Collective effects in Single Molecule Magnets

by

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Prof. Andrew D. Kent
From ignorance, lead me to truth;
From darkness, lead me to light;
Dedication

To my family, especially to my wife and my mother, for their love, support and encouragement.
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Abstract

Single molecule magnets (SMMs), such as Mn$_{12}$-acetate, are composed of transition metal ions and consists of identical molecules with large ground-state spin ($S = 10$) and a strong uniaxial anisotropy (65 K). Below about 3 K, Mn$_{12}$-acetate exhibits magnetic hysteresis with steps at specific values of longitudinal magnetic field due to resonant quantum tunneling between spin up and down projections along the easy axis. The intermolecular exchange interactions between spins on molecules are quite small and spins are considered to be independent and non-interacting.

However, the molecules do interact with each other both through magnetic dipolar interactions and through the lattice (e.g. phonons). I have investigated collective effects in SMMs due to these intermolecular interactions. In the thesis I will present experiments that explored magnetic ordering due to magnetic dipole interactions in Mn$_{12}$-acetate and Mn$_{12}$-acetate-MeOH. I will also present experiments on the onset of magnetic deflagration in Mn$_{12}$-acetate due to a thermal instability.

The magnetic ordering studies involved investigating the effect of transverse fields on the susceptibility of single crystals of Mn$_{12}$-acetate and Mn$_{12}$-acetate-MeOH. Transverse fields increase quantum spin fluctuations that suppress long-range order. However, the suppression of the Curie temperature by transverse fields in Mn$_{12}$-acetate is far more rapid than predicted by the Transverse-Field Ising Ferromagnetic Model (TFIFM) and instead agrees with the predictions of the Random-Field Ising Ferromagnet Model. It appears that solvent disorder in Mn$_{12}$-acetate gives rise to a distribution of random-fields that further suppress long-range order. Subsequent studies on Mn$_{12}$-acetate-MeOH, with the same spin and similar lattice constants but without solvent disorder as Mn$_{12}$-acetate, agrees
with the TFIFM.

The magnetic deflagration studies involved studying the instability that leads to the ignition of magnetic deflagration in a thermally driven Mn$_{12}$-acetate crystal. When spins prepared in a metastable state reverse, Zeeman energy is released that diffuses away. In some circumstances, the heat released cannot be compensated by thermal diffusion, resulting in an instability that gives rise to a front of rapidly reversing spins traveling through the crystal. We observed a sharp crossover from relaxation driven by heat diffusion to a self-sustained reversal front that propagates at a constant subsonic speed.
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Chapter 1

Introduction

Magnetism is one of the fundamental properties of matter and in recent years there has been much effort in understanding magnetism at nanometer length scales. There are two approaches to study magnetism at these length scales – artificial structured ferromagnet and magnetic molecules. The former represents a top-down approach where nanofabrication techniques combined with thin film deposition are used to create magnetic nanostructures. The nature of interaction between the conducting electrons and the magnetization of the structure can be studied in such structures. The latter is a bottom-up approach where 3-dimensional molecular structures are chemically synthesized. Each molecule within a crystal can behave as tiny magnets and have the same composition, structure, spin, anisotropy and orientation and hence these materials are named single molecule magnets (SMMs). In SMMs the intermolecular exchange interactions between molecules are typically quite small but the spins interact with each other by magnetic dipolar interactions that lead to quite notable effects. Moreover, the molecules are arranged in an ordered lattice and hence spins also interact through the lattice (e.g. phonons). In
my thesis research I studied collective effects in SMMs due to dipolar interactions and interaction through the lattice.

1.1 Single Molecule Magnets

Single molecule magnets (SMMs) are metalorganic compounds composed of transition metal ions and organic ligand molecules [2]. At low temperature, due to strong exchange interactions between spins on neighboring ions, each molecule can be considered as having one giant collective spin [3–5]. SMMs exhibit magnetic hysteresis at low temperature due to slow relaxation of these giant spins that are much larger than the electron’s spin ($S \gg \hbar/2$). The slow relaxation is associated with thermal activation over a magnetic anisotropy barrier [6]. Hence, SMMs can be treated as tiny classical magnets. However, the magnetic hysteresis loops have steps at regular interval of applied magnetic field. These steps are clear evidence of quantum tunneling of magnetization [7], as will be discussed further below. Therefore, SMMs exhibit classical thermal activation over a barrier as well as quantum tunneling of the magnetization. This makes SMMs excellent model systems to study the regime between the classical and quantum magnetization dynamics. This realm of physics that is intermediate between microscopic objects such as electrons and atoms and macroscopic objects is know as mesoscopic physics. Mesoscopic systems show unique properties such as quantum conductance [8] and quantum Hall effect [9] due to their confined dimensions. Hence, studies of these systems allow understanding of fundamental properties of matter at the border between classical and quantum worlds.

Among the mesoscopic magnetic systems, SMMs represent excellent model sys-
tems for the studies of the behavior of giant spins. Unlike an ensemble of magnetic nanoparticles where there is an inevitably distribution of sizes of the particles that leads to undesired distribution of energy barriers [10], all molecules in a single crystal of SMMs are nearly identical. Due to this mono-dispersity, the effects of quantized magnetic energy of an individual molecule can be observed while measuring an ensemble of molecules in a single crystal. This allows the study of quantum phenomena such as quantum tunneling of magnetization [7] and Berry phase oscillations [11] in SMMs. In addition, SMMs are versatile systems as their properties, such as spin, magnetic anisotropy and crystal symmetry can be easily controlled and manipulated via chemical synthesis. They can be easily dissolved in the organic solvent and the molecules retain their identity and intrinsic properties in solution [4, 12]. Since there is a continuous diffusion of the ligands while the molecules are in solution, different variant of the same SMMs can be synthesised by adding desired ligand molecules to the solution. As will be described later in the thesis, this substitution of the ligands can have a dramatic effect on the magnetic (as well as electronic) properties of the molecule. Due to these properties SMMs are an interesting magnetic system that enable fundamental studies such as the quantum origin of magnetization, quantum relaxation processes and spin decoherence. They are also proposed candidates for application in high density data storage and quantum computation [13].

1.1.1 Spin Hamiltonian

SMMs have a strong uniaxial magnetic anisotropy that leads to Ising-like behavior, with the giant spin oriented either up or down along the easy axis. The magnetic anisotropy depends on the molecule site symmetry and the symmetry of the crys-
talline field. In the presence of an applied field $\mathbf{H} = (H_\perp, H_z)$ the simplest spin Hamiltonian has the form,

$$\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z - g\mu_B H_\perp S_\perp. \quad (1.1)$$

$S_z$ is the component of the spin operator for the magnetic moment $\mathbf{S}$ along the anisotropy axial direction and $D > 0$ is the uniaxial anisotropy constant. The first term defines the anisotropy barrier and the second and third terms specify the effect of the magnetic field applied parallel and perpendicular to the anisotropy axis. In the absence of the applied field, the eigenstates of the above Hamiltonian $\psi_i = |m_i\rangle$, where $m_i$ is the spin projection along the $z$ axis, correspond to the spin states of the system with eigenvalues $E_i = -Dm_i^2$. There are $2S + 1$ energy states and the ground state of the system correspond to $m_i = \pm S$. The height of the energy barrier separating positive and negative projections along the anisotropy axis is $U = DS^2$. The energy barrier reflects the bi-stability of the system. In zero applied field, except for $m_i = 0$ state, the energies for the Hamiltonian of Eq. 1.1 are degenerate and have two corresponding eigenstate, $m_{\pm i}$ (see Fig. 1.1a).

