to a perpendicular magnetic field. The phenomenon was discovered by E. H. Hall in 1879 while working with a thin metallic gold foil. He found that the generation of the voltage difference (the Hall voltage) is proportional to the current flowing through the conductor and flux density perpendicular to the current.

![Figure 26: Electric and magnetic field in metallic strip illustrating Hall Effect](image)

His experiment can be illustrated as shown in Figure 26. Consider the current is flowing through the metal strip in the $x$-direction and a magnetic field $B$ is applied along the $z$-axis; then the Lorentz force acting on the charge carriers can be written as [97, 98]

$$ F = q(E + v \times B) $$

(15)
where, \( q \) is the charge and \( v \) the drift velocity of the charge carriers. The Lorentz force is directed towards the negative \( y \)-direction, generating the electrostatic potential \( E_y \). Under equilibrium; \( eE_y = ev_x B_z \) with the current flowing along the \( x \)-direction. The Hall voltage is thus given by

\[
V_H = wE_y = v_x B_z = \frac{j_x B_z}{ne}
\]

where, \( w \) is the width of the conductor, \( j_x \) the current density along \( x \)-axis and \( n \) the charge carrier density. Since, \( j = I = wt \) (where, \( t \) is the thickness), the final relation is;

\[
V_H = R_H IB_z
\]

where, \( R_H \) is the hall co-efficient and is defined as;

\[
R_H = \frac{R_H}{j_x B} = \frac{1}{ne}
\]

### 2.7 Hall Effect Magnetometers (HEM)

Hall Effect sensors have a substantial market demand, finding use in technologies as various as pressure and fluid flow sensors, current sensors, and robust switches. They are also used to study superconductors and magnetic systems at the micron scale. In particular, Hall magnetosensors (also called Hall Effect magnetometers or HEM for short) based on 2DEG (two-dimensional electron gas) heterostructures have provided a considerable contribution to the study of magnetic systems. The sub-micron sized active sensing area, high sensitivity and wide temperature and magnetic field range of strength make them versatile measurement devices. In our group, we use HEMs to study the quantum dynamics of single molecule magnets, as will be explained in detail in chapter 2.

We fabricate our HEM devices (fabrication recipe given in appendix B) from a 0.6 mm thick GaAs/AlGaAs substrate containing a high-mobility 2-DEG layer ~70 nm underneath the surface. The carrier density, \( n = 5.46 \times 10^{11} \text{ cm}^{-2} \) and mobility, \( \mu = 67,400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) for our 2-DEG were determined from Hall measurements carried out at \( T=77 \text{ K} \).
A 50×50 µm² cross-shaped HEM is patterned on the surface by means of optical lithography and with a 100 nm deep chemical etch to produce the mesa structure. Figure 27 shows the schematic of our HEM. A zoom at the center of the sensing area of the device is shown in Figure 28 (b) where the current and the voltage leads for the operation of the HEM are indicated. The leads that widen go to the sides of the wafer where macroscopic Au/Ge pads are patterned (see Figure 28 (a)). Thermal annealing of the contacts in inert atmosphere was performed to diffuse the germanium into the wafer and obtain Ohmic contacts to the 2-DEG layer. A preliminary magnetic characterization of the HEM was carried out at low temperatures (4 K) by applying a magnetic field perpendicular to the sensor plane. Monitoring of the Hall voltage across the sensor was performed via a lock-in amplifier in the presence of a low-frequency (<100 kHz) AC signal of 1 µA. The Hall coefficient, $R_H = 2200 \, \Omega/T$, was extracted from the dependence of the Hall voltage on the external field and the geometry of the sensor. The density of carriers, $n = 1/eR_H = 4.2 \times 10^{11} \, \text{cm}^{-1}$, extracted from the Hall coefficient, agrees well with the value found at 77 K.
2.8 Gradiometers

While using HEM to study magnetic systems (in our case SMMs), weak magnetic anomalies in the ambient magnetic field may affect the response of the device, appearing as background noise and affecting the data. Most of the time, these effects are very small as compared to the response of the magnetic system under test and thus can be ignored, but for small magnetic samples background anomalies can act to mask the real signal. In order to overcome this issue, we designed a gradiometer by placing two independent Hall magnetometers next to each other on the 2DEG substrate as shown in Figure 29. For measurements, we place our sample on one magnetometer and use the other magnetometer as a reference to compensate for anomalies. We then use a subtraction circuit (explained in appendix C) to subtract the signals and produce a resulting signal which is the difference in flux between two magnetometers and corresponds predominantly to the response of the sample under test, while background signals are completely eliminated.
2.9 Integrated EPR/Magnetometry Sensors

In this section we discuss a novel sensor which integrates high frequency EPR spectroscopy and high sensitivity Hall effect magnetometry on a single semiconductor chip. A microstrip resonator (described in section 1) is patterned on the surface of the HEM, with the center of the resonator line located on top of the HEM cross, making the area where the microwave magnetic field of the fundamental resonant mode is maximum coincident with the active area of the HEM (see Figure 30).

A thin dielectric separates the sensor from the heterostructure material (detailed recipe in appendix D). The ends of the reflection and transmission feed lines are connected to the inner conductor of a 0.086 in. semi-rigid coaxial line ($f \leq 50$ GHz) through opposite walls of the microwave housing box.
as shown in figure 31 (a), the zoom at the center of device where resonator intersects the active area of HEM is shown in figure 31 (b).

![Figure 31](image)

**Figure 31:** (a) Photograph of the device placed in a low temperature housing box. (b) Optical micrograph of the center part of the resonator. The 50×50 µm² cross-shaped HEM can be seen underneath the resonator. The green pyramidal-shaped sample is a single crystal of a Ni₄ SMM.

To demonstrate the feasibility of our integrated sensor, we carried out simultaneous measurements of the magnetization and the EPR absorption spectra of a single crystal of Ni₄ SMMs. For this, a pyramidal-shaped crystal (~60×60×120 µm³) is placed on top of both sensors, as shown in Figure 31 (b). Ni₄ is known to have its easy axis oriented parallel to the long axis of the pyramid [62]. In our case, a large field is applied transverse to the easy axis to generate tunnel splittings of the order of the microwave radiation energy employed. Thus the crystal is aligned with its easy axis in the direction of the ac magnetic field ($h \perp H_{dc}$). The magnetization of the Ni₄ single crystal recorded at 200 mK during excitation with microwave radiation of $f=15$ GHz is shown in Figure 32 (a) (red curve). Deviations from the equilibrium magnetization in the absence of radiation (black curve) are observed at both polarities of the magnetic field, corresponding to photon induced transitions between quantum superposition states of the spin of the molecules (see Ref. 16 for details). The microwave-induced magnetization change is
shown in Figure 26 (c). The corresponding microwave power absorbed by the sample is shown in Figure 32 (b), estimated from the change in the transmitted power through the resonator, $S_{21}$, which is recorded simultaneously. The results presented in Figure 32 demonstrate that our EPR-HEM integrated sensors allow the simultaneous measurement of the magnetization and the EPR spectra. This is of crucial importance for the study of the magnetization dynamics in nanoscale systems, since the simultaneous measurement of $\Delta M$ and $P_{\text{abs}}$ allows the direct determination of the energy relaxation time of the sample, associated with the coupling of the spin and the lattice (i.e., spin-phonon relaxation time), provided that only the two lowest lying spin states are significantly populated. The relation (derived in ref 19) is given as

$$\tau = \frac{hf N_0 \Delta M}{2M_{eq} P_{\text{abs}}} \quad (19)$$

where $N_0$ is the population difference between the two spin levels at equilibrium and is a function of the temperature $T$ and the total number of molecules in the sample $N_T$. Taking the results shown in Figure 32, we obtain an energy relaxation time for this sample of $\sim 30$ ms. In this sample, a phonon bottleneck is known to slow down the energy relaxation of the molecular spin states. This makes the extracted relaxation time larger than the spin-phonon relaxation time of this sample ($\tau > T_1$) [82].
2.10 Real Time Magnetization Dynamics using Integrated Hall Sensors

Our EPR-HEM sensor can also be used to perform time resolved measurements. Using a fast $p-i-n$ diode switch operating up to 40 GHz and controlled by a pulse generator, it is possible to generate very short (the typical switching time of our pin switch or pulse generator is 5 ns) microwave pulses. An RF amplifier (with 40 dB gain and 30 dBm maximum output power) amplifies the microwave pulse power after the switch, before it is sent to the microstrip resonator, through the coaxial lines. Using the PNA, it is also possible to detect the microwave power absorbed during such short high power pulses. With standard pulse EPR capabilities, our integrated sensor adds the capability of time-resolved measurements of the magnetization of the sample during and after microwave pulses. This direct measurement is very useful for the investigation of relaxation processes, for instance, in SMMs [59, 99]. Figure 33 shows an example of such an experiment on a Ni$_4$ single crystal. Here, the microstrip resonator patterned on top of
the HEM has a resonance frequency of 26 GHz, and a transverse field of 2.75 T is applied in order to
generate the desired tunnel splitting between the two lowest-lying spin states of the $S = 4$ SMM, as in the
experiment presented in the previous section.

Figure 33: (a) Time-resolved magnetization measurements for three different applied longitudinal
fields under microwave pulse irradiation. (b) Magnetization curves at six different times, during
and after the microwave pulse. The dashed line indicates the resonant field corresponding to the
transition between the two lowest-lying tunnel split spin states.

The presented data was obtained at 0.4 K. In order to perform these real-time measurements, a
constant DC field of 10 µA is used to bias the HEM, and a low noise preamplifier with a 1 MHz
bandwidth is used to amplify the Hall voltage, which is read and averaged on an oscilloscope. The typical
Hall voltage is a few µV, and a gain of 1000 is used in order to amplify it to microvolt levels. The
presented data are averaged over a few thousands traces, with the $W = 2$ ms long microwave pulse being
there repeated every 100 ms (hence, the duty cycle is $\text{dc} = 2\%$). It is possible to record the magnetization
behavior during the pulse and after it has been turned off, for different applied longitudinal fields (Figure
33 (a)). The magnetization decreases during the pulse, and then relaxes toward equilibrium on a few
millisecond time scale. The diminution of the magnetization at the end of the pulse is maximum when $Hz$
=0.12 T, i.e., when the splitting between the two lowest lying spin states matches the microwave energy $h\nu$. It is also possible to analyze “time slices” of the magnetization curve, as shown in Figure 33 (b). In that case, magnetization changes induced by the microwave irradiation are plotted as a function of $H_z$, at different times during and after the application of the pulse. During the first stage of the pulse (filled circles and squares), the magnetization change is maximum at $H_z = 0.12$ T, and small for large longitudinal fields, where the resonant condition is not fulfilled. However, large magnetization changes develop even far from resonance, at later times. This is due to the direct heating by the microwaves. As the pulse is turned off, the full magnetization curve relaxes toward equilibrium, which is almost recovered after 20 ms (the open triangles). This behavior is well reproduced by a phenomenological model taking into account the heat transfers between the Ni$_4$ crystal, the chip of the integrated sensor, and the bath, as well as a resonant part corresponding to the microwave absorption by the spins around $H_z = 0.12$ T. Finally, we point out that the data presented in Figure 33 demonstrate a time resolution of about 10 µs, limited in this case by the bandwidth of the amplifier, and that the intrinsic dynamics of the sample studied is much longer, in the millisecond time scale. Measurements of the magnetization with pulse lengths down to ~50 ns have been successfully obtained with our resonator (not shown here). In fact, the performance of the EPR-HEM for time-domain studies is only limited by the wiring and the Ohmic contacts to the 2D electron gas, as well as by the electronics employed to amplify the Hall voltage to a level measurable by an oscilloscope.
CHAPTER 3: GSA vs. MS DESCRIPTIONS OF THE MIXED VALENCE Mn₄ COMPLEXES

The second part of the chapter can be found in the following publications;

“EPR and magnetic quantum tunneling studies of the mixed valent [Mn₄(anca)₄(Hedea)₄(ede)₄].2CHCl₃,EtOH single molecule magnet”, Junjie Liu, Christopher C. Beedle, Hajrah M. Quddusi, Enrique del Barco, David N. Hendrickson, Stephen Hill, Polyhedron 30, 2965 (2011)


Magnetic materials, appearing in the accounts of ancient Greeks from millennia ago, have become indispensable to modern technology. They appear as components of electromechanical and electronic devices widely used at both the domestic and industrial levels, and their application in information technology grows rapidly. In the endeavor to gratify an ever-increasing need for high-density information storage materials, ultra-small mesoscopic and even nanoscopic magnetic materials are being continuously developed. Extensive research in nanoscience has taken devices to the limit of miniaturization, where quantum phenomena dominate the classical effects. This is also true in the case of nanomagnetism, where future specialized applications require mono-disperse nanoscale magnetic systems. These efforts have led to the birth of metal organic complexes called “single molecule magnets” (SMMs) which exhibit superparamagnetic-like properties [3, 6].