![Figure 1.1: Energy diagram due to magnetic anisotropy for a $S = 10$ system. (a) At zero longitudinal field, the energies of levels $m_i$ and $m_{-i}$ coincide. (b) Small fields shift the energy levels and decrease the height of the barrier. (c) At certain value of the longitudinal field $H_z = kH_\tau$ the energies of levels $m_i$ and $m_{-i+1}$ coincide.](image)
The second term in the above Hamiltonian corresponds to Zeeman energy

\[ E_{Zeeman} = g\mu_B H_z S_z, \]

where \( g \) is the Landé factor, \( \mu_B \) is the Bohr magneton and \( H_z \) is the longitudinal magnetic field applied along the anisotropy direction. Application of a longitudinal field removes the above mentioned degeneracy as the energies of the spin states with \( m > 0 \) decrease (for \( H_z > 0 \)) while the energies of with \( m < 0 \) will increase (see Fig. 1.1b). As a result, the height of the energy barrier will be modified:

\[
U = DS^2 - g\mu_B H_z S_z \left( 1 - \frac{g\mu_B H_z}{4DS} \right). \tag{1.2}
\]

As shown in Fig. 1.1c, at particular values of the longitudinal field \( H_r \), the energies of some spin states, \( m_i \) and \( m_j \) with \( |m_i| \neq |m_j| \) will coincide, \( E_{m_i} = E_{m_j} \), and two levels \( m_i \) and \( m_j \) come into resonance. This resonance condition is given by:

\[
H_r = -\frac{kD}{g\mu_B}. \tag{1.3}
\]

where \( k = m_i + m_j \) is an integer that characterizes the level crossing and resonant field. \( k = 1 \) gives the first resonant field, \( H_{r1} = \frac{D}{g\mu_B} \). The resonant fields are equally spaced and when two energy levels are in resonance, all other levels are also in resonance (for this Hamiltonian which only contains a first order uniaxial anisotropy term). For large longitudinal fields \( H_z > \frac{2DS}{g\mu_B} = H_A \), the bi-stability of the system is removed. Here, \( H_A \) is the anisotropy field and a field of this magnitude applied transverse to the easy axis also eliminates the energy barrier.

The third term of Equation 1.1 shows the effect of the magnetic field applied perpendicular to the anisotropy axis. The spin projections \( S_{x,y} \) of the spin operator \( \mathbf{S} \) do not commute with \( S_z \) and consequently with the Hamiltonian. Application
of the transverse field removes the degeneracy at resonant fields as the degenerate levels $E_{m\pm i}$ splits into two levels $E_{m\pm i} = E_{m_i} \pm \Delta m_i$. Also, the eigenstates $\psi_{m\pm i}$ are mixed states corresponding to the spin projections along $z$ direction and can be written as:

$$\psi_{m\pm i} = \frac{1}{\sqrt{2}} ( |m_i \rangle \pm |m_{-i} \rangle ) .$$  \hspace{5cm} (1.4)

Figure 1.2: Avoided energy level crossing of energy levels of state $m_i$ and $m_{-i}$. At the crossing, due to the symmetry breaking transverse field term, the two state will not cross, and symmetric and anti-symmetric terms of $m_i$ and $m_{-i}$ become the eigenstates.

Figure 1.2 plots the crossing of two energy levels $E_i$ and $E_{-i}$ for given applied transverse field. $\Delta$ is the separation between the two split levels and generally increases with the applied transverse field. However, for systems with a biaxial anisotropy, such as Fe$_8$, the splitting can be a non-monotonic function of the applied field [11]. The split states are actually responsible of quantum tunneling of the magnetic moment as spins can flip from $m_i$ to $m_{-i}$ and irreversibly decay to the ground state once the resonance is crossed. The splitting of the states is the
origin of quantum tunneling of the magnetic moment, as neither \( m_i \) or \( m_{-i} \) is an eigenstate of the spin-Hamiltonian. A spin initially in the state \( i \) may go to \( -i \) as the field is ramped through the avoided crossing as shown in the Figure 1.2.

1.1.2 Quantum Tunneling of Magnetization

At non zero temperature the population of spins in the states \(|m_i\rangle\) follows a Boltzmann distribution and is proportional to \( \exp \left[ -\frac{E_i}{k_B T} \right] \). The population of spins in the state \( m_i \) is given by:

\[
  n_i = \frac{1}{Z} \exp \left[ -\frac{E_i}{k_B T} \right], \quad Z = \sum_j \exp \left[ -\frac{E_j}{k_B T} \right].
\]  

(1.5)

The total magnetization along \( z \) direction is the sum of the population multiplied by the corresponding spin projections, \( M_z = \sum_i n_i m_i \). The magnetization dynamics can be described by equations for the number of spins in the left \( n_+ \) and right wells \( n_- \),

\[
  \dot{n}_\pm = \pm \Gamma_\mp n_\mp \mp \Gamma_\mp n_\pm = \Gamma(n_\pm^{eq} - n_\mp).
\]

(1.6)

Here \( \Gamma_\pm \) are the escape rates from the positive/negative wells and are described by the following equations:

\[
  \Gamma_- = \Gamma_0 \exp \left[ -\frac{U}{k_B T} \right], \quad \Gamma_+ = \Gamma_0 \exp \left[ -\frac{U + \Delta E}{k_B T} \right],
\]

(1.7)

where \( U \) is the energy barrier, \( \Delta E \) the energy difference between the two wells and \( \Gamma_0 \) is the attempt frequency.

Finally, using \( \Gamma = \Gamma_+ + \Gamma_- \), we get the total relaxation rate (neglecting resonant
tunneling for the moment):

\[
\Gamma = \Gamma_0 \exp \left[ -\frac{U}{k_B T} \right] \left( 1 + \exp \left[ -\frac{\Delta E}{k_B T} \right] \right) .
\] (1.8)

At high temperatures the spins in SMMs are thermally activated and the time the spins remain in one state is much shorter than the measuring times. The magnetic moments are in thermal equilibrium \( M \propto 1/T \). Since they show paramagnetic behavior and have giant spins, SMMs are known as superparamagnets.

At low temperature, \( k_B T \ll U \), the spins in SMMs do not have enough energy to jump over the double well potential energy barrier. The system relaxes slowly and stays in a metastable state for a long time. When the time scale of spin relaxation becomes longer than the measuring time, \( t_{\text{meas}} \), hysteresis will be observed in the magnetization curve due to “blocking” of the spins in one well [6]. The hysteretic behavior in SMMs is different than in a conventional ferromagnet, where hysteresis is due to nucleation, propagation and pinning of magnetic domains. The blocking temperature, \( T_B \), is defined as the temperature below which SMMs show hysteretic behavior. Solving \( t_{\text{meas}} = 1/\Gamma \), we get the blocking temperature,

\[
T_B = \frac{U}{k_B \ln(t_{\text{meas}}/\Gamma_0)} .
\] (1.9)

In addition to classical thermal relaxation, tunneling between spin states must be taken into account at low temperature. In section 1.1.1, we described how the longitudinal field, \( H_z \), could drive the system in and out of resonances and how the transverse field spits the resonant levels and is responsible of quantum tunnelling of the magnetic moment. The tunnel splittings \( \Delta_{m_i,m_j} \), which is the energy difference between resonant states can be obtained by diagonalizing the
Hamiltonian of Eq. 1.1 in the presence of a longitudinal and a transverse field. For small transverse fields, using perturbation theory, we can obtain the expression for the tunnel splitting between resonant levels \( m_i \) and \( m_j \) [14],

\[
\Delta_{m_i,m_j} = \frac{2D}{[(m_j - m_i - 1)!]^2} \sqrt{\frac{(S + m_j)!(S - m_i)!}{(S - m_j)!(S + m_i)!}} \left( \frac{g\mu_B H_x}{2D} \right)^{m_j - m_i}. 
\tag{1.10}
\]

The splitting is larger for the higher resonance step, \( k \). In addition, increasing the transverse fields also increases the splittings and hence promotes the tunneling effect. The rate of quantum transitions between two resonant levels is determined by the tunneling frequency [14],

\[
\Omega_{m_i,m_j} = \frac{\Delta_{m_i,m_j}}{\hbar}. 
\tag{1.11}
\]

Figure 1.3a shows the magnetization of a common SMM, Mn\(_{12}\)-acetate, when the magnetic field is swept along the easy axis at 10 mT/s between 0.3 K and 3.0 K. The steps indicate that the magnetization is relaxing faster at resonant fields and presents a clear evidence of quantum tunneling of magnetization [7, 15–17]. At resonant fields, a pair of spin states are brought to the same energy by the external longitudinal magnetic field, and the transverse field provides the splitting and promotes tunneling of the spins through the energy barrier as shown in Figure 1.3c. The quantum tunneling provides the system an additional way to reach equilibrium, and thus promotes the spin relaxation. Increasing the transverse field increases the tunnel splitting and hence increases the relaxation rate. This is clearly shown in Figure 1.3b. As the transverse field is increased from 1.5 T to 4.5 T, the relaxation process is accelerated, the width of the hysteresis loops decreases, steps disappear and the magnetization curve is non-hysteretic, indicative
Figure 1.3: Quantum tunneling of magnetization. (a) Longitudinal magnetization of a crystal of Mn$_{12}$-acetate for several temperatures between 0.3 K to 3.0 K. (b) Longitudinal magnetization as a function of the longitudinal field for various transverse magnetic fields at $T = 2.0$ K. (c) The double-well potential at the resonant magnetic field $H_z = 3.01$ T for $k = 6$ resonant tunneling step.
of an equilibrium magnetization response.

1.1.3 Materials: Mn$_{12}$-acetates

One of most studied SMMs is [Mn$_{12}$O$_{12}$(O$_2$CCH$_3$)$_{16}$(H$_2$O)$_4$]·2CH$_3$CO$_2$H·4H$_2$O commonly known as Mn$_{12}$-acetate. The magnetic core of Mn$_{12}$-acetate molecule consists of a tetrahedron of four Mn$^{4+}$ ions surrounded by a ring of eight Mn$^{3+}$ ions as shown in Figure 1.4a. The four Mn$^{4+}$ ions (spin = 3/2) couple via superexchange antiferromagnetically to the eight surrounding Mn$^{3+}$ ions (spin = 2) by eight $\mu_3$-O$^{2-}$ bridge ions to form a ferrimagnetic magnetic ground state spin $S = 10$ with a magnetic moment $m \approx 20\mu_B$. Four of the eight outer Mn$^{3+}$’s (labeled as Mn2) are bridged to a Mn$^{4+}$ by two $\mu_3$-O$^{2-}$ ions; the other four Mn$^{3+}$’s (labeled as Mn3) are each bridged to two Mn$^{4+}$ ions by two $\mu_3$-O$^{2-}$ ions. This dodecanuclear cluster has $S_4$ symmetry [3, 4, 18–20].

Mn$_{12}$-acetate crystallizes in a body centered tetragonal lattice (space group $I\bar{4}$) with unit cell parameters at 83 K of $a = b = 17.1668(3)$ Å, $c = 12.2545(3)$ Å, molecules per unit cell(Z) = 2, $V = 3611.39$ Å$^3$ [21]. Since the exchange interaction between the transition metal ions is much stronger than all other terms in the spin Hamiltonian, each Mn$_{12}$ molecule behaves as a nanomagnet with giant spin oriented along the crystallographic c axis by a strong uniaxial magnetic anisotropy $D S^2 = 65$ K, where $D$ is the first order uniaxial anisotropy constant [22–25]. The magnetic centers are well separated by the organic ligands and intermolecular exchange is small compared to the intermolecular magnetic dipole interactions [26], $E_{\text{dip}} = (g\mu_B)^2 S^2/(a^2c) \sim 0.08$ K, which is one order of magnitude larger than intramolecular hyperfine interactions. In the absence of applied fields, magnetic ordering with a Curie temperature of about 0.9 K has been predicted [27, 28].
Figure 1.4: Molecule structure of the magnetic core of Mn$_{12}$-acetate and Mn$_{12}$-ac-MeOH. Mn$^{4+}$ ions, Mn$^{3+}$ ions, Oxygen atoms, and Carbon atoms are represented by green, purple, red, and gray solid spheres respectively. Hydrogen atoms are not displayed. The elongated Jahn-Teller axes that give the spin anisotropy are represented by the black bonds. The blue solid spheres in Mn$_{12}$-ac-MeOH represent the carbon atoms of the four terminal methanol molecules that substitute the terminal water molecules in Mn$_{12}$-acetate.
[Mn_{12}O_{12}(O_2CMe)_{16}(MeOH)_4]\cdot MeOH, hereafter referred as Mn_{12}-ac-MeOH, is a new high-symmetry variant of the original SMM Mn_{12}-acetate. Each molecule in Mn_{12}-ac-MeOH has the same magnetic core (see Figure 1.4c) with the same ground state spin of $S = 10$ and similar anisotropy of $DS^2 = 66.7$ K as the molecules in original Mn_{12}-acetate. Mn_{12}-ac-MeOH also crystallizes in the space group $I\bar{4}$ with unit cell parameters at 173 K of $a = b = 17.3500(18)$ Å, $c = 11.9971(17)$ Å, $Z = 2$, $V = 3611.4$ Å$^3$ [29–31]. All the parameters are nearly identical to that of Mn_{12}-acetate.

### 1.1.4 Isomer Disorder

Although the two compounds have similar lattice parameters, ground state spin and anisotropy, there are some crucial differences relevant to the studies of magnetic ordering in my thesis, which originate from the organic ligand and solvent molecules that form the local molecular environment. In Mn_{12}-ac-MeOH, the four terminal water molecules of Mn_{12}-acetate are replaced by terminal methanol molecules, the two acetic acid and four water solvent molecules are replaced by only one methanol that resides on a symmetry element making the overall structure highly symmetric and leading the crystal to retain the molecular $S_4$ symmetry [30].