This chapter is divided into two parts. The first gives a brief introduction to SMMs and their associated phenomena. It also explains a few analytical approaches used to understand the physics exhibited by these systems. The second part discusses the magnetization and EPR measurements
performed on two mixed valence Mn₄ SMMs where a multi-spin description is shown necessary to explain the QTM behavior of the molecules.

3.1 Introduction to SMMs

SMMs function as single-domain magnetic particles that exhibit slow relaxation of magnetization at low temperatures and represent a bottom-up approach to nanoscale magnets, thus possessing many advantages over other magnetic materials. Molecular magnets are composed of one or more transition metals or rare-earth ions serving as a magnetic core (which are responsible for the magnetic properties) and are surrounded by organic or inorganic ligands acting to minimize inter-molecular interactions. The most prominent early SMM, [Mn₁₂O₁₂(O₂CCH₃)₁₆(H₂O)]₄H₂O.2CH₃CO₂H (often called simply Mn₁₂-acetate) [11, 12] was synthesized in 1980 but was not recognized and discovered as a SMM until 1991. Since then, many SMMs with different magnetic cores and features have been synthesized and studied in the venture of finding one with a slow relaxation of the magnetization at higher temperatures. Figure 34 shows the structures of different SMMs including (l) Mn₄ and (m) Mn₃, which are the primary focus of this dissertation.

SMMs have generated interest for their application to fields such as spintronics and quantum information and computation [45, 57, 100, 101]. These molecules are effectively quantum objects and have been proposed as candidates for qubits, the units of quantum information. It is possible to couple the spins of molecular nanomagnets, each acting as a quantum bit, to make the entangled state useful in quantum computation and communication. They are attractive compounds in spintronics because of their magnetization relaxation time, which is extremely long at low temperatures and can provide high density information storage. Because of their well defined structure with well characterized spin ground state and magnetic anisotropy, they are the most promising candidates for observing quantum phenomena [47, 102] such as the quantum tunneling of magnetization or quantum phase interference.
Figure 34: Examples of molecular nanomagnets. (a) ‘Mn$_{12}$’ (Mn$_{12}$O$_{12}$(CH$_2$COO)$_{16}$(H$_2$O)$_4$) ($S=10$) (b) ‘Fe$_8$’ ([tacn]$_6$Fe$_8$O$_2$(OH)$_{12}$) ($S=10$) ; (c) ‘Mn$_9$’ (Mn$_9$O$_7$(OAc)$_{11}$(py)$_3$(H$_2$O)$_2$) ($S=17/2$); (d) [Mn$_{84}$O$_{72}$(O$_2$CMe)$_{78}$(OMe)$_{24}$(MeOH)$_{42}$(H$_2$O)$_{42}$(OH)$_6$.xH$_2$O.$y$CHCl$_3$ ($S=6$); (e) Fe$_{19}$(metheidi)$_{10}$ (OH)$_{14}$O$_6$ (H$_2$O)$_{12}$NO$_3$.24H$_2$O ($S=(33/2)$; (f) keplerate containing twelve {Mo$^\text{VI}$}Mo$_5^\text{VI}$} units fixed by thirty V$^{IV}$ linkers; (g) Ni$_{12}$(chp)$_{12}$(thf)$_6$(H$_2$O)$_6$($S=12$);(h) (Mn$_{12}$)$_{10}$Mn$_7^{\text{II}}$ (µ$_4$-O)$_8$(µ$_3$-$\eta^1$-N$_3$)$_6$(HL)$_{12}$–(MeCN)$_6$.Cl$_2$.10MeOH.MeCN ($S=83/2$); (i) ‘Cr$_8$’ homometallic wheel ([CrF(O$_2$C$t$Bu)$_2$])$_8$; (j) ‘Cr$_7$Ni’ heterometallic wheel ([H$_2$N$_2$Pr$_2$]Cr$_7$NiF$_8$(O$_2$C$t$Bu)$_{16}$]); (k) [{Ni(cyclen)$_2$ Cr$_{12}$ NiF$_{18}$(O$_2$CCMe$_3$)$_{24}$}], a wheel which failed to close, producing an S-shaped molecule [6]; (l) ‘Mn$_4$’ [Mn$_4$(Bet)$_4$(mdea)$_2$(Hmdea)$_2$](BPh$_4$)$_4$ ($S=9$); (m) ‘Mn$_3$’ [NET$_4$]$_3$[Mn$_3$Zn$_2$(solax)$_3$O(N$_3$)$_6$Cl$_2$] ($S=6$) ; (n) ‘Ni$_{12}$’ [Ni(hmp)(t-BuEtOH)Cl]$_4$ ($S=4$); (o) ‘Mn$_{12}$-wheel’ [Mn$_{12}$(Adea)$_8$(CHCOO)$_{14}$].7CH$_3$CN ($S=7$) [103]
A SMM derives its unusual properties from a combination of large spin ($S$) and easy-axis type anisotropy (negative axial zero-field splitting parameter $D$). $S$ and $D$ describe a double potential well, and give rise to a significant parabolic shape energy barrier (also known as a tunnel barrier) which separates opposite spin projections. This barrier resists the thermally activated magnetization relaxation, with upper limits given by $S^2D$ or $(S^2-1/4)D$ for integer and half integer spin, respectively. Figure 35 shows the energy diagram of the opposite spin projections ($m$ and $m'$) separated by an anisotropy barrier $\sim DS^2$.

![Energy diagram of the $2S+1=21$ projections of spin $S=10$ (separated by anisotropy barrier $DS^2$) along the easy axis of magnetization of the Mn$_{12}$-ac SMM for the first resonance at $k=0$](image)

**Figure 35: Energy diagram of the 2$S$+1=21 projections of spin $S$=10 (separated by anisotropy barrier $DS^2$) along the easy axis of magnetization of the Mn$_{12}$-ac SMM for the first resonance at $k=0$**

### 3.1.1 Spin Hamiltonian

The Spin Hamiltonian is a quantum-mechanical Hamiltonian and is the most prominent tool for interpreting the data used to understand the magnetic features exhibited by SMMs. This approach depends on the spin coordinates and ignores any spatial coordinate thus eliminating orbital angular momentum and
replacing it with the spin angular momentum of the system with the spin-orbit coupling redefined into the zero-field splitting parameters (i.e, anisotropy tensors). The general expression for this Hamiltonian is given by

\[ H = H_{zfs} + H_{zeeman} \]  

where \( H_{zfs} \) is the Hamiltonian corresponding to zero field splitting (“zfs” for short, and defined as the removal spin microstate degeneracy for magnetic systems with spin \( S > \frac{1}{2} \) in the absence of an applied magnetic field), primarily originating from spin-orbit coupling. \( H_{zeeman} \) is the Zeeman Hamiltonian which corresponds to the Zeeman energy resulting from the coupling of the spin with an applied external field. This term is given by

\[ H_{zeeman} = \mu_B H \cdot \hat{g} \cdot S \]  

where, \( \hat{g} \) is the Landé tensor. The most widely used approximations in solving the spin Hamiltonian are the Giant spin approximation (GSA) and the Multi-spin (MS) description. The Hamiltonians based on these approximations are explained in the next sections and have been used extensively to interpret and understand the experimental data presented in this dissertation.

### 3.1.2 The Giant Spin Approximation

The GSA description is based on the fact that the exchange interaction between the metal ions (constituting magnetic core) is very strong and it can be modeled as an isolated and well defined ground spin \( S \). This approximation is valid at low temperatures, where the excited levels corresponding to different spin-multiplets are not populated, especially at large exchange couplings, where the ground state is well isolated. Considering this model the molecule behaves as a single domain particle with its energy levels corresponding to various orientations of the total spin \( S \) into the main quantization axis.
The GSA Hamiltonian can be developed by using Steven’s operators [104, 105] as expressed in the following equation [102]

$$\mathcal{H}_{Zfs} = \sum_{n,m} B_n^m O_n^m$$  \hspace{1cm} (22)

where the sum runs over all positive even integer values for $n$ ($2 \leq n \leq 2S$) and the integer $m$ gives the rotational symmetry of the operator about the $z$-axis and satisfies the limit $-n \leq m \leq +n$. $B_n^m$ are anisotropy parameters and $O_n^m$ are the Steven’s operators (Appendix E list terms up to $4^{th}$ order). Higher order terms are relatively small compared to $2^{nd}$ order terms in complexes with relatively small spin-orbit coupling (e.g. transition metal ions) and can be ignored, thus giving rise to a simpler form of the zero-field splitting Hamiltonian

$$\mathcal{H}_{Zfs}^{(2)} = DS_z^2 + E(S_x^2 - S_y^2)$$  \hspace{1cm} (23)

where, the parameter $D$ ($=3B_2^0$) is the second order uniaxial anisotropy while $E$ ($=B_2^2$) gives the second order transverse anisotropy found in SMMs with rhombic symmetry, such as Fe$_8$ [54]. For systems with spin $S \geq 2$, inclusion of $4^{th}$ order terms may become necessary in order to explain the characteristics of the SMM. The zero-field splitting Hamiltonian then becomes

$$\mathcal{H}_{Zfs} = \mathcal{H}_{Zfs}^{(2)} + \mathcal{H}_{Zfs}^{(4)}$$  \hspace{1cm} (24)

$$\mathcal{H}_{Zfs}^{(4)} = -BS_z^4 + C(S_+^4 + S_-^4)$$  \hspace{1cm} (25)

where, $BS_z^4$ gives the $4^{th}$ order uniaxial anisotropy parameter and $C$ is the $4^{th}$ order transverse anisotropy. These are the lowest order anisotropy allowed in systems with tetragonal symmetry and have been observed in SMMs with 4-fold symmetry, such as Mn$_{12}$-ac, Ni$_4$ [106, 107]. The influence of different terms on the ZFS Hamiltonian can be visualized by plotting the potential energy of a classical spin as a function of cartesian co-ordinates as shown in Figure 36. The classical anisotropy barrier is separating the anti-parallel orientations of the spin $z$-projections (distinguished by colored arrows).
Figure 36: Anisotropy barrier in SMMs. The colored arrows represent the preferred orientation of the spin along the z-axis. (a) Uniaxial anisotropy barrier, (b) Second order transverse anisotropy barrier. The lines represent the hard (H) and medium (M) axes which are separated by 90° (c) Fourth order Anisotropy barrier, with two hard and two medium transverse axes separated by 45°[49]

Figure 36(a) gives the anisotropy barrier determined by uniaxial anisotropy of the molecule (first term in equation (23)). This determines a hard anisotropy plane between opposite spin orientations along the easy magnetic z-axis. The barrier itself is isotropic in the x-y plane. Figure 36(b) shows the modification of the anisotropy barrier by the addition of a second order transverse term $E(S_x^2 - S_y^2)$, characteristic of systems with rhombic symmetry. This anisotropy introduces a hard and a medium axis (separated by 90°) within the x-y hard plane. Figure 36(c) depicts the anisotropy barrier in the presence of
fourth order transverse anisotropy term \( C(S^4_+ + S^4_-) \), characteristics of systems with tetragonal symmetry. This term gives rise to two medium and two hard axes (with 45° separation) in the hard plane.

The most relevant characteristics of SMMs can be explained fairly well within the giant-spin approximation, by which the molecule is modeled as a rigid magnetic unit of spin \( S \) weakly interacting with the environment. This model accounts for the basic properties of the quantum tunneling of the magnetization (QTM, explained later in this chapter) and associated phenomena observed in these molecules, including the remarkable observation of QTM quenching due to Berry phase interference (BPI, discussed in chapter 3) between equivalent tunneling trajectories. Unfortunately, the giant-spin model fails to explain many other phenomena (e.g. excited spin states, mixing of states of different spin lengths, etc.) or when looking at details of the basic QTM properties (e.g. selection rules, symmetry etc.). As a matter of fact, a complete understanding of the fascinating physics in these systems has become only possible during the last few years when looking at the effect of internal molecular degrees of freedom on the QTM behavior.

### 3.1.3 The Multi-Spin Description

In cases where the single ion anisotropies dominate the exchange coupling between the magnetic ions, a multi-spin interaction Hamiltonian is the preferred method for understanding the details of the QTM. Using the multi-spin model, the molecule is considered as a group of magnetic ions coupled through exchange interactions, in contrast to the GSA where it is considered as a single entity with one rigid spin. The zfs interaction Hamiltonian in multi-spin description of a SMM is given by:

\[
\mathcal{H}_{zfs} = \sum_i (\vec{s}_i \cdot \vec{R}_i \cdot \vec{d}_i \cdot \vec{s}_i) + \sum_{i,j,(i \neq j)} \vec{s}_i \cdot \vec{f}_{ij} \cdot \vec{s}_j
\]

where the first term represents the local anisotropy of the \( i^{th} \) ion, \( \vec{s}_i \) is the spin operator, and \( \vec{d}_i \) is the second order zfs tensor represented as
\[ \tilde{d}_i = \begin{pmatrix} e_i & 0 & 0 \\ 0 & -e_i & 0 \\ 0 & 0 & d_i \end{pmatrix} \] (27)

with \(d_i\) and \(e_i\), the axial and rhombic anisotropies respectively and \(\tilde{R}_i\) are Euler matrices (defined by Euler rotation angles \(\alpha, \beta, \gamma\)) specifying the orientations of these tensors with respect to the laboratory frame. The second term represents the exchange interaction between the \(i^{th}\) and \(j^{th}\) ions.