In a perfect crystal, every molecule’s easy axis lies along the crystal $c$-axis. However, in Mn_{12}-acetate, each molecule is surrounded by four acetic acid solvent molecules. Each acetic acid can form only one OH…O hydrogen-bond with the two Mn_{12} molecules it lies between. Thus each Mn_{12} molecule can have $n$ ($n = 0 – 4$) hydrogen-bonds around it, which results in six different isomers [32], and three different easy axis tilts (the molecules easy-axis forms an angle with the crystal
c-axis). So although the molecule itself has $S_4$ symmetry, Mn$_{12}$-acetate does not retain this symmetry in a crystal. As explained in detail later, in the absence of an applied magnetic field these small tilts of the magnetic easy axis of Mn$_{12}$-acetate molecules have negligible effect on the magnetic properties. However, when a field is applied these small tilts can play an important role.

The relationship between the six isomers and easy axis tilts are illustrated below in Fig. 1.5:

a) For $n=0$ or $n=4$, the Mn$_{12}$ molecule retains $S_4$ symmetry; for $n=2$ (trans) case, the Mn$_{12}$ molecule has $C_2$ symmetry. In these three isomer cases, there are no easy axis tilts since the hydrogen-bonds’ net effect in the x-y plane is zero in these high symmetry cases (Fig. 1.5a).

![Figure 1.5: Two examples of different isomer in crystral lattice. Blue spin represents Mn$_{12}$ molecule with untilted easy axis and the red spin represents Mn$_{12}$ molecule with tilted easy axis. Green arrows indicate the acetic acid solvent molecules with a hydrogen-bond on one side of it. Red arrow represents the acetic acid solvent molecule that forms hydrogen bond with the Mn$_{12}$ molecule of interest.](image)

b) For $n=1$ or $n=3$, the Mn$_{12}$ molecule has only $C_1$ symmetry. The hydrogen-bonds will give a net effect pushing the easy axis to tilt towards one of the corners of the unit cell. Density functional calculations [1] predict a tilt angle $\theta$ around
0.4 degree; while HFEPTR experiments [33] found tilt angles up to 1.7 degree. The azimuthal tilt angle \( \varphi \) can be 45°, 135°, 225° or 315° (Fig. 1.5b).

c) For the \( n=2 \) (cis) case, the easy axis will tilt towards one of the unit cell edge centers. \( \theta \) is 0.5 degree in theoretical calculations, but around 1.7 degree in experiments. However, in this case, the value of the azimuthal tilt angle \( \varphi \) are different from case b). It can be 0°, 90°, 180° or 270°.

![Figure 1.6](image_url)

**Figure 1.6:** (a) The six isomers of Mn\(_{12}\)-acetate. The yellow Mn\(_{12}\) unit represents \( n=1 \), \( n=2 \) (trans) and \( n=4 \) isomers. In these three isomer cases there are no easy axis tilts. The blue Mn\(_{12}\) unit represents \( n=1 \) and \( n=3 \) isomers. In these isomer cases the hydrogen-bonds will give a net effect of tilting of the easy axis. The red Mn\(_{12}\) unit represents \( n=2 \) (cis) isomer. In this isomer there is also the tilt of easy axis as the blue isomers but the tilt differs in azimuthal angle. (b) A schematic diagram of possible isomer distribution in the crystal. A real distribution is three dimensional with additional bonds lying between different layers.

Fig. 1.6a gives a top view (looking along the z-axis) of the six isomers and the corresponding direction of tilts. At first glance, the distribution of isomers in a Mn\(_{12}\)-acetate crystal, as shown in Fig. 1.6b, seems to be random. But a closer analysis reveals that there are restrictions between the nearest neighbors, for example, it is impossible to have \( n=0 \) and \( n=1 \) molecules next to each other as
shown in the first row of Figure 1.6a. In this case the acetic acid solvent molecule lying between them would not form a hydrogen bond with either and will be frustrated.

These restrictions will impose some short range correlations on the system, but whether these correlations will lead to observable long-range correlations, is a question outside the scope of this thesis and awaits future study. In this thesis, we ignore the nearest neighbor restriction and assume that all the isomer cases have equal probability. In this case the probability of the tilt angles are summarized in Table 1.1.

<table>
<thead>
<tr>
<th>i</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
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<td>$\theta_0$</td>
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<td>$\theta_0$</td>
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<tr>
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<td>0</td>
<td>$\pi/4$</td>
<td>$\pi/2$</td>
<td>$3\pi/4$</td>
<td>$\pi$</td>
<td>$5\pi/4$</td>
<td>$3\pi/2$</td>
<td>$7\pi/4$</td>
</tr>
<tr>
<td>$P_i$</td>
<td>1/4</td>
<td>1/8</td>
<td>1/16</td>
<td>1/8</td>
<td>1/16</td>
<td>1/8</td>
<td>1/16</td>
<td>1/8</td>
<td>1/16</td>
</tr>
</tbody>
</table>

Table 1.1: Table of probability distribution of the polar $\theta$ and the azimuthal $\phi$ angles for isomer $i$ of Mn$_{12}$-acetate molecule. $\theta_0$ is found to be 0.4° or 0.5° by DFT calculation and measured up to 1.7° in experiments.

### 1.2 Magnetic Ordering

The intermolecular exchange interactions between molecules are typically quite small in Mn$_{12}$-acetates and this has led to the commonly used approximation that the large spins on each molecule are independent and do not interact with one another. Indeed, much of early research on SMMs did not consider intermolecular interactions or collective phenomena. Such studies include the famous observation of quantum tunneling of magnetization in Mn$_{12}$-acetate [7], and the study of Berry phase oscillations in Fe$_8$ [11]. However, the molecules do interact with each other and the dominant interaction is often magnetic dipolar interaction and, while the
strength of the intermolecular dipole interactions is much less than the scale of the anisotropy energy of the molecules, there are quite notable effects of intermolecular interactions. This has lead to a renewed interest in studies of collective phenomena due to dipolar interactions in SMM single crystals [34–37].

For spins on an ordered lattice, dipolar interactions lead to long range order with a ferromagnetic or antiferromagnetic ground states that depend on the lattice structure and sample shape. In several SMMs, finite temperature transitions to a dipolar ferromagnetic state have been observed or predicted theoretically [27, 28, 34, 38–41]. In Mn$_{12}$-acetate, a transition to dipolar ferromagnetism was inferred from neutron scattering experiments by Luis et al. [34]. This finding was supported by Monte Carlo simulations [41]. Calculations based on the Mean Field Approximation (MFA) by Garanin and Chudnovsky [27] and Millis et al. [28] have predicted the existence of an ordered state in elongated crystals of Mn$_{12}$-acetate at low temperature. Our measurements of the longitudinal magnetization and susceptibility of Mn$_{12}$-acetate (described in Chapter 3) are consistent with the occurrence of a transition to dipolar ferromagnetism at finite temperature [35]. In our experiments we apply transverse fields to induce quantum fluctuations (i.e. increase the rate of quantum tunneling of magnetization) and study the interplay between intermolecular interactions and quantum fluctuations by observing the field and temperature dependence of the magnetic susceptibility [35, 37].

1.2.1 Transverse-Field Ising Ferromagnet Model

The Ising Model is the most famous and simple non-trivial model used in the study of phase transitions in statistical mechanics. The application of a magnetic field in a direction transverse to the Ising axis induces quantum spin fluctuations
that compete with the long-range order by mixing the eigenstates of $S_z$ \[42\]. A fundamental model used to study the interplay between the long range order and spin fluctuations is the Transverse-Field Ising Ferromagnet Model (TFIFM) \[43\], which is described by following Hamiltonian:

$$H = -\sum_{<i,j>} J_{i,j} S_i S_j - \sum_i H_i S_i$$  \hspace{1cm} (1.12)

where $S_i$ is spin at lattice site $i$, $J_{i,j}$ are exchange coupling constants that are translationally invariant, $J_{ij} = J(|r_i - r_j|)$. The external field $H_i$ is usually taken to be homogenous, $H_i = H(r_i) = H \forall i$.

1.2.2 Random-Field Ising Ferromagnet Model

In real systems there is compositional disorder, impurities, vacancies, lattice dislocations etc. that break the translational symmetry. The Ising model fails in these systems. To take into account these nonideal effects present in any real system the following modifications could be made:

- $J(|r_i - r_j|) \rightarrow J(|r_i - r_j|) + \delta J_{ij}$,
- $H \rightarrow H + \delta h_i$.

Here, $\delta J_{ij}$ and $\delta h_i$ are not translationally invariant but random quantities that are characterized by their probability distributions. In general, $\delta J_{ij}$ and $\delta h_i$ have a zero average but a non-zero mean square average.

There are several limiting cases one can consider. For the case with $\delta h_i = 0$ and $\delta J_{ij} << J_{ij}$, the influence of randomness on the phase transition is negligible. When $\delta h_i = 0$ and $\delta J_{ij} >> J_{ij}$, the ferromagnetic order will be destroyed.
completely, and at low temperature there will be a spin-glass phase [44].

The interesting physical model is the limiting case $\delta J_{ij} = 0$, $h_i \neq 0$, which is referred as Random-field Ising Ferromagnet Model (RFIFM) [44–46]. The Hamiltonian is modified as:

$$
\mathcal{H} = -\sum_{<i,j>} J_{i,j}S_i S_j - \sum_i h_i S_i
$$

(1.13)

$$
\tilde{h}_i = 0 \quad \overline{h_i h_j} = h^2 \delta_{ij} \quad \text{and} \quad h << J_{ij} = J
$$

Here, $h_i$ is the site random-field that follows a probability distribution with $h$ the strength of the random-field and the overbar ($\bar{x}$) denotes the average over the disorder configurations. We can divide disorder systems into two separate categories.

“Quenched” site disorder is where the configuration averages are independent of the thermal averages. The ‘disordered’ variables remain fixed while the spins fluctuate. Experimentally, we can understand it as the system where dynamical time scale of the disorder is much longer than the time scale of the spin fluctuations.

“Annealed” site disorder is where the averages of site disorder variables as well as the spins, $S_i$, are carried out. In annealed system, in addition to the spins, the disorder parameters are themselves thermodynamic variables. Here timescale of the disorder and of spin fluctuations are comparable and it is much harder to perform calculations. In this thesis, the system in consideration to be quenched.

The random-field model was first proposed by Larkin for modeling defect pinning of vortices in superconductors [47]. The first discussion about whether ordering could occur in random-field system was by Imry and Ma [48]. Since then there have been many interesting realizations of random-field Ising systems in nature.
The most important in terms of experimental work is that the site diluted anti-ferromagnets in a uniform external field is random-field effect for the staggered magnetization [49, 50]. Other realizations of random-field are adsorbed monolayers on impure substrates (for e.g. Xe on a Cu surface), binary liquids in porous media, mixed Jahn-Teller systems, Anderson-Mott transition of disordered interacting electrons, impurities on ferromagnet, liquid crystal, etc. [44]. The only ferromagnetic material found to date that shows characteristics of random fields is the rare earth dipolar ferromagnet LiHo$_x$Y$_{1-x}$F$_4$[51]. Recently we discovered that Mn$_{12}$-acetate is an experimental realization of random-field Ising model [28, 35] and it will be discussed in Chapter 3 of the thesis.

1.3 Magnetic Deflagration

In previous section I described magnetic ordering in SMMs due to dipolar interactions between the molecules on different lattice sites. In this section I will describe a case in which the interaction between molecules is through heat flow or the lattice. When the spins prepared in metastable state reverse, the difference in the energy between metastable and stable state can be released through the emission of phonons. The released phonons increase the temperature of neighboring molecules. Therefore, magnetic relaxation can be described as a reaction-diffusion process. Here the reaction is the reversal of spins that releases Zeeman energy and the diffusion serves to transmit the energy to adjacent material. When the rate at which the energy released due to spin-reversal is lower than the rate at which heat diffuses away, the temperature of the sample remains constant. However, if during a short amount of time many molecules in a localized region of the sample reverse
then the magnetic relaxation process can become uncontrolled. In this case the heat from energy released cannot be compensated by thermal diffusion and leads to increase in temperature of the crystal. Due to the increase in temperature, the spin of the neighboring molecules can reverse from the excited states which in turn releases more phonons resulting in an instability that gives rise to a front of rapidly reversing spins traveling through the sample at constant speed as shown in Figure 1.7. This process has been described as magnetic deflagration—i.e. propagation of a well defined self sustained spin-reversal front.

In SMMs the role of the chemical energy is played by the Zeeman energy, and the activation energy is the energy barrier between the metastable and the stable state (See Fig. 1.8). Both activation and Zeeman energies can be varied independently via external applied transverse and longitudinal fields. The analogy
Figure 1.8: The activation and Zeeman energy in the deflagration process. As the bias magnetic field is swept, the spins relax from metastable state (left well) to the stable state (the right well) and release the Zeeman energy. This stored Zeeman energy is released through phonons that heat neighboring molecules. The activation energy is the energy required by the molecules in metastable well to overcome the anisotropy energy barrier to relax to stable well. The Zeeman energy is set by the longitudinal field and both longitudinal and transverse fields set the activation energy.

of the fuel and the ashes in the magnetic system are the spins in a metastable state and stable state respectively. The burnt ashes in the magnetic deflagration can be converted back to the fuel by reversing the magnetic field direction. Hence, the magnetic deflagration allows comprehensive non-destructive studies of deflagration that is not possible with flammable chemical substances.

The abrupt complete reversal of the magnetic moment of Mn$_{12}$-acetate crystals was first reported by Paulsen and Park [56] and later shown to take the form of a propagating spin-reversal front [52]. Magnetic deflagration has been studied by sweeping the magnetic field or by raising the crystal’s temperature. Thresholds for
both temperature [57] and applied Zeeman fields [58] were found to be governed by quantum laws due to quantum tunneling of magnetization [7]. In the experiments reported in this thesis, the spin reversal was triggered using a heat pulse at one end of the sample.