As a consequence, the Multi-spin model takes into account the internal molecular degrees of freedom and provides an understanding of quantum phenomena (such as mixing of the ground spin state with excited states) in SMMs, which are out of reach for the GSA [16-18, 108-110]. Note that this model can only be used for SMMs of low nuclearity where a low number of ions generate a Hilbert space that is computationally tractable. It has been shown to work well with Mn\(_3\), Mn\(_4\), and Ni\(_4\) (molecules with three and four ions). In molecules of high nuclearity (e.g. Mn\(_{12}\)), the GSA remains as the only practical option.

### 3.1.4 Quantum Tunneling of the Magnetization

Quantum tunneling is typically thought of as a microscopic phenomenon in which a particle can penetrate through a classically impassable potential barrier. However, a more general description accounts for any system which sees two of each states interchanged in the absence of the required potential to overcome the energy barrier separating them. This is also true for the magnetic nano-particles where up and down spins relax by penetrating through the potential barrier. The exchange interaction within the particle restricts the electronic spins to stay parallel to each other while allowing the level spin to tunnel from one state to the other in the absence of thermal energy to overcome the magnetic anisotropy barrier. This process of magnetic particles to undergoing the tunneling process is called “quantum tunneling of the magnetization” (QTM). The possibility of QTM was first suggested by Chudnovsky in 1988 [111] and it was first observed and reported in magnetic nanoparticles by Tejada and collaborators [112] and later in a SMM (Mn\(_{12}\)) in 1993 [11] with a further confirmation of its resonant nature in 1996 [15].
Figure 37 shows a magnetic hysteresis loop that is not smooth, but exhibits steps in the magnetization at regular intervals of the field, a behavior indicative of resonant QTM which in this case corresponds to Mn$_{12}$-ac. The fields of the steps are known as QTM resonant fields and are to a good approximation, equally spaced according to $H_k \sim kD/g\mu_B$ (where, $k$ is the number of resonance (or step) =0,1,2,...). These steps in the magnetization move down in field with an increase in temperature due to thermally assisted tunneling for which tunnel splittings are larger as compared to the lower splittings.

The general GSA Hamiltonian used to understand the QTM is expressed as [49]

$$\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z + \mathcal{H}_T + \mathcal{H}_d$$ \hspace{1cm} (28)

The first term describes the uniaxial anisotropy, the second term represents the Zeeman Effect due to the component of magnetic field along the easy axis of the SMM and third and last terms represent the off-diagonal transverse field and transverse anisotropy respectively. These off-diagonal terms affect the characteristics of QTM and their inclusion in the Hamiltonian aids in determining various aspects related to the physics of QTM. $\mathcal{H}_T$ in the expression above can be defined as [49];

$$\mathcal{H}_T = -g\mu_B H_T (S_x \cos \phi + S_y \sin \phi)$$ \hspace{1cm} (29)

This gives the Zeeman energy for external magnetic field in $x$-$y$ plane at an angle $\phi$ with respect to the $x$-axis. The tunnel splitting, $\Delta_k$, between the lowest lying states at a given resonance $k$, depends crucially on the transverse field ($H_T = \sqrt{H_x^2 + H_y^2}$), for small $H_T$ ($H_T \ll H_D = 2DS/g\mu_B$) and is given by [49];

$$\Delta_k(H_T) = g_k \left(\frac{H_T}{H_D}\right)^{\zeta_k}$$

with

$$g_k = \frac{2D}{[(2S - k - 1)]^2} \times \sqrt{\frac{(2S - k)! (2S)}{k!}}$$

and

$$\zeta_k = 2S - k$$

50
The above expression clearly specifies a change in tunnel splitting by many orders of magnitude for transverse fields within a very small range (<10 Tesla) and allows studying of QTM via a broad range of experimental techniques.

![Hysteresis loop of Mn\textsubscript{12}-ac recorded as a function of longitudinal magnetic field \(H_L\) at 0.6K and at field rate of 0.4T/min. The steps in the hysteresis are indicative of quantum tunneling of the magnetization.](image)

**Figure 37:** Hysteresis loop of Mn\textsubscript{12}-ac recorded as a function of longitudinal magnetic field \(H_L\) at 0.6K and at field rate of 0.4T/min. The steps in the hysteresis are indicative of quantum tunneling of the magnetization.

The transverse anisotropies (second order and fourth order, discussed in the previous section) influence the QTM as their inclusion in the Hamiltonian affects the tunnel splitting, introducing the hard and medium axes and are the only source of tunneling in experiments performed in the absence of transverse magnetic fields. If a transverse magnetic field is applied along the medium axis, it produces a
larger tunnel splitting than the same field applied along the hard axis. This results in a tunnel splitting showing a non isotropic pattern of oscillation as a function of the angle ($\phi$) of the transverse field.

In presence of second order anisotropy, the tunnel splitting show the 2-fold pattern of oscillation as a function of $\phi$ as shown in figure 38(a) and in the presence of fourth order anisotropy, the tunnel splitting will have a 4-fold pattern of oscillations with maxima and minima spaced by a 45° (see Figure 38(b)). These transverse anisotropy terms (in addition to oscillation patterns) also dictate the QTM spin selection rules, where the transverse anisotropy allows tunneling only at some resonances which mixes states differing by a given spin number, depending on the symmetry term. For the case of second order anisotropy, only even resonances ($k = 2n$) are allowed, where connected states are separated by a multiple

![Figure 38: (a) 2-fold and (b) 4-fold symmetries imposed by second and fourth order anisotropy terms respectively for Mn12-ac SMM when a transverse field is applied in the hard magnetic plane of the molecule [49].](image)
of two in their spin value. For the case of fourth order anisotropy, only $k = 4n$ is allowed (i.e. the connected states are separated by a multiple of four).

Disorder in SMMs is another influencing factor in QTM. It enhances the lower order anisotropy terms by lowering the average molecular site symmetry in SMM crystals and tilting the easy axis from the crystallographic easy-axis [50, 106, 113-117]. As a consequence of disorder in the crystal, the QTM does not follow selection rules imposed by the symmetry of the molecule and results in the observation of non-exponential magnetic relaxation [49].

Extensive research has been done to study the quantum phenomenon in SMMs; in Fe$_8$ [10], Mn$_{12}$-ac [50], Mn$_{12}$ wheels [109], Mn$_6$ [118], Mn$_4$-dimers [68], Mn$_{18}$ [119], and Mn$_{30}$ [120]etc.

3.2 Study of Mixed Valent Mn$_4$ SMMs

This section focuses on our experimental study of a Mn$_4$ SMM, and the numerical analysis carried out to understand the observations. We have shown that the GSA may not fully explain the QTM results and that a more rigorous approach, such as the MS model, is required in order to take into account the role of individual ions and the interactions between them. The Mn$_4$ SMM examined was synthesized by Dr. David Hendrickson’s group at the University of California-San Diego and EPR measurements were performed by Dr. Steve Hill’s group at the National High Magnetic Field Laboratory in Tallahassee. The magnetization studies, numerical analysis and comparative studies for both the Mn$_4$ SMMs (-anca and -bet) were done in UCF.

3.2.1 Complex I: The Mn$_4$-Anca SMM

3.2.1.1 Crystallographic Configuration of the Mn$_4$ Complex

The [Mn$_4$(anca)$_4$(Hdea)$_2$(edea)$_2$].2CHCl$_3$.2EtOH complex (henceforth Mn$_4$-anca) is tetranuclear manganese dicubane [19, 22, 40, 41, 121-125] and crystallizes in the triclinic $P\overline{1}$ space.
group, with one symmetry independent molecule per unit cell, where anca is the anion of 9-
anthracenecarboxylic acid, and Hdeea and edea are the monoanion and dianion of N-ethyl-
diethanolamine, respectively. One half of the molecule makes the asymmetric unit while the other half is generated by inversion.

Figure 39: Magnetic core of Mn$_4$-anca with Jahn-Teller axes shown in black. The Mn$^{III}$ occupy the inside “body” and the Mn$^{II}$ are on the outside “wing” positions

The synthesis and chemical properties of this complex have been addressed in detail elsewhere [126]. The magnetic core [Mn$_4$O$_6$] of the molecule (shown in figure 39) is composed of two Mn$^{III}$ ions (pink in color) in “body” and two Mn$^{II}$ ions (purple in color) in “wing” position, bridged by oxoatoms from coordinated anthracenecarboxylate and N-ethyl-
diethanolamine ligands that form a dicubane topology. The oxo bridges (Mn-O-Mn) between Mn ions work as the super-exchange pathways making $J_{wb}$, Mn$^{III}$-O-Mn$^{II}$ wing-body interaction and $J_{bb}$ the Mn$^{III}$-O-Mn$^{III}$ body-body interaction within the magnetic core. The inversion symmetry dictates that all four Mn ions lie in the same plane, and that the Jahn–Teller axes of the Mn$^{III}$ ions are collinear; these JT axes, and thus the uniaxial anisotropy axes, are nearly perpendicular to the plane formed by the four Mn ions. Figure 40 illustrates the crystal packing of Mn$_4$-anca and indicates the JT axes in black. Analysis of variable temperature and variable field dc...
magnetic susceptibility data suggest that the molecule possesses a large spin ground state (S = 9) with positive values of $J_{wb}$ (exchange interaction between Mn$^{II}$ and Mn$^{III}$) and $J_{bb}$ (exchange interaction between Mn$^{III}$ and Mn$^{III}$) [32], indicating ferromagnetic exchange pathways, with Mn$^{III}$-Mn$^{III}$ distances of 3.25-3.38 Å, Mn$^{II}$-Mn$^{III}$ distances of 3.24-3.31 Å, Mn$^{III}$-O-Mn$^{III}$ bond angles of 99-101 degrees and Mn$^{II}$-O-Mn$^{III}$ bond angles of 92-96 degrees and 107-114 degrees [126].

![Figure 40: Crystal packing of Mn$_4$-anca SMM](image)

### 3.2.1.2 Low Temperature Magnetization Measurements

Our Mn$_4$-anca sample was studied via high sensitivity micro-Hall effect magnetometry.[127] The crystal was placed on the magnetometer with its easy axis aligned with the z-axis of the magnetic field of a 3D vector superconducting magnet. The low temperature magnetization studies were carried out in a He$^3$ cryostat with a base temperature of 230mK. Figure 41 (a) shows magnetization hysteresis loops obtained while applying magnetic field along the easy magnetization axis of the crystal in the temperature range from 0.23 to 1.4 K. The longitudinal field was swept at a constant rate of 0.1 T/min. The observation of hysteresis with clear steps in the magnetization (indicating QTM) is considered a hallmark of SMM behavior. The observed blocking and crossover temperatures are ~ 1.4K and ~0.3K. Figure 41
(b) shows the derivatives of magnetization curves, indicating three prominent resonances ($k=0, 1$ and $2$) at lower temperatures with the field spacing $\Delta H_k \sim 0.65T$ (between $k = 0$ and $1$) and $\sim 0.45T$ (between $k = 1$ and $2$), demonstrating that the peaks do not follow the regular pattern predicted by the GSA Hamiltonian ($H_k \sim kD/g\mu_B$). Also, as we went higher in temperatures ($\sim 0.7K$), we observed additional resonances around $0.3T$. The irregular spacing between the steps and observation of resonances at higher temperatures is considered to be due to the presence of low-lying excited states [18, 109]. It is also indicative of a not-so-well isolated (rigid) spin ground state and is most likely due to the weak exchange interactions between the ions.

![Image](image.png)

**Figure 41:** (a) Hysteresis loops recorded as a function of longitudinal magnetic field $H_L$ at different temperatures at field rate of $0.1 T/min$. (b) Derivatives of the hysteresis loops of Mn$_4$-anca at different temperatures and at a field sweep rate of $0.1 T/min$.

### 3.2.1.3 EPR Measurements

EPR experiments were carried out in a $17 T$ superconducting magnet with temperature control achieved by a $^4$He flow cryostat. A Millimeter-wave Vector Network Analyzer (MVNA) was used as a microwave source and detector, and a cavity perturbation technique was employed to measure the signal.
from a micron-sized crystal [128, 129]. Figure 42 shows the EPR spectra obtained at 165 GHz in a temperature range of 1.7 to 15K with the magnetic field aligned close to the easy axis.