1.3.1 Deflagration Ignition

At low temperature, $k_B T \ll U$, a fully magnetized crystal of SMMs exhibits two modes of relaxation. The first, slow mode, is the slow relaxation of a giant spin that is usually observed in magnetic hysteresis by slowly sweeping the magnetic field. The relaxation is in the form of series of steps in a hysteresis curve [7] due to quantum tunneling of the magnetic moment between crossing spin states as discussed in Sec. 1.1. The second relaxation mode is an abrupt, complete reversal of magnetization due to an instability throughout the slow relaxing process. During the abrupt reversal process, the heat released in reversal of small region of spins preheats the neighboring spins and accelerates the relaxation process. It typically lasts a few milliseconds [56, 59].

To understand the ignition process of deflagration we should consider basically two processes involving heat. The first one is related with the transport along the sample, $C \dot{T} = \nabla \cdot k \nabla T$ where $k$ is the thermal conductivity and $C$ the heat capacity. The other thermal phenomenon is the energy released by the spins when a molecule makes a transition from the metastable state to the minimum energy stable state, $\Delta E = 2g\mu_B H_S$. When this energy is thermalised it leads to a change in temperature $C \Delta T = \Delta E$.

At low temperature, an exponentially small number of molecules will react and release heat. This heat will flow out of the sample, creating a steady and smooth
temperature profile along the substance with a slightly higher temperature in the bulk compared to the temperature at the surface, $T_s$, which can be found by equating the heat flow through the boundary to the heat production due to the chemical reaction inside the substance. The temperature profile is entirely determined by $T_s$, the shape of the flammable substance, and the thermal conductivity. As $T_s$ goes up, so does the temperature difference between the surface and the bulk. It turns out that, above a certain value of $T_s$, the smooth and steady temperature profile becomes unstable against formation of a narrow high-temperature burning front which propagates through the substance.

### 1.3.2 Deflagration Propagation

In a deflagration process there are two characteristic timescales that are important. The first is the thermal diffusion timescale $\tau_d \simeq \delta^2/\kappa$, where $\kappa = k/C$ is the thermal diffusivity and $\delta$ is the width of the flame. The second is the burning timescale $\tau_b \simeq \epsilon/\Gamma$ where $\epsilon$ is the total energy released by burning per unit mass, and $\Gamma$ is the burning rate (e.g., the rate of increase of specific thermal energy). This rate of chemical reaction associated with burning is given by $\tau_0^{-1} \exp[-U/(k_B T_f)]$, where $U$ is the activation energy, $T_f$ is the temperature of the burning flame, $k_B$ is the Boltzmann constant and $\tau_0$ is the attempt time. The width of the flame front $\delta$ can be found by setting the two rates equal, $\tau_b \simeq \tau_d$. Since the burning timescale $\tau_b$, which is the total energy released per molecule when reversing its magnetic moment and the diffusion timescale $\tau_d$ are:

$$
\tau_b = \tau_0 \exp \left[ \frac{U(H)}{k_B T_f} \right] \quad \tau_d = \delta^2/\kappa .
$$

\hspace{1cm} (1.14)
We can get the flame width as

$$\delta \simeq \sqrt{\frac{\epsilon \kappa}{\Gamma}} \simeq \sqrt{\kappa \tau_b} = (\kappa \tau_0)^{1/2} \exp \left[ \frac{U(H)}{2k_B T_f} \right].$$  

(1.15)

Thus, the thermal flame front propagates at a characteristic speed $v$, which is simply equal to the thermal diffusivity over the burning rate:

$$v \simeq \frac{\delta}{\tau_b} \simeq \sqrt{\frac{\kappa}{\tau_b}} = \left( \frac{\kappa}{\tau_0} \right)^{1/2} \exp \left[ -\frac{U(H)}{2k_B T_f} \right].$$  

(1.16)

The temperature of the flame, $T_f$ is given by the energy released from the reversing spins and can be written as:

$$T_f = \frac{\Theta_D}{\pi} \left[ \frac{5 n_i \Delta E(H)}{3 k_B \Theta_D} \right]^{1/4},$$  

(1.17)

where $\Theta_D$ is the Debye temperature and $n_i$ is the fraction of spins in the metastable state [60].

1.4 Thesis Overview

In this thesis, I will present an experimental study of collective effects due to dipolar interactions and the lattice in single molecule magnets. First, I will present a detailed study of magnetic ordering in Mn$_{12}$-acetate single crystals due to dipolar interactions. The magnetic ordering experiments investigates the temperature dependence of the magnetic susceptibility of Mn$_{12}$-acetate as a function of transverse field. We develop a theoretical model to explain our susceptibility data and find that Mn$_{12}$-acetate single crystals are a random-field Ising ferromagnet due to their isomer disorder. We test this finding with another SMM that does not have dis-
order but is closely related to original Mn$_{12}$-acetate and find that the new system, Mn$_{12}$-ac-MeOH (discussed in Sec. 3.4), is described by different physical model, that of a transverse-field Ising ferromagnet model.

Next, I will present a detailed study of magnetic deflagration in Mn$_{12}$-acetate single crystal. Here, using a trigger heat pulse and transverse and longitudinal magnetic fields, we investigate the deflagration ignition and control the crossover between thermally driven magnetic relaxation and magnetic deflagration in single crystals of Mn$_{12}$-acetate. Moreover, we study the steady state propagation of deflagration and find that the speed of spin-reversal front is strongly dependent on the applied transverse field and the prepared magnetic state.

The thesis is organized in such a way that each chapter is self contained. Chapter 2 is devoted to describing the experimental setup and the relevant experimental techniques used to make measurements. I made several technical improvements to the setup and these are documented in the chapter. In Chapter 3, I describe the experiments carried out on magnetic ordering in Mn$_{12}$-acetate and Mn$_{12}$-ac-MeOH. The chapter presents both the experiments carried out on the two systems and also the theoretical calculations made using appropriate Hamiltonian and lattice parameters. It also includes a section on the comparison between the calculations and the data and also a section comparing the data of the two systems. Chapter 4 presents the experiments on magnetic deflagration. Here, the experimental results on the speed of deflagration front and final state of the magnetization after the deflagration is presented. A theoretical model that explains the onset of deflagration in the experiments is developed. A section on the propagation of the reversal front is presented as well. In Chapter 5 the thesis is summarized and concluded with future research perspectives.
Chapter 2

Experimental Setup

2.1 Sample Preparation and Handling

2.1.1 Samples

For the experiments on magnetic ordering we measured more than twenty single crystals from Prof. G. Christou’s group at University of Florida, Gainesville [12, 29, 61]. We studied three Mn$_{12}$-acetate and three Mn$_{12}$-ac-MeOH thoroughly and data obtained from these samples will be presented in this thesis. The samples are:

Mn$_{12}$-ac-MeOH:
Sample A, dimensions $\sim 0.2 \times 0.2 \times 0.95$ mm$^3$,
Sample B, dimensions $\sim 0.085 \times 0.085 \times 0.68$ mm$^3$, and
Sample C, dimensions $\sim 0.075 \times 0.075 \times 0.85$ mm$^3$.

Mn$_{12}$-acetate:
Sample D, dimensions $\sim 0.4 \times 0.4 \times 2.17$ mm$^3$,
Sample E, dimensions $\sim 0.4 \times 0.4 \times 2.4$ mm$^3$, and
Sample F, dimensions $\sim 0.3 \times 0.3 \times 1.85 \text{ mm}^3$.