The peaks in the spectra are sorted as either A or B series depending on their temperature dependence and the relative spacing between peaks within each series. The stronger peaks preserved with lower temperatures are labeled as A₁, A₂, etc., whereas the weaker peaks that appear between the A peaks at higher temperatures are labeled as B₁, B₂, etcetera. At the lowest temperature (1.7K), only one strong transition (A₉) is observed, indicating a well separated ground state. The high temperature (15K) spectrum indicates nine successive peaks in the A series, distributed in the field range of 1.8 to 6 T, which is the g = 2.00 position for 165 GHz. These nine peaks correspond to the nine transitions, \( m_s = -9 \rightarrow -8 \) (A₉), -8 \( \rightarrow \) -7 (A₈), \ldots, -1 \( \rightarrow \) 0 (A₁), where \( m_s \) is the spin projection onto the molecular easy axis. The
number of peaks observed confirms the approximate ground state spin of \( S = 9 \). On the basis of the GSA, one expects the high-field EPR peak spacing associated with the transitions to be uniform, but the irregular spacing between the A series peaks indicates the admixing of low lying excited spin states with the ground state.

### 3.2.1.4 Numerical Analysis of the Experimental Observations

The GSA model clearly does not account for all the observed features found in magnetization and EPR studies. This can be tested further by applying the model directly to the data and considering Mn₄ as a rigid molecule with giant spin \( S = 9 \). The Hamiltonian is then

\[
\mathcal{H}_{\text{GSA}} = -DS_z^2 + g\mu_B H_z S_z
\]  

The energy spectrum obtained by the exact diagonalization of the Hamiltonian as described above using values of \( D = 399 \) mK, \( g_x = g_y = 1.95 \), and \( g_z = 2 \) is shown in figure 43. For the chosen parameters, the spin projections of \( S = 9 \) cross at regularly spaced values of the fields, giving QTM resonances at fields spaced by 0.33 T, a condition satisfied by only a few peaks in the \( dM/dH \) data - there are still several peaks which cannot be explained by incorporating this approximation.

The non-uniform spacing of the peaks seen in the EPR data can be reproduced by including high order anisotropy terms (2\(^{\text{nd}}\), 4\(^{\text{th}}\) and 6\(^{\text{th}}\)) in the GS Hamiltonian. Figure 44 shows the fits to series A peaks with the parameters: \( D = -0.398 \) K, \( E \geq 0.038 \) K (the \( \geq \) symbol represents the fact that the precise field orientation within the hard plane is not known), \( B_4^0 = 3.65 \times 10^{-4} \) K and \( B_6^0 = -2.64 \times 10^{-7} \) K. Although the sixth order axial anisotropy value used in above parameters is quite small it is necessary to include it in order to obtain a good quality fit with the experimental data. The addition of higher order parameters does not provide enough insight into the underlying physics of this molecule, and thus completely fails to account for the existence of low lying excited spin states.
Since the resonances obtained by magnetization and EPR studies of Mn$_4$-anca cannot be justified by GSA, a more realistic model that involves a multi-spin Hamiltonian may be required. The Hamiltonian for multi-spin model is expressed by the equation

$$\mathcal{H}_{MS} = \sum_{i} (\vec{s}_i \cdot \vec{R}_i \cdot \vec{R}_i \cdot \vec{s}_i) + \sum_{i} m\mu_B gH \cdot \vec{s}_i + \sum_{i,j,(i>j)} \vec{s}_i \cdot \vec{J}_{ij} \cdot \vec{s}_j$$ \hspace{1cm} (31)

This model considers the zfs associated with the constituent magnetic ions, Zeeman energy and the super-exchange coupling between them. Figure 45(a) shows the schematic of the Mn$_4$-anca complex where $S_1=S_3=5/2$ and $S_2=S_4=2$. The interaction between 2 and 4 ($J_{bb}$) is strong compared to the interaction ($J_{wb}$) between 1 and 2. Therefore, for simplicity, we have considered 2 and 4 to be rigidly coupled and acting as a single ion with spin $S = 4$, thus converting a four ion body into a three as shown in Figure 45(b).
Figure 44: Simulated plots of frequency versus magnetic field (using giant spin model) for the observed EPR peak positions obtained at 15 K and at multiple frequencies, with the magnetic field along the molecular easy axis. The black solid lines represent simulations of the A series of peaks (red squares).

Figure 45: (a) Schematic of Mn₄ crystal. 1 & 3 represent Mn^{II} while 2 & 4 represent Mn^{III} ions. (b) Schematic of the three ion model (trimer)
In doing so the dimension of the multi-spin Hamiltonian is reduced from $900 \times 900$ to $324 \times 324$, which allows much faster computations. DC susceptibility versus temperature data also provide independent support for this approximation [126]. The corresponding multi-spin Hamiltonian describing the molecule is thus

$$
\mathcal{H} = d_1 s_1^2 + d_2 s_2^2 + d_3 s_3^2 + e_2 (s_2^2 + s_2^2) + J(\mathbf{s}_2 \cdot \mathbf{s}_1 + \mathbf{s}_2 \cdot \mathbf{s}_3) + g\mu_B \mathbf{H} \cdot (\mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3) 
$$

The first four terms represent the anisotropies of the individual spins, where $d_2$ and $e_2$ are the axial and transverse anisotropies of the central spin ($s_2 = 4$), respectively, and $d_1$ and $d_3$ are the axial anisotropies of the external spins ($s_1 = s_3 = 5/2$). In this model, we did not include transverse anisotropy (being weak) on the outer spins which are equivalent due to inversion symmetry. The fifth term in equation (32) is the isotropic exchange coupling between the three spins, and the final term is the Zeeman interaction.

Figure 46 shows the energies of the Mn₄-anca $m_t$ levels as calculated by exact numerical diagonalization of the Hamiltonian in equation (32), with $d_1 = d_3 = 115$ mK, $d_2 = 2220$ mK, $e_2 = 182$ mK, $J=5420$ mK and $g=2$, as a function of the applied magnetic field. Levels associated with the ground state ($S = 9$) and the first excited state ($S = 8$) are indicated in red and blue, respectively. Note that some of the observed QTM transitions originate from states of different spin length, while others originate from crossings between excited projections of the same spin multiplet, explaining the irregular spacing between QTM steps observed in the experiments.
Similarly, the multi-spin Hamiltonian can be used to explain the EPR data. The black solid lines in Figure 47 represent simulations of EPR transitions between the lowest lying sub-levels (ascribed to a nominal $S = 9$ ground state) using the same parameterization of equation 32. These parameters were constrained by the A series of EPR peaks. As can be seen, the multi-spin model provides good overall agreement for all EPR transitions from the ground state spin multiplet. This provides further confirmation for weak exchange (comparable to the single-ion anisotropy) in this molecule and the resultant low-lying excited spin multiplets.
The focus of the dissertation is to study the low nuclearity molecules so that one can understand the effect of internal degrees of freedom on the QTM. GSA can be employed in the strong coupling regime where the QTM and EPR spectra are insensitive to $J$ and both the hysteresis steps and the high-field EPR peaks are expected to be evenly spaced. While studying Mn₄-anca we observed characteristic resonances which were irregularly spaced and could be explained only by including higher order anisotropy terms into the GSA. The addition of these terms indicates a mixing of excited spin states into the ground state, and this mixing is eventually related to the exchange coupling within the molecule. Therefore, it is preferable to use the multi-spin approach, which is efficient to apply to low nuclearity
molecules, as solving high nuclearity ions require a larger matrix which is mostly outside of computational resources.

### 3.2.2 Complex II: The Mn₄-Bet SMM

This section is divided into three sub-sections; discussing structure, magnetization and EPR studies performed on the Mn₄-Bet SMM.

#### 3.2.2.1 Crystallographic Structure of Mn₄ SMM

The [Mn₄ (Bet)₄ (mdea)₂(Hmdea)₂](BPh₄)₄ complex (henceforth Mn₄-Bet) also belongs to the family of Mn₄ dicubane SMMs. The [Mn²⁺Mn³⁺O₆]⁴⁺ ion constituting the magnetic core is similar to two face sharing cubanes missing opposite vertices with two hepta-coordinate Mn²⁺ ions (Mn1) in the “wing” positions and two hexa-coordinate Mn³⁺ ions (Mn2) in the “body” positions. It is similar in structure to Mn₄-anca presented and discussed in the previous section. The centro-symmetric Mn₄-Bet crystallizes in the triclinic $P\bar{1}$ space group with half of the molecule in the asymmetric unit. The other half is generated by inversion, resulting in the four Mn ions lying in a plane (the molecular plane), with the Mn³⁺ Jahn-Teller (JT) axes oriented along the Mn³⁺-N bonds, which lie 122.61 degrees out of this plane, i.e., roughly perpendicular to the molecular plane [130]. Figure 48 provides a sketch of the magnetic core of Mn₄-Bet. The cationic Mn₄-Bet contains four BPh₄⁻ anions per Mn₄ core.

The presence of these anions increases steric isolation and is expected to decrease the intermolecular- through-bond magnetic exchange and -through-space dipolar interaction. Mn₄-Bet is an ideal candidate for magnetization studies since it crystallizes without any lattice solvate molecules, thus reducing the disorder associated with ligands and solvate molecules. Figure 49 shows the ORTEP (Oak Ridge Thermal Ellipsoid Plot) of Mn₄-Bet.
Figure 48: Magnetic core of Mn₄-Bet. The principal magnetic axes of the molecule are indicated, with the easy (z) axis determined by the JT elongation associated with the Mn³⁺ ions (Mn³⁺-N line). The y axis lies in the plane defined by the two Mn³⁺ ions and their JT axes.

Figure 49: ORTEP of Mn₄-Bet with BPh⁺ anions.

3.2.2.2 Magnetization Studies

The analysis of DC susceptibility measurements performed at relatively higher temperature (T > 2 K) gives the ground state spin S = 9 and a barrier of ~20 K for the molecule [130].
We performed low temperature studies of the molecule’s magnetization by placing a single Mn$_4$-bet crystal on a high-sensitivity micro-Hall effect magnetometer in a He$^3$/He$^4$ dilution refrigerator, which was then placed in a 3D vector superconducting magnet. The temperature dependent magnetization ($M/M_s$) versus longitudinal field ($H_z$, the magnetic field applied along the easy axis of the molecule) data was collected in the temperature range from 35 to 1200 mK. The hysteresis loops observed for Mn$_4$-Bet are shown in Figure 50. The magnetization data reveals extremely sharp and evenly spaced vertical steps in the hysteresis loops, indicative of QTM and confirming the high quality of the crystal.

The hysteresis is temperature-independent below ~200 mK where pure ground-state tunneling plays an effective role. Thermally assisted tunneling is observed as the temperature is increased until the blocking temperature of ~1.2 K is reached, at which point the “loop” disappears. The vertical steps in the hysteresis plots at $H_z = 0$, 0.2, and 0.4 T can be assigned to QTM transitions between $m_S = -9$ and $(9 - k)$ states, where $k = 0$, 1, and 2, respectively. These sharp QTM resonances occur at a regular interval of 0.2 T ($\Delta H$), as shown in the figure 51, which displays the first derivative plot of the magnetization hysteresis loops. The small shift of ~0.02 T for all resonances is observed, and also some other minor peaks (mostly in the $k = 2$ resonance and at higher temperatures) which are considered to be due to dipolar effects. Using the GSA the axial zfs parameter $D$, associated with the $S = 9$ ground state, was calculated to be ~0.28 K. This value is in excellent agreement with the activation barrier ($E_a = |D S^2|$) calculated from ac susceptibility measurements. We note that the GSA is capable of explaining the basic QTM behavior of this molecule, as opposite to the case in Mn4-anca. We will discuss the difference between two molecules (Mn$_4$-anca and Mn$_4$-Bet) in the last section of this chapter.
Figure 50: Temperature-dependent magnetization hysteresis loops for Mn₄-Bet recorded as a function of applied longitudinal magnetic field $H_L$.

Figure 51: Derivatives of the hysteresis loops of Mn₄-Bet at different temperatures and at field rate of 0.02 T/min.
3.2.2.3 EPR Studies

EPR spectra at 139.5 GHz were obtained for Mn$_4$-Bet at different temperatures with the magnetic field directed along the easy axis of the molecule. Figure 52 shows extremely sharp EPR resonances. There are two different sets of resonances and the most prominent and sharpest ones are labeled as set A. Resonances belonging to set A appear at low temperature and the other resonances between the existing set A peaks appear at higher temperatures. The set A shows nine resonances in the 20 K spectrum in the range of 1.15 T to 4.75 T. These belong to the $S = 9$ ground state and are labeled as $A_1$, $A_2$, ..., $A_9$, with the subscript representing the absolute value of spin projection associated with the level from which the resonance occurred. It also indicates the presence of many low-lying excited spin states ($S < 9$).

![EPR spectra obtained for Mn$_4$-Bet at different temperatures with the magnetic field applied close to the easy axis at a frequency of 139.5 GHz](image)

Figure 52: EPR spectra obtained for Mn$_4$-Bet at different temperatures with the magnetic field applied close to the easy axis at a frequency of 139.5 GHz
The EPR spectra of Mn₄-Bet are almost identical to that of Mn₄-anca. Both of these support that the complexes are spin $S = 9$ ground state and the ZFS associated with $A_9$ (the ground state easy axis resonance) is equal to 110GHz, indicating that both the complexes have the same axial anisotropy. The difference in line width of $A_9$ for Mn₄-bet and Mn₄-anca is most likely due to the presence of solvate molecules in Mn₄-anca which give rise to the disorder.

3.2.3 Comparison of Mn₄-Anca and Mn₄-Bet SMMs: Concluding Remarks

Mn₄-anca and Mn₄-Bet belong to the family of Mn₄ dicubane SMMs. They share the same magnetic core [Mn²⁺Mn³⁺O₆]⁴⁺ (shown in previous sections) and possess a ferromagnetic exchange interaction between ions with Mn³⁺-Mn³⁺ distances of 3.25-3.38 Å and Mn²⁺-Mn³⁺ distances of 3.24-3.31 Å. Although these molecules crystallize in the triclinic $P\bar{1}$ space group, Mn₄-Bet SMM crystallizes without any lattice solvent molecule, while the Mn₄-anca co-crystallizes with Et-OH (which introduces ligand disorder to the SMM).

Since the magnetic cores of these two molecules (Mn₄-anca and -Bet) possess the exact same topology they can be characterized with the same spin Hamiltonian with different parameters. The high temperature ac susceptibility and EPR measurements support that both the compounds acquire an $S = 9$ ground state. Also (extracted from the EPR measurements), the ZFS associated with the ground state easy-axis transitions ($A_9$) for the both complexes is $\sim 110$ GHz, which indicates that the Mn₄-Bet and Mn₄-anca SMMs have similar axial anisotropy. The EPR spectra for both compounds can be seen and compared in the figure 53 ((a) and (b)). They both show the nine transitions ($A_1, A_2, \ldots, A_9$) but one can see a significant difference between the line-widths of the same transitions from different compounds. For instance, the line-width of the easy-axis ground transition ($\sim 0.02$ T) observed in the Mn₄-Bet SMM is less than 1/5 of that of Mn₄-anca ($\sim 0.1$ T). The difference in sharpness of the transitions is most likely due to
the fact that Mn$_4$-Bet does not have any lattice solvent molecules (and thus getting rid of the major source of disorder).

Figure 53: Comparison between Mn$_4$-anca and Mn$_4$-Bet’s (a and b) EPR, (c and d) magnetization data and (e and f) energy spectra obtained by solving multi-spin trimer model.
Low temperature magnetization studies also show characteristic differences between the complexes. Figure 53((c) and (d)) give the hysteresis loops for these SMMs, in which one can clearly see that Mn₄-Bet shows extremely sharp QTM resonances \((k = 0, 1 \text{ and } 2)\) equi-spaced by \(~0.20\text{T}\), which is different from that of Mn₄-anca, where the resonances are not regularly spaced. Also, some resonances appear at higher temperatures only, making it difficult for GSA to account for all the features. We associate this difference with varying distances between the Mn ions in the molecules due to the different molecular surroundings of the two complexes (crystals WITH vs. WITHOUT solvent). Note that small changes in the separation between the magnetic ions and the bond angles may result in a big change of the exchange coupling constants, which will in turn affect the magnetic configuration of the molecule, in particular the separation between the ground and first excited total spin states of the system. This can be visualized by comparing Figure 53 (e) and (f), which give the energy spectra for Mn₄-anca and -bet, respectively, obtained by solving the Hamiltonian with a multi-spin trimer model. The ZFS parameters \(d_{1} = d_{3} = -115\text{mK}, e_{1} = e_{3} = 0, e_{2} = -182\text{mK}\), are identical and the value of \(d_{2}\) very close \((-2200\text{mK}\) for Mn₄-anca and \(-2000\text{mK}\) for Mn₄-bet) for both molecules, but the exchange coupling \(J\) is significantly different, almost more than double in Mn₄-anca \((5420\text{mK}\) for Mn₄-anca & 1900mK for Mn₄-bet). It makes the lowest spin projections \(m_{s} = \pm 8\) of first excited state \(S = 8\) to be much lower in Mn₄-bet than in Mn₄-anca.
4.1 Introduction: Quantum Interference

Studies of the QTM, as seen in SMMs, further our understanding of the underlying physics and reveal them as candidates to be incorporated in new storage devices and quantum computation applications. It also exploits the interesting set of phenomena associated with the topology and symmetry of the molecule. Quantum phase interference [131-135], also known as Berry Phase interference (BPI), is a topological effect in which two tunneling paths interfere. The theory behind it was proposed by Loss [136] and Garg [137] for nanoscale magnetic particles and SMMs, respectively, and was successfully observed for the first time in Fe₁₈ in 1999 [54]. The degeneracy that occurs at a level crossing can be lifted by the inclusion of transverse anisotropy terms in the spin Hamiltonian (as discussed in Chapter 3). Resonance between two spin projections is achieved when the applied longitudinal magnetic field is sufficient to bring the system near an avoided level crossing. The energy gap between symmetric and anti-symmetric superposition states, the so-called “tunnel splitting” Δ, can be tuned by means of an applied transverse field. In the case of rhombic symmetry, the transverse term $E(S_x^2 - S_y^2)$ takes a form which leads to oscillations of the tunnel splitting when the transverse field is applied along the $x$-axis (hard axis) with a period of oscillations given by

$$\Delta H_T = 2k_B(2E[E + D])^{1/2} / g\mu_B$$  \hspace{1cm} (33)
The oscillations are explained by constructive (maxima) or destructive (minima) interference between the Berry phases of two equivalent tunnel paths. The probability of spin tunneling is estimated by using the Landau-Zener-Stuckelberg formula [138-141] given below [102]

$$P = 1 - \exp \left( -\frac{\pi \Delta^2_{mm'}}{2h g \mu_B (m' - m) \alpha} \right)$$

(34)

where \(m\) and \(m'\) are opposite spin projections and \(\alpha\) is the sweep rate of longitudinal magnetic field, The limits of the above equations are defined by \(\alpha\) in such a way that if \(\lim_{\alpha \rightarrow 0}, P \rightarrow 1\) and for \(\lim_{\alpha \rightarrow \infty}, P \rightarrow 0\).

The above formula satisfies the experimental observations for fast sweeps only and does not seem to agree with the behavior seen in slow sweeps [102] (as it is valid for a single spin but neglects spin-spin interactions). Figure 54 shows the dependence of the tunnel splitting of resonance \(k=0\) on the external field applied along \(\phi = 0\) (hard \(E\) anisotropy axis) and \(\phi = 90^\circ\) (medium \(E\) anisotropy axis). The drawings represent the \(x-y\) plane projections of the anisotropy barrier for Fe\(_8\) in the presence of a transverse field \((H_T)\) applied at different angles \(\phi\). The white lines show two hypothetical quantum tunneling trajectories. When \(H_T\) is applied along the hard anisotropy axis, \(\phi = 0\), the barrier remains symmetric with respect to the field. In this case, the trajectories interfere. For transverse fields not aligned with the hard axis, an asymmetric distortion of the barrier leads to non-equivalent tunneling trajectories, destroying the interference.

In this chapter we present asymmetric BPI patterns (with respect to the polarity of the transverse component of the applied field \(H_T\)) observed in the Mn\(_4\)-Bet SMM. As we show below, the asymmetric behavior results from a competition between non collinear magneto-anisotropy tensors at the two crystallographically distinct Mn ions, which is also responsible for an unusual motion of the Berry-phase minima within the transverse field magnitude-direction phase-space. We also observed that the asymmetry can be inverted upon reversal of the longitudinal field \((H_L\) parallel to easy axis) - i.e. the BPI
pattern is invariant with respect to a full inversion of the applied field, consistent with the time-reversal symmetry of the underlying zero-field Hamiltonian.

**Figure 54:** Berry phase interference pattern for resonance $k=0$ as a function of a transverse magnetic field applied along the hard (HE) and medium (ME) anisotropy axes of the Fe$_8$. The drawings above represent the $x−y$ plane projections of the anisotropy barrier for Fe$_8$ [49].

### 4.2 Observation of Asymmetric Berry Phase Interference (BPI) Patterns

We performed studies of the magnetization of Mn$_4$-bet using a dilution refrigerator at 35mK. Figure 55 gives the magnetization hysteresis loop when we applied magnetic field along easy axis ($z$-axis) of the SMM. In order to determine the hard axis we applied a constant transverse field (along $x$-axis) of
0.2T in different directions (0-360°) in the hard x-y plane for resonance $k = 0$ in addition to longitudinal field.

**Figure 55: Hysteresis loop for Mn₄-Bet recorded at 35mK at constant rate of 0.02T/min.**

From the change in magnetization ($\Delta M_{k=0}$) at resonance $k = 0$ for various directions of the transverse field we determined the angular dependence of the QTM probability ($P_{k=0} = \Delta M_{k=0}/2M_s$). Here, $\Delta M_{k=0} = (M_f - M_i)$, where $M_i$ and $M_f$ are the magnetizations before and after tunneling for resonance $k = 0$, respectively. Figure 56 shows the two fold modulation of QTM probability ($P_{k=0} = \Delta M_{k=0}/2M_s$). The minima in the modulation show the probability to tunnel is nearly zero and hence indicates the hard axes (direction of maximum energy and spontaneous magnetization is unfavorable). The hard axis was found to be at 123° or 303° which lies ~30° away from one face of the crystal. We also
noted the slight misalignment ~3° of the field rotation plane during the measurements and considered it while solving the Hamiltonian and analyzing data. This misalignment, however does not contribute significantly towards the observation of the interesting results discussed below.

After deducing the hard axis, we oriented the magnetic field exactly along it (ϕ = 0°) and performed extensive QTM measurements in order to study the symmetry of the QTM in resonances k=0 and k=1. Figure 57 shows the QTM probability \( P_k = (M_f - M_i)/(M_{sat} - M_i) \) for resonance \( k=0 \) as a function of the magnitude of the transverse field with ϕ = 0. \( M_i \) and \( M_f \) are the magnetization before and after the resonance, respectively. \( M_{sat} \) is the saturation value. The observed oscillations in \( P_0 \) correspond to BPI, with minima at regularly spaced field values (\( \Delta H_T = 0.3 \) T). A maximum in \( P_0 \) is found at \( H_T = 0 \), as expected for an integer spin value.

Figure 56: Two-fold angular modulation of \( P_0 \) for \( H_T = 0.2 \) T, providing clear evidence for a significant 2nd-order rhombic anisotropy
Within the GSA, \( \Delta H_T = 2k_B(2E[D])^{1/2}/g\mu_B \) [137], yielding a 2\textsuperscript{nd}-order rhombic ZFS parameter \( E = \pm 60 \text{ mK} \). Note that the regularly spaced \( k = 0 \) BPI minima are invariant under inversion of \( H_T \); i.e., they are symmetric with respect to \( H_T = 0 \).

![Graph](image)

**Figure 57: Modulation of the QTM probabilities for resonances \( k = 0 \)**

Interestingly, this is not the case for the resonance \( k = 1 \), for which the behavior of the QTM probability is very different. This can be seen in Figure 58, which illustrates the dependence of \( P_I \) on \( H_T \), for \( \phi = 13.5^\circ \) (the angle for which the first BPI minimum at \( H_T = 0.30 \text{ T} \) is the sharpest).

In fact, for resonance \( k = 1 \), different BPI minima appear at different field orientations \( \phi \) of the transverse field within the \( xy \) (hard) plane of the molecule (see Figure 59); i.e., the first minimum (\( H_T = 0.3 \text{ T} \)) appears at \( \phi = 13.5^\circ \) while the second (\( H_T = 0.6 \text{ T} \)) occurs at \( \phi = 6^\circ \), contrary to what is found for the \( k = 0 \) resonance (all \( P_0 \) minima are seen most clearly at \( \phi = 13.5^\circ \)). This kind of behavior has been predicted theoretically [49, 142], though never observed experimentally.
4.3 Time Reversal Symmetry of Spin Orbit Coupling

Before considering this aspect in detail, we first discuss the asymmetric nature of the BPI oscillation pattern in resonance $k = 1$. As seen clearly in Figure 58, reversal of the longitudinal field, $H_L$, results in a reflection of the $P_1$ BPI pattern about $H_T = 0$. In other words, the BPI minima are in fact invariant under a full magnetic field inversion, as required on the basis of the time-reversal invariance of the spin-orbit Hamiltonian responsible for this physics.
As noted above, the symmetries of BPI patterns must respect the symmetry of the zero-field spin Hamiltonian. If one considers only 2\textsuperscript{nd} order zfs within the GSA, then the resulting Hamiltonian necessarily belongs to the orthorhombic point group and possesses the following symmetry elements: (i) three mutually orthogonal twofold rotation axes $(x, y, z)$, (ii) three mutually orthogonal mirror planes $(xy, xz, yz)$; and (iii) an inversion center. (ii) guarantees invariance with respect to reversal of $H_T$; i.e. it enforces symmetric BPI patterns, irrespective of whether a longitudinal field is applied ($k > 0$) or not ($k = 0$). As we show below, one must break the $xy$ mirror symmetry in order to obtain asymmetric BPI patterns with respect to inversion of $H_T$. Reversal of $H_L$ results in different patterns, and the time-reversal...
symmetry then guarantees that these two patterns are mirror images. Nevertheless, no matter how many spatial symmetries are broken, the time-reversal invariance of the spin-orbit interaction guarantees that the BPI minima should be invariant under a full reversal of the applied field, that is, a simultaneous reversal of $H_L$ and $H_T$, as we have confirmed experimentally. It is possible to reproduce the essential features of the experiments by introducing 4th-order terms into the GSA. The $xy$ mirror symmetry can then be broken by rotating the coordinate frames of the 2$^\text{nd}$ and 4$^\text{th}$-order tensors.