For the magnetic deflagration experiments three Mn$_{12}$-acetate single crystals from Prof. G. Christou’s group were studied and the data from the third sample will be presented. The samples are:

Sample I, dimensions $\sim 0.3 \times 0.3 \times 2.1 \text{ mm}^3$,
Sample II, dimensions $\sim 0.35 \times 0.35 \times 1.75 \text{ mm}^3$, and
Sample III, dimensions $\sim 0.4 \times 0.4 \times 1.6 \text{ mm}^3$.

### 2.1.2 Handling Mn$_{12}$-acetates Single Crystals

In both the magnetic ordering and magnetic deflagration experiments we apply large (several tesla) transverse fields and thus a magnetized sample experience a large mechanical torque as the samples try to align with the field. This often resulted in samples breaking and flying off the Hall sensors. To counteract the problem, we coated the Mn$_{12}$-acetate crystals with a thin layer of DOW CORNING high vacuum grease (silicon based) and added suitable amount of STYCAST 1266 epoxy to cover the crystal and let it cure for 24 hours. After transferring the samples on to the Hall sensors we further applied GE-varnish to fix the encased crystal to the Hall sensor chip as shown in Figure 2.1a. We used the epoxy to provide the mechanical strength and prevent the crystal from breaking and flying off. GE-varnish was used as an adhesive to balance out the torque.

The samples were coated with vacuum grease for protection before putting the Stycast as we found that the solvents used in STYCAST 1266 epoxy (Aliphatic Amine) and GE-Varnish (Toluene and Ethanol) are corrosive to the Mn$_{12}$-acetate crystal. Fig. 2.2a shows the Mn$_{12}$-acetate placed in different solutions used in the sample preparation for a week. We found that Isopropanol did not dissolve the
crystals, and in Toluene and Xylene the crystal dissolved a little bit. However, the crystal placed in Ethanol completely dissolved. Figure 2.2b shows the crystal in epoxy without the grease coating. The curing agent of STYCAST 1266 epoxy, Aliphatic Amine, is a strong oxidizer and it is likely that it reacts with Mn_{12}-acetate and changes the surface property and degrades the crystals.

The procedure for handling Mn_{12}-ac-MeOH crystal is different as the crystals
are stored in the mother liquor to prevent solvent loss. The solvent molecules in these crystals evaporate at temperatures below the room temperature. When the crystal are taken out of the mother liquor and exposed to vacuum or atmosphere, the crystal will lose solvent molecules and disintegrate. To prevent degradation we coated Mn\textsubscript{12}-ac-MeOH crystals with a mixture of Paratone\textsuperscript{®} N and paraffin oil [30]. Since Mn\textsubscript{12}-ac-MeOH crystals are smaller in size than Mn\textsubscript{12}-acetate, the magnetic torque experienced by Mn\textsubscript{12}-ac-MeOH is also smaller. It was found that the samples coated in Paratone\textsuperscript{®} N and paraffin oil mixture and placed on a Hall sensor with a large amount of vacuum grease on top was enough to fix the samples in transverse fields up to 6.5 T.

2.2 Measurement Techniques

We used Hall-effect magnetometry to measure the magnetization of the samples. The samples were mounted on a one-dimensional array of Hall sensors (active area $20 \times 100$ $\mu m^2$ with 200 $\mu m$ separation). The magnetization, $M_z$, along the easy direction ($c$-axis) of the crystal was measured by each micro-Hall sensor via measurement of the stray field $B_x$, which is a linear function of $M_z$. Care was taken to align the sample and the Hall array (placed in the y-z plane) relative to each other and relative to the magnet axes. The relative position between crystal and Hall sensor array is shown in Figure 2.1b.

2.2.1 Hall-effect Magnetometry

Hall magnetometry uses Hall-effect devices whose operation is based on the classical Hall effect to detect the magnetic field. The Hall effect was discovered by
Edwin Hall in 1879 [62]. When a current is flowing through a sample the charge carriers are deflected due to Lorentz force acting on moving charges in the magnetic field and accumulate at the sides resulting in a potential difference across the sample (see Figure 2.3).

![Hall Sensor](image)

Figure 2.3: Hall effect.

In a uniform magnetic field this voltage is:

\[ V_H = R_H \frac{I}{t} B, \]  

where \( R_H = \frac{1}{n_3 d q} \) is the Hall coefficient of the device, \( n \) is the charge carrier density, \( q \) is the magnitude of the charge of the carriers, \( t \) is the thickness of the conducting layer, \( I \) is the current through the device and \( B \) is the magnetic field perpendicular to the current. Eq. 2.1 is for a free electron gas or single band model of the Hall-effect [63]. We used a GaAs/AlGaAs quantum well Hall sensor in which a two-dimensional electron gas (2DEG) forms at the GaAs/AlGaAs interface. Eq. 2.1 can be rewritten in terms of 2DEG carrier concentration \( n_{2d} = n_{3d} t \) and electron
charge \( q = -e \) \((e > 0)\):

\[
V_H = -\frac{IB}{n_2d}e. \tag{2.2}
\]

### 2.2.2 Two Dimensional Electron Gas

Although Hall-effect devices have been used for a century, the interest was revived a few decades ago through the progress in micro- and nano-fabrication along with the advances in growing high mobility 2DEG heterostructures. We fabricated our Hall sensors using GaAs/AlGaAs heterostructure shown in Fig. 2.4a that was grown in Prof. H. Ohno’s Laboratory at Tohoku University.

![GaAs/GaAlAs QW heterostructure and energy band diagram](image)

Figure 2.4: GaAs/GaAlAs QW heterostructure and the energy band diagram.

In such a structure, as shown in Figure 2.4b, two n-type semiconductor materials with different band gaps are used: a material with a large band gap is labeled
as N-type and that with a narrow band gap is labeled as n-type material. When the two materials are joined to form a heterostructure, their equilibrium chemical potentials must coincide and therefore their bands must bend at the interface. The band bending causes the electrons to move from the larger band gap N-side to the narrower band gap n-side, leaving an uncompensated positive charge on the N-side (depletion layer) and causing an upward bending of its conduction band. On the n-side, an excess negative charge is accumulated, and a conduction band bends down, forming a potential well for the carriers at the interface. The motion in $z$ direction is frozen out as the level spacing in the QW is much larger than $k_B T$ and usually only the lowest subband is occupied. As a result, the electrons form a two-dimensional gas (2DEG). The doping level of the n-type material is usually chosen to be very low so that there are few ionized donors in this material. The mobility of these 2D electrons is limited mostly by the phonon scattering at high temperature that decreases dramatically at lower temperature. Note that at the lowest temperature the mobility is limited by impurity and defect scattering and determines the ultimate sample mobility.