### 4.4 Internal Degrees of Freedom and Quantum Interference

Interestingly, the approach followed in the previous section also reproduces the complex motion of the $P_1$ minima within the $H_T - \phi$ phase-space shown in Figure 59. However, a complete GSA analysis for Mn$_4$-Bet requires many parameters and provides little insight, while the same physics can be naturally understood within a multispin description which considers the internal structure of the Mn$_4$-Bet molecule. Note that the emergence of significant higher-order anisotropy terms within the GSA is a manifestation of mixing of the ground spin state with excited states, which can only be captured within a multispin model. In this context, the $xy$ mirror symmetry may be trivially broken by rotating (tilting) the ZFS tensors at the two inequivalent magnetic sites in the molecule so that their local $z$ axes no longer coincide. To explain the experimental findings we have diagonalized the multispin Hamiltonian, where the four Mn ions are coupled according to the sketch in Figure 11 and the Hamiltonian is given by

$$
\mathcal{H}_{MS} = \sum_{i=1}^{4} (\vec{s}_i \cdot \vec{R}_i^T \cdot \vec{d}_i \cdot \vec{R}_i \cdot \vec{s}_i - g \mu_B \vec{s}_i \cdot \vec{H}) + \sum_{i,j,(i\neq j)} \left(\vec{s}_i \cdot \vec{J}_{i,j} \cdot \vec{s}_j - \frac{\mu_0 (g \mu_B)^2}{4\pi r^3_{i,j}} \vec{s}_i \cdot \vec{\Delta}_{i,j} \cdot \vec{s}_j\right)
$$

The first term represents the local anisotropy of the $i$$^\text{th}$ ion, $\vec{d}_i$ being the 2nd-order ZFS tensor ($d_{ixx} = e_i$, $d_{iyx} = -e_i$, and $d_{izz} = d_i$, with $d_i$ and $e_i$ representing the axial and rhombic anisotropies, respectively). The $\vec{R}_i$ are Euler matrices (defined by Euler rotation angles $\alpha_i$, $\beta_i$, & $\gamma_i$) specifying the orientations of these tensors. The second term is the Zeeman coupling to the applied field, and we assume an isotropic Landé
factor, $g = 2.00$. The third and fourth terms represent the exchange and dipolar interactions, respectively. These terms are also time-reversal invariant, and do not change any of the preceding arguments. As depicted in Figure 60 three independent near-neighbor exchange coupling constants, $J_a$, $J_b$ and $J_c$, are considered: $J_{1,2} = J_{3,4} = J_a$, $J_{2,3} = J_{1,4} = J_b$, $J_{2,4} = J_c$ and $J_{1,3} = 0$. The dipolar matrix, $\tilde{\Delta}_{\ell \ell'}$ has been chosen to exactly reproduce all of the dipolar couplings within the molecule, with no fitting parameters.

![Figure 60: Sketch of the Mn$_4$ core indicating the interaction parameters used to explain the results](image)

Figure 61 shows the contour plots of the QTM probabilities for resonances $k = 0$ and $k = 1$ as a function of $H_T$ and $\phi$ obtained via diagonalization of Equation 35. This simulation takes into account the small misalignment of the experimental field rotation plane and employed the following parameters: $d_2 = d_4 = -4.99$ K and $e_2 = e_4 = 0.82$ K, with the easy and hard anisotropy axes along $z$ ($\alpha_2 = 0$) and $x$ ($\beta_2 = 0$), respectively; $d_1 = d_3 = -0.67$ K & $e_1 = e_3 = 0$, with the axes rotated with respect to the central spin by identical Euler angles $\alpha_{1,3} = 45^\circ$, $\beta_{1,3} = 0^\circ$ (as required by inversion symmetry); $\gamma$ being zero for all ions; isotropic ferromagnetic exchange constants $J_a = -3.84$ K, $J_b = -1.20$ K and $J_c = -3.36$ K are used.
Figure 61: Contour plots of the QTM probabilities for resonances \( k = 0 \) and \( k = 1 \) as a function of \( H_T \) and \( \phi \), calculated by using multi-spin Hamiltonian. All of the \( k = 0 \) minima lie approximately along the \( \phi = 0^\circ \) axis, whereas the \( k = 1 \) minima appear at different orientations for different \( H_T \) values.

Figure 62 plots the locations of BPI minima extracted from Figure 61 to clearly compare the experimental and numerical results. The parameters used to justify the results are constrained by the locations of hysteresis loop steps as well as by the extensive angle dependent EPR measurements. Figure 63 shows the calculated frequency dependence of the set A resonances when the magnetic field is applied along easy axis. The resonances within \( S = 9 \) ground state are represented as color coded solid lines to distinguish different transitions within set A. These simulations were performed using the same parameters explained earlier for asymmetric BPI and motion of minima for \( k = 1 \) resonance.
Figure 62: Measured (open black symbols) and calculated (solid red symbols) $\phi/H_T$-dependence of the BPI minima for resonances $k = 0$ (circles) and 1 (squares).

Figure 63: Plots of frequency versus field for Mn$_2$-Bet showing the observed ground state EPR peak positions. The data was collected with the applied field close to the molecular easy-axis at 3 K. The solid lines are the simulations of A series peak positions (black squares) using the Hamiltonian and parameters provided in the main text.
Moreover, the obtained anisotropy values for the Mn$^{III}$ ions are very similar to related Mn$^{III}$ complexes [16], while the $d_{1,3}$ value lies within the bounds reported for other Mn$^{II}$ systems [143]. The quantitative agreement with experiment is also excellent.

The motion of the $P_1$ minima can be understood as a result of the competition between different anisotropic interactions within the molecule, without a need to invoke unphysical 4th and higher-order anisotropies. Importantly, the angular positions ($\phi$) of the $k = 1$ minima move with $H_T$, while the $k = 0$ minima remain stationary, as found experimentally (Figure 59).

Finally, the multispin model perfectly reproduces the $H_T$ asymmetry of the $k = 1$ BPI pattern. As seen in Figure 64 the asymmetry is reversed upon inversion of $H_L$, as required by the time-reversal invariance of the anisotropic interactions in equation 35, and observed experimentally [Figure 58].

![Figure 64: Calculated tunnel splittings for resonance $k = 1$, for $\phi = 9.5^\circ$, as a function of $H_T$ for $H_L > 0$ (black line) and $H_L < 0$ (blue line)](image)
The crucial ingredient is the tilting of the ZFS tensors of the external spins, $s_1$ & $s_3$, relative to the central spins $s_2$ & $s_4$, so that the $xy$ mirror symmetry is broken (depicted in figure 65(a)). Figure 65(b) shows the classical energy landscape which is invariant under full field inversion (blue vs black arrows), while this is not the case when only $H_T$ is reversed (red vs black arrows). The Euler angle $\alpha_{1,3} = 45^\circ$ results in a significant projection of the relatively weak anisotropy associated with the Mn$^{\text{II}}$ ions into the hard ($xy$) plane. This, together with the finite $e_{2,4}$ parameters and the dipolar interactions, results in competing transverse interactions and the complexity of the BPI patterns observed in Figure 59. We note that the dipolar interaction has a very significant effect on the energy levels of the molecule; the ZFS within the $S = 9$ multiplet varies by as much as 10% when dipolar interactions are omitted and the location of the $k = 1$ QTM step is shifted by $\sim 0.02$ T.

![Figure 65](image-url)  
*Figure 65: (a) Sketch of the Mn$_4$ core indicating the interaction parameters and tilts in ZFS parameters (b) Representation of classical anisotropy barriers of Mn$^{\text{III}}$ and Mn$^{\text{II}}$ separately and the resultant anisotropy barrier generated by the noncolinear ZFS tensors and the different perspectives resulting from permutations of $H_T$ and $H_L$*  

The asymmetric BPI patterns have been seen in other centro-symmetric SMMs but a clear explanation is still lacking [109, 144, 145]. The present results may help shed light on the effect that symmetric anisotropic interactions can have in magnetic systems with inversion symmetry, where a net antisymmetric interaction is strictly forbidden. In this chapter we have clearly demonstrated that the
studies of simple low nuclearity systems can address fundamental symmetry considerations related to QTM in molecular nanomagnetism.
CHAPTER 5: EXPLORATION OF QUANTUM INTERFERENCE PATTERNS IN A TRIGONAL SYMMETRY SINGLE-MOLECULE MAGNET

BPI patterns have been observed in SMMs with rhombic and tetragonal symmetry, and explained with second and fourth order transverse anisotropy terms in the GSA Hamiltonian [146-148]. In addition, special cases, where the BPI patterns present peculiar symmetry behaviors (e.g., Mn_{12} wheel [109] or Mn_{4}-Bet [65]) have also been reported. This chapter presents our efforts devoted to study the same phenomenon (BPI) in a molecule with trigonal symmetry [16, 17, 149-154] for which BPI has not been observed yet. We have selected Mn_{3} SMM (symmetry = C_{3}) as our target to explore the physics related to these systems. The motivation to study a Mn_{3} SMM comes from an aim of continuing the exploration of internal degrees of freedom and molecular symmetries on the QTM of SMMs. Mn_{3}, a low nuclearity molecule with pure trigonal symmetry, serves as the perfect prototype for such endeavors.

5.1 Crystallographic Structure of Mn_{3} SMM

The complex [NEt_{4}]_{3}[Mn_{3}Zn_{2}(salox)_{3}O(N_{3})_{6}Cl_{2}] (henceforth Mn_{3}-Cl) was synthesized by Dr. David Hendrickson’s group at the University of California at San Diego [154]. The magnetic core of the molecule (shown in figure 66) is composed of a $\mu_{3}$-oxo-centered triangle of Mn$^{3+}$ ions and two capping Zn$^{2+}$ ions located above and below the Mn_{3} plane which results in a rigid trigonal bipyramidal structure. The Zn$^{2+}$ ions and [NEt_{4}]^{+} cations isolate the Mn_{3} magnetic core from intermolecular magnetic interactions. The complex crystallizes in the trigonal space group $R3c$ as racemic mixtures of $C_{3}$-symmetric chiral molecules. This means that the single crystal contains two equal populations of molecules with opposite chirality, rotated by 27° about the $C_{3}$ axis with respect to each other. Similar to the Mn_{4}-Bet discussed in chapter 3, this molecule lacks solvate molecules, resulting in extremely high resolution spectroscopic data. The ground state spin $S = 6$ is dictated by the ferromagnetic exchange
interactions between Mn$^{3+}$ ($S=2$) ions (propagated by the central $\mu$3-oxo ion and through the coordinating oxime).

![Figure 66: Magnetic core of Mn$_3$ SMM, Mn ions are in pink while Zn is in green](image)

**5.2 Quantum Tunneling of Magnetization**

The magnetization studies on Mn$_3$-Cl were previously performed and published by our group (del Barco group at UCF) in 2009. Figure 67 shows the derivatives of the magnetization recorded at various temperatures ranging from 0.3 K to 2.6 K while applying the magnetic field along the easy magnetization axis of the molecule. In this SMM, the quantum tunneling of magnetization (QTM) exhibits clear evidence of quantum mechanical selection rules. The molecular symmetry enforces the spin selection rules in tunneling and allows only transitions with a change of spin projection $\Delta m_s$ equal to the order of the spin ladder operators in the transverse anisotropy terms in the Hamiltonian (in zero transverse field). This means molecules with $S_4$ symmetry (e.g., Mn$_{12}$/BuAc; tetragonal crystal lattice) only allow $|\Delta m_s| =$
4n, where n is an integer, and molecules with C₃ (e.g., Mn₃; trigonal lattice) or D₂ (e.g., Fe₈; triclinic lattice) symmetries only permit |Δmₛ| = 3n and 2n, respectively.

The plots for Mn₃-Cl of dM/dH vs the longitudinal field H_L (i.e., along the molecular easy axis), at different temperatures, show narrow peaks corresponding to the k = 0, 1, 2, and 3 QTM resonances at almost regular field intervals (ΔH ~ 0.85 T). Resonance k = 1 (0.85 T) is invisible at low temperature; it emerges only upon application of a transverse field or above 1.5 K, when it appears suddenly at a lower field value (0.80 T). The absence of a QTM resonance within a series of resonances was observed for the first time and represents evidence of the manifestation of spin selection rules for QTM.

The absence of QTM spin selection rules in all other SMMs studied so far can be attributed to many possible reasons: (i) Intrinsic disorder (from solvent loss, ligand disorder, or crystal defects) lowers the local symmetry, so that an applied longitudinal field induces a distribution of transverse magnetic field components [49, 116]; (ii) dynamic fields from nuclear spins [155]; (iii) dipolar interactions [156]; and (iv) internal transverse fields.

Following spin selection rules, one would also expect resonance k = 2 to be absent in figure 2 at low temperatures since only k = 3n are allowed. However, the presence of this resonance can be understood in terms of tilting of the Jahn-Teller axes of the Mn ions within the molecule and can be explained by exact diagonalization of MS Hamiltonian given below;

\[ H_{MS} = \sum_i (\vec{s}_i \cdot \vec{R}_i \cdot \vec{d}_i \cdot \vec{R}_i \cdot \vec{s}_i) + \sum_i \mu_B g H \cdot \vec{s}_i + \frac{1}{2} \sum_{i,j,(i \neq j)} \vec{s}_i \cdot \vec{J}_{i,j} \cdot \vec{s}_j \]  \hspace{1cm} (36)

Here the first term represents the magnetic anisotropy of the i-th ion, being the ZFS (diagonal) tensor given by \( d_{xx} = e, \ d_{yx} = -e \) and \( d_{zx} = -d \), with d and e the uniaxial and second-order transverse anisotropy parameters, respectively. \( \vec{R}_i \) is the Euler matrix specifying the anisotropy axes of the three Mn ions in the molecule, defined by the Euler rotation angles \( \theta_i, \phi_i \) and \( \psi_i \). The second term is the Zeeman
coupling to the applied magnetic field, and the last term is the exchange interaction between neighboring ions.

The positions of the QTM resonances observed can accurately be accounted for by using the following set of parameters: \( s_i = 2, d = 4.2 \text{ K}, e \sim 0.9 \text{ K}, \) isotropic \( g = 2 \) and \( J = -4.88 \text{ K} \). The anisotropy axes for the three Mn\textsuperscript{III} ions are rotated such that \( \theta = 8.5^\circ \) (with \( \psi_i = 0 \)), and \( \phi_1 = 0, \phi_2 = 120^\circ \) and \( \phi_3 = 240^\circ \), in order to account for the local tilts of the Jahn-Teller axes and to preserve the \( C_3 \) symmetry.

Figure 68 shows the tunnel splittings associated with resonances \( k = 0, 1, 2 \) and \( 3 \) plotted against the transverse field for opposite polarities using the above parameters and MS Hamiltonian. The finite field splitting of the \( k = 0 \) and \( k = 3 \) resonances, allowed by symmetry when \( H_T = 0 \), is mainly generated by the molecular anisotropy and shows weak variation for moderate \( H_T \) values. However, for the
‘forbidden’ $k = 1$ and $k = 2$ resonances, the transverse field is the only source of level mixing, and this mixing is strongly amplified by the Jahn-Teller tilts. This figure also shows the quenching of tunnel splitting for the case of resonances $k = 1, 2$ and $3$, at the transverse fields of ~0.7, ~0.6 and ~0.4T respectively, comparing to BPI.

![Graph](image)

**Figure 68:** Calculated BPI patterns by solving multi-spin Hamiltonian using parameters extracted from aforementioned experimental data

Figure 69 shows the color contour polar plot of the tunnel splitting of resonance $k=1$ as a function of transverse field $H_T$, calculated using the MS Hamiltonian in equation (36) and the above parameters. The interference pattern shows the three fold modulation expected from the trigonal symmetry possessed by Mn$_3$ SMM.
5.3 Theoretical Studies on Trigonal Symmetry SMMs

Recently, theoretical studies [157] have been done to study the QTM in trigonal symmetry SMM. These studies are focused on the origin of the three-fold transverse anisotropy $O^3 = \frac{1}{4}[S_z (S^+_z + S^-_z)]$ and phenomena generated by this interaction. The QTM in Mn$_3$ with trigonal symmetry has been studied by mapping the spectrum of Mn$_3$ obtained by multi-spin Hamiltonian (in Equation (36)) onto that of a giant spin model. The giant spin Hamiltonian used is expressed below;

$$\mathcal{H}_{gs} = D S_z^2 + B^3_4 O^3_4 + B^3_6 O^3_6 + B^6_6 O^6_6 + \mu_B g H \cdot S$$

(37)

The first four terms represent the ZFS anisotropy while the last term gives the Zeeman interaction. The effect of transverse magnetic field and hence the visibility of BPI patterns is predicted based on theoretical models. In case of multi-spin ($s = 2$ for each Mn ion) description the interaction is considered strong with $J = 10K$ while in GSA the trigonal $O^3_4$ and hexagonal $O^6_6$ operators play the leading role. Figure 70 shows the BPI patterns for resonance $k = 0$ and $k = 3$ in Mn$_3$ SMM. These patterns are generated purely from the $B^3_4 O^3_4$ interaction. The $k = 0$ pattern in (a) is hexagonal. However, the
coloring indicates the polarity of the compensating longitudinal magnetic field, $H_\ell$. Thus, on the basis of the sign of $H_\ell$, one sees that the BPI minima exhibit a three-fold rotational symmetry. In contrast, the $k = 3$ BPI minima exhibit obvious trigonal patterns, regardless of the behavior of the compensating $H_\ell$ field.

Figure 70: The BPI patterns for the ground QTM resonances of the Mn$_3$ SMM. The Color contour plots show tunnel splittings for $k = 0$ (a) and $k = 3$ (b) as a function of $H_T$, calculated using equation (37) with $B^0_6 = 0$ [157]

5.4 Exploration of BPI in Mn$_3$SMM

Based on the experimental and theoretical studies mentioned above, we were motivated towards exploring the BPI patterns in Mn$_3$-Cl. The observation of BPI is complex due to strong avalanches at high transverse fields ($H_T > 0.55T$) for resonances $k > 0$ and the presence of two species rotated by $\sim 27^\circ$. We started our exploration by considering Figure 69, which shows the BPI minima for resonance $k = 1$ using the MS description based on experimental observations. The three-fold minima position ($120^\circ$ away from each other) is attributed to the trigonal symmetry of the Mn$_3$ SMM. $k = 1$ is considered due to the presence of minima below applied transverse field of 1T, which is the limitation of the transverse coils of
our 3D vector superconducting magnet. Also for \( k > 0.1 \) the avalanches are very strong and is almost impossible to register the magnetization properly.

![Contour plot showing the expected BPI minimum for \( k = 1 \) following trigonal symmetry, yellow lines specify the range -35° to +35° and red lines specify range 145° to 215°](image)

**Figure 71**: Contour plot showing the expected BPI minimum for \( k = 1 \) following trigonal symmetry, yellow lines specify the range -35° to +35° and red lines specify range 145° to 215°

We placed a single crystal on a high sensitivity Hall Effect magnetometer and applied the transverse field in the hard plane of the SMM in various directions. These directions were selected by considering at least the three fold pattern of BPI minima. Firstly, we swept the transverse field in the range of -35° to 35° (70° range) (range specified by yellow lines in Figure 71) with intervals of 5° to examine the case of resonance \( k = 0 \).

Figure 72 shows the modulation of QTM probability \( P_k = (M_f - M_i)/(M_{sat} - M_i) \) for resonance \( k = 0 \) as a function of the transverse magnetic field applied at different angles \( \phi \). \( M_i \) and \( M_f \) are the magnetization before and after the resonance, respectively. \( M_{sat} \) is the saturation value. \( P_{k=0} \) is explored at high field rate of 1 T/min, with the transverse magnetic field applied in the range of \( H_T = 0 \) to 1 T (which is the upper limit for the magnitude of our 3D vector superconducting magnet). The angles are scanned in
the range of 145° to 215° with an increment of 5°, while the longitudinal field is swept up and down. This covers a 70° scan.

![Figure 72: Modulation of QTM probabilities for resonance k = 0 for ϕ = ((a)-35 to +35°) ((b)145-215°)](image)

As seen in figure 72(a), there is no minimum for the k = 0 resonance in the explored range of angles. So following the trigonal symmetry (since the SMM is trigonal symmetry so the BPI minima if then existed will follow 3n fold, i.e., trigonal, hexagonal, etc.) one can expect it to be on the opposite angle side (i.e. in the range of 145° to 215°), the area enclosed by red lines in figure 71. Sweeping field in opposite directions with the angle range of 70° should be enough to detect at least one minimum. Figure 72 (b) shows the QTM probability in the angle range of 145° to 215°. This also does not show any indication of BPI pattern. Following the trigonal symmetry, a scan range of 70° +70° should be enough to detect a BPI minimum if it lies below 1T. The observation of no minimum for k = 0 is in agreement with the prediction in Figure 68 (parameters based on experimental observations).
We repeated the same experiments for the case of resonance \( k = 1 \), starting with the angle range of -35° to 35° (since minimum for \( k = 1 \) is expected near 0.8T). Figure 73 (a) shows the QTM probability for \( k = 1 \) \((P_k = 1)\) in angle ranging from -35° to 35°. \( P_k = 1 \) has been measured at the field rate of 1 T/min below \( H_T \sim 0.6\)T and at 0.1 T/min from 0.6 T up to 1 T due to avalanches at higher transverse fields. The decrease in rate above the transverse field of 0.6 T is necessary to avoid avalanches. The change in rates for \( P_k = 1 \) appears as a jump for each angle as can be seen in the figure 73 (a). Due to the absence of minimum in this range (-35° to 35°), we studied the opposite angle range by applying the transverse field from 145° to 215°. Figure 73 (b) shows the QTM probability \( P_k = 1 \) for \( k = 1 \), indicating the absence of BPI minima.

![Figure 73: Modulation of QTM probabilities for resonance \( k=1 \) for \( \phi = ((a)\text{-35 to } +35^\circ)((b)145-215^\circ)\)](image)

One can be satisfied with the results obtained by resonance \( k = 0 \), since the predictions in figure 70 (also figure 68) expect the first minima to appear above 1T transverse field, while the case for resonance \( k = 1 \) is not consistent with the predictions. There are several reasons which explain the absence of BPI minima for resonance \( k = 1 \) in our experiments. The positions of the BPI minima depend extensively on the transverse anisotropy \( E \), while the energy levels do not depend considerably on \( E \).
which means changing $E$ in the MS description will not have any drastic effect on the energy levels of Mn$_3$ SMM. It is possible that the value of $E$ is underestimated from the results, and the calculations in Figure 68 are wrong and the BPI minima appear for field values greater than 1T (which could not be checked due to field limitations of our superconducting magnet system). Also the presence of two different chiralities in the SMM can affect the observations.

Observation of BPI patterns in the trigonal symmetry SMM (Mn$_3$) is of extreme interest since it has not been observed yet. We are planning to continue further experiments with our collaborators, using magnets that allow applying transverse magnetic fields greater than 1T.
APPENDIX A: FABRICATION RECIPE OF MICROSTRIP RESONATORS
Fabrication recipe of Microstrip resonators (Line and cross)

The following steps are followed in order to make microstrip resonators (Line and cross):

1. Clean the piece of GaAs wafer using three solvent cleaning process (acetone 5min, ethanol 5 min and isopropanol 5 min) in the ultrasonic cleaner.
2. Spin coat photoresist LOR-3A at 500rpm (2 seconds) followed by 3000rpm (30 seconds).
3. Bake on hotplate at 170C (175°C in our plate) for 5 minutes.
4. Spin coat photoresist S1813 at 500rpm (2 seconds) followed by 5000rpm (30 seconds).
5. Bake on hotplate at 115C (120°C in our plate) for 2 minutes.
6. UV-expose for 7 seconds.
8. Hotplate bake at 125C (130°C in our plate) for 5 minutes.
9. Undercut etch in CD26 for 1 minute (do not move the sample while developing in this step).
   Rinse in DI-water and blow dry.

Depositing the metal:

1. (Optional. This step is not required if the sample has been prepared right before deposition)
   Removal of the oxide layer on the surface of the sample: Dip the sample in DI H2O: Ammonium Hydroxide (4:1) for 5 seconds immediately before putting the sample inside the UHV chamber.
2. Dip the sample in DI water for 15 seconds.
4. Deposit the metal: Use small deposition rates for this.
   - 5nm thickness Pt (Bulk density 21.37, z-ratio 0.245)
   - 100nm thickness metal to be evaporated (copper, gold or aluminum)
   - Optional: 50-100nm thickness Au on top (if metal evaporated is not gold)
   - Use the tooling factor for the thermal and e-beam evaporators.
5. Lift-off the metal outside the microstrip resonator: dip the sample in remover PG and ultrasound for short periods of time (1 second each period or less) until having all the photoresist out. Ultrasound bath is a very aggressive method that can peel off the contacts pads, so its use at this stage must be minimized.

6. Clean the sample with acetone/isopropanol/ethanol WITHOUT ultrasounds.
APPENDIX B: FABRICATION RECIPE OF MICRO HALL-EFFECT MAGNETOMETERS
Micro-Hall effect magnetometers fabrication process

The GaAs-2DEG micro hall sensors were fabricated using GaAs/AlGaAs heterostructures purchased from University of Glasgow with the spacer width of 25 nm and carrier density of 2 e 11. The 2 DEG wafer is cut into the piece of dimension 0.8×0.8 cm² and the fabrication was done using the following three steps;

1. Active area delineation by optical lithography and wet chemical etching
2. Definition of Ohmic contacts by optical lithography and e-beam evaporation
3. Thermal annealing in He atmosphere

Active area delineation

Definition of active “cross” area is the first step in the fabrication of the hall sensor which is done by the depletion of the 2DEG with a careful patterned etching. In our case, 2DEG was depleted by etching the epilayer surface by 100nm. The etching depth was tested and optimized with previous trials. The etch pattern was designed to use with a positive resist Shipley.

The pattern classifies the region on the wafer where the resist will be exposed with UV, consequently leading to etch of the wafer and depletion of 2DEG. In the process of UV exposure and chemical etching, the edges of the feature get curved off and loose the sharpness. The 2DEG depletes in lateral dimension in addition to the physical etch and is referred as the depletion width. Depletion width is of the order of the depth of the 2DEG for a comparatively deep etch. If active area is too small then depletion regions can overlap and pinch off the leads to the active area. The procedure used to etch the 2DEG wafer is explained in the following steps;

1. Clean the piece of wafer using three solvent cleaning process (acetone 5min, ethanol 5 min and isopropanol 5 min) in the ultrasonic cleaner.
2. Spin coat Shipley on the clean wafer for 2 seconds at 500 rpm followed by 30 seconds at 5000 rpm. This would give a 1.2 µm layer thickness.
3. Bake the Shipley coated wafer for 2 minutes at 115°C.
4. Expose to UV at 260 W and 60 V for 7 sec.
5. Develop in CD-26 developer for 45 sec followed by dip in DI water to get rid of the residual.
7. Remove photoresist by dipping consecutively in acetone, ethanol and isopropanol for 2 min.

**Definition of ohmic contacts**

The following steps are followed in order to make ohmic contacts for the Hall sensor;

1. Spin LOR-3A at 500rpm (2seconds) followed by 3000rpm (30 seconds).
2. Bake on hotplate at 170°C (175°C in our plate) for 5 minutes.
3. Spin S1813 at 500rpm (2seconds) followed by 5000rpm (30 seconds).
4. Bake on hotplate at 115°C (120°C in our plate) for 2 minutes.
5. UV-expose for 7 seconds.
7. Hotplate bake at 125°C (130°C in our plate) for 5 minutes
8. Undercut etch in CD26 for 1 minute (do not move the sample while developing in this step).
   Rinse in DI-water and blow dry.

**Depositing the contacts:**

1. (Optional. This step is not required if the sample has been prepared right before deposition)
   Removal of the oxide layer on the surface of the sample: Dip the sample in DI H₂O: Ammonium Hydroxide (4:1) for 5 seconds immediately before putting the sample inside the UHV chamber.
2. Dip the sample in DI water for 15 seconds.
4. Deposit the contacts: Use small deposition rates for this.
   
   a. 5nm thickness Pt (Bulk density 21.37, z-ratio 0.245)
   b. 100nm thickness Au/Ge 12% alloy (bulk density 14.68, acoustic impedance 22.45)
   c. Optional (50-100nm thickness Au on top)
   d. Use the tooling factor for the thermal and e-beam evaporators.

5. Lift-off the metal outside the contacts: dip the sample in remover PG and ultrasound for short periods of time (1 second each period or less) until having all the photoresist out. Ultrasound bath is a very aggressive method that can peel off the contacts pads, so its use at this stage must be minimized.

6. Clean the sample with acetone/isopropanol/ethanol WITHOUT ultrasounds.

**Annealing the contacts**

1. Check what are the approximate values of the current needed for each of the temperatures of the annealing procedure before placing the sample into the annealing box.

2. If possible, place a microscope on top of the box to check how the metal melts during the annealing process.

3. Place the sample on the grid inside the Rapid Thermal Annealing box close to the reference sample. The thermometer must be touching the surface of a similar thickness and composition piece of wafer to have similar reading of the temperature of the surface of the sample.

4. A continuous flow of He needs to be generated inside the box. Tune the flow with the needle valve.

5. To anneal the contacts follow the next procedure:

   - 110°C for 60 seconds
   - 250°C for 10 seconds
   - 410°C for 20-30 seconds
Checking the Hall sensor at low temperature

1. Make contacts to the leads of the sensor with the wire bonder.
2. Measure the resistance at RT using the low current voltmeter (analog). Never use a digital voltmeter in doing this, high currents will break the sensor.
3. RT resistances for a 50μm × 50μm sensor should be in the order of 20-50kΩ.
4. Helium temperature (4.2K) resistance should be in the order of 1-10kΩ.
5. Apply a low frequency (100Hz-100kHz) ac current of 1-5μA between two of the leads of the sensor.
6. Measure the Hall voltage between the opposite set of leads of the sensor. Use a Lock-in amplifier at the same frequency of the current to increase sensitivity.
7. Sweep a magnetic field from negative 1-2T to positive 1-2T. The field needs to be applied perpendicular to the plane of the sensor.
8. This can be done in the homemade closed cycle cryostat at 10 K using electromagnet.
9. The Hall voltage is proportional to the field magnitude:

\[ V_H = \frac{R_H}{t} GIB \]

10. The Hall coefficient is calculated as follows:

\[ R_H = \frac{V_H}{IB} \left[ \frac{V}{AT} = \frac{\Omega}{T} \right] \]

A typical value for our sensors is 1,800 Ω/T.

11. To calculate the density of carriers use:

\[ n = \frac{1}{eR_H} \left[ \frac{T}{\Omega C} = \frac{1}{m^2} \right] \]

A typical value for our material is \(2 \times 10^{11}\) cm\(^2\)
APPENDIX C: SUBTRACTION CIRCUIT BOX
SUBTRACTION CIRCUIT BOX

The purpose of the subtraction circuit is to get rid of the background noise coming from either magnet or some other equipment during measurements. The main component of the circuit is the INA 116 differential op-amp (data sheet attached). The idea of using op-amp is to match the signal before you subtract.

The following sections explain the working of the subtraction circuit box.

FRONT PANEL

The above figure shows the front panel of the box. It is divided into three sets namely; set 1, set 2 and set 3. Each set works independently and either of it can be used for the subtraction. Every set is further divided into fixed and variable. Fixed and variable signifies two independent INA 116 op-amps (explained in circuitry) in the circuit. In case of “Fixed” the resistance $R_g$ (explained in circuitry) is fixed and can not be changed whereas in “Variable” the resistance $R_g$ can be varied with the two knobs in blue labeled as 0-5 kohms and 0-100 kohms on the front panel. The 0-100 kohms range knob is used as coarse adjustment while 0-5 kohms is for fine tuning. The red color represents two inputs + and – to the INA 116 op-amp. The voltage leads of the hall sensor to be measured will be connected to the two inputs (+ & -). The outputs (in green) from variable or fixed will go into the lock –in’s A and B.
The rear of the box has power plug and switch to supply power to the subtraction circuit.

**CIRCUITRY**

The above picture shows the subtraction circuit. It has six INA 116 op-amps. The subtraction circuit itself needs just two op-amps. From the data sheet of the INA 116 op-amp you can see that it has a (–) and a (+) input at pin 3 and 6 respectively, which are connected via red wires to the BNC connector labeled as – and + inputs in red on the front panel. The $R_G$ is connected to the pins 1 and 16 of op-amp. In case of “Fixed” these pins are not connected, providing high resistance and thus giving Gain 1 whereas, in case of “Variable” $R_G$ is given by potentiometers (blue in the circuit and connected via blue wires to op-amp) and can be varied or adjusted by the knob at the front panel in blue. $RG$ is related to the Gain by equation (1) on page 7 of the data sheet for INA 116 op-amp. Also the table in Figure 1 on the same page
gives desired Gains and RG related to them. The output of the signal is collected through pin 11 of op-amp connected to BNC connector labelled as output on front panel via green wires in the circuit. The supply voltage of +12V and -12V is given to the pins 13 and 8 of op-amp respectively by a voltage source (black colored block in the circuit).

**OPERATION**

The above figure on left shows the schematic of the hall sensor with main and the reference cross and on right the schematic of two INA 116 op-amps. Before operating the subtraction circuit, the voltages from both the sensors should be checked independently by applying the current of 1microamps. And depending on the voltage signal, the larger one should be connected to the “Fixed” and small signal should go in “Variable”. The output from respective should go into the Aand B of the lock-in amplifier.

Considering example of the above sensor we suppose that the voltage signal of the main sensor is greater than that of the reference cross. After checking the signals, we will short the current leads of both the senors (see O9 nad O7); in this case 1microA current is going through lead O16-O9-O7-O21. Since
we assumed that the voltage signal from the main is larger so we will connect voltage leads O8-O11 to
the inputs of sub-set “Fixed” on the front panel. The voltage signal from reference will go to the inputs of
“Variable” on the front panel. And the output from both will go to the A and B of the lock-ins. When you
will apply magnetic field and measure the hall voltage the data will appear with certain slope. That slope
can be reversed or changed by changing the resistance of the “Variable” via two knobs on the front panel.
The resistance should be adjusted in a way that it shows no slope. Zero slope will indicate the complete
subtraction of the background.
APPENDIX D: FABRICATION RECIPE OF INTEGRATED MICROSTRIP EPR AND MICRO HALL-EFFECT MAGNETOMETRY SENSORS
Fabricating microstrip on top of a Hall Sensor

The idea of our recipe is to have a dielectric layer between the 2DEG wafer and the microstrip, and to be able to remove it, if needed, without damaging the Hall bar.

Photoresists: LOR-3A, HSQ and AZ resist
Developer: AZ developer
Remover: PG
Other Chemicals: Acetone, Isopropanol, ethanol, H₂O₂, H₂SO₄, DI-water, Hydrogen peroxide, Ammonium Hydroxide.
Metals for evaporation: Platinum and gold
Wafer: 2DEG GaAs/AlGaAs
Tools: glass slides, pipettes, diamond knife, lint-free paper, hot plate, ultrasound bath, spinner, mask aligner and evaporation chamber.

1. Prepare AZ developer by mixing (1:4 with DI water).
2. Take AZ resist and HSQ out of the refrigerator to let them warm up, wait 30 minutes at least.
3. Pour only the HSQ amount that will be used into the white ceramic beaker and use the plastic pipette to place on wafer. AZ can be poured into a glass vile, cover with Al foil to prevent contamination, use a glass pipette to place on wafer.
4. Take hall sensor and clean by spraying acetone, IPA and ethanol followed by blow dry in N₂ gas.
   Use sonic only if needed, but only as last resort.
   Acetone (5 min.) – Isopropanol (5 min.) – Ethanol (5 min.)
5. Blow dry with N₂ gas.
6. Spin LOR photo resist on top of a hall sensor at 500 rpm (2 seconds) followed by 3000rpm (40 seconds). This layer can be removed in EBR-PG in case something wrong happen later.
7. Bake for 5 minutes at 170 C
8. Spin HSQ resist at 500 rpm (2 seconds) followed by 3000rpm (40 seconds). This is the dielectric layer, which is generally known to be resistant to solvent

9. Bake for 20 minutes at 190 C

10. Spin AZ resist at 500 rpm (2 seconds) followed by 4000rpm (40 seconds). This can be removed by isopropanol

11. Bake for 10 minutes at 100 C

12. Align the hall cross with the very center of either the microstrip or the polarizer using the mask aligner dials.

13. Expose desired pattern in the UV lamp for 15 seconds.

14. Develop in the AZ developer for 70 seconds (very important that this time is tracked as accurately as possible)

15. Immediately dip sensor into DI water to stop the development and wave it around a bit in the water.

16. Blow dry with N₂ gas

17. Deposit 3 nm of Pt (0.1 A/s, 150 -180 nm of Cu (0.4A/s) and 5-10 nm of Au (0.1/s) following the standard chamber procedure, but evaporating slowly to keep the resist from cracking.

18. Lift off the metal with warm (60°C) isopropanol. Use ultrasound at the end to help, if necessary.

19. Rinse with DI water

APPENDIX E: STEVEN’S OPERATORS
Steven’s Operators $O^m_n$ are defined below:

$O^0_2 = 3S_z^2 - s(s + 1)$

$O^2_2 = \frac{1}{2}(S_x^2 + S_y^2)$

$O^0_4 = 35S_z^4 - [30s(s + 1) - 25]S_z^2 + 3s^2(s + 1)^2 - 6s(s + 1)$

$O^2_4 = \frac{1}{4}[7S_z^2 - s(s + 1) - 5](S_x^2 + S_y^2) + \frac{1}{4}(S_x^2 + S_y^2)[7S_z^2 - s(s + 1) - 5]$

$O^3_4 = \frac{1}{4}S_z(S_x^3 + S_y^3) + \frac{1}{4}(S_x^3 + S_y^3)S_z$

$O^4_4 = \frac{1}{2}(S_x^4 + S_y^4)$
LIST OF REFERENCES