2.2.3 Fabrication of micro-Hall Array Sensors

Our micro-Hall magnetometers were fabricated by photolithography from the two dimensional electron gas GaAl/AlGaAs heterostructure. Fig. 2.5 shows the mesa of the Hall array that I used to fabricate the devices used in the experiments. The active area is $20 \times 100 \ \mu m^2$ and the distance between neighboring sensors is 200 $\mu m$. Compared to the typical size of the crystal ($\text{Mn}_{12}$-acetate is $\sim 0.3 \times 0.3 \times 1.5 \ mm^3$, $\text{Mn}_{12}$-ac-MeOH is $\sim 0.15 \times 0.15 \times 1 \ mm^3$), the sensor size is small enough to probe the local magnetization and also provide good signal to noise ratio.
The GaAs/AlGaAs heterostructure substrate was cut by first slightly scribing the edges in a preferred crystalline direction using a diamond scriber and then applying pressure at one end with a q-tip. The substrate was cleaned with ultrasound by immersing in Acetone, Isopropanol and Ethanol for 10 minutes each. After each cleaning process the substrate was dried with extra dry and filtered $N_2$.

The main steps of the fabrication process of a micro-Hall device are shown in Figure 2.6. These steps include defining the mesa structure, deposition of contacts, exposure of the photoresist layer with UV light, developing the photoresist, etching the structure into the substrate, and removing the photoresist.
(second exposure, metal deposition and lift-off) and thermal annealing of contacts.

In the first step the wafer is coated with a photoresist and exposed by UV light through a contact mask with the pattern of Hall array. The resist is developed by immersing the wafer in the 351 developer (DI water: 351 developer = 3.5:1). Next, the structure is etched in Pirahna solution (a mixture of sulphuric acid, hydrogen peroxide and deionized water, $H_2SO_4:H_2O_2:DI$ water=1:8:160 ) at a rate of 41.7 Å/sec. The etchant removes parts of the materials that are not covered with the resist leaving a mesa structure. After the etching the wafer well below 120 nm from the surface, where the 2DEG layer lies, the wafer is immersed in DI water and cleaned before removing the remaining resist with Acetone.

The next step involved coating the wafer with a new layer of photoresist and exposing through a mask with the contact pad layout. The device is developed to remove the resist from the contact pad. The wafer is then cleaned with Ammonium hydroxide solution ($\text{NH}_3 : \text{H}_2\text{O} = 4 : 1$) for 5 sec to remove oxides and rinsed with DI water for 15 seconds before placing in the Ultra-High Vacuum chamber. The contacts are deposited by e-beam and thermal deposition. We deposit 2-5 nm adhesion layer of Pt at 0.1 Å/sec by e-beam followed by 100 nm of Au/Ge layer by thermal deposition. After deposition, the sample was cleaned in Acetone and ultrasound to remove the photoresist. Next, the contacts were carefully annealed in an annealing chamber so that the metal diffuses into the semiconducting heterostructure.

### 2.2.4 Background micro-Hall Sensor

In addition to one dimensional of Hall array sensors, we have a background sensor at a distance of about 3 mm on the same semiconductor wafer as the main
Hall array as shown in Figure 2.5. Although the external fields (both the longitudinal field in $z$ direction and transverse field in $x$ direction) are applied parallel to the Hall sensor surface as shown in Fig. 2.1b, due to flux trapping and non-ideal wiring, the field generated by the superconducting magnet is not completely uniform and the Hall array sensors pickup some background signal. We use the background Hall sensor to monitor the signal and remove the non-linear effects. The background effects were removed using a differential amplifier circuits made with operational amplifiers as shown in Figure 2.7a. The subtraction of the background sensor signal from the sample sensor signal is shown in Fig. 2.7b.

![Background subtraction circuit](image1)

![Subtracting background signal](image2)

**Figure 2.7**: Background subtraction

### 2.3 Instrumentation

The low temperature Hall effect magnetometry setup is shown in Figure 2.8. A micro-Hall array sensor wafer was mounted on a homemade chip holder that was designed and made from a Copper-Clad PCB. The sensor wafer was glued on the
heat sink by MG Chemicals® Pure Silver Conductive Epoxy. A thick piece of copper braid was glued by GE-varnish and bolted on the chip holder to transfer the heat to the cold finger. The sample temperature is obtained via four-point measurement of the resistance of a Lakeshore Cernox™ cryogenic temperature sensor that was glued next to the Hall array on the heat sink by thin layer of GE-varnish. The whole setup was mounted on the tip of the probe of a Heliox $^3\text{He}$ system (Oxford Instruments) with the base temperature of 0.3 K. The probe is inserted into an American Magnetics, Inc.’s LN$_2$ shielded Helium dewar with a 3-Axis superconducting vector magnet. The vector magnet consists of an 8 T solenoid with its axis in the vertical direction and two Helmholtz coils in the horizontal plane generating up to 1 T and 0.7 T respectively.

![Figure 2.8: The low temperature Hall effect magnetometry setup](image)

The measurements in the magnetic ordering experiments were performed with a lock-in technique. A 200 Hz ac current of 10 $\mu\text{A}$ is supplied by a floating battery
powered low-noise current source. The Hall voltage is detected with a lock-in amplifier at a time constant of 300 ms with a band pass filter with slope of 12 dB/octave and the amplified dc signal is passed on to a National Instruments data acquisition card. In magnetic deflagration experiments, a dc current of 20 µA was supplied to the array of Hall sensors and the signal from each sensor was amplified by a factor of 1000, filtered, and recorded by the data acquisition card.

### 2.4 Measurement of Crystal Geometry and Position

![Microscope images](image1.jpg)  
(a) BX60M microscope image of Mn$_{12}$-acetate.  
(b) Microscope image on measuring slide

**Figure 2.9:** Microscope photos taken for measuring a crystal.

As shown in Fig. 2.9, we took images of the crystal on a microscope scale using an Olympus BX60M microscope. We took pictures of all four surfaces of the crystal and extracted the information regarding the size of the crystal by examining the images later with a computer.

Moreover, we took images of the magnetometry setup after mounting the sample on to the Hall sensors as shown in Figure 2.8. We employed normal point-
and-shoot digital camera to take pictures directly from the eyepiece of an optical microscope. By superimposing the image of the crystal mounted on the Hall sensor on the mesa of the Hall sensor shown in Fig. 2.5, we were able to determine the exact crystal’s position relative to different Hall sensors. The result of the superposition process is quite accurate and is shown in Figure 2.10.

![Figure 2.10: Measurement of crystal position on the Hall sensor.](image)

(a) The image of the crystal mounted on the Hall sensor is superimposed on the mesa of the Hall sensor. b) The zoom of the Figure 2.10a with a scale superimposed on the image. This procedure allows the precise measurement of the crystal geometry and also relative position of the Hall sensor with respect to the crystal.

After taking the images of the setup, we closed the Heliox probe with the brass IVC (Internal Vacuum Chamber) can that makes a vacuum seal with the probe. Next we pumped the IVC with a turbo pump for few hours to reach pressure of \( \approx 1 \times 10^{-5} \) mbar and then precooled the probe in liquid nitrogen before inserting it in the Helium dewar with a 3-Axis superconducting vector magnet.
In summary, after many trials and errors, I developed a careful procedure for preparing and handling the single crystal of SMMs. I also improved our measurement setup by designing and fabricating the Hall array sensor that included the background sensors to remove any background signal. Moreover, documenting the crystal’s geometry and position on the Hall sensor array allowed me to determine the crystal’s size and its position relative to the Hall sensor array.
Chapter 3

Magnetic Ordering

Interacting Ising spins that preferentially orient either “up” or “down” form a basis for understanding a broad range of complex natural phenomena, including phase transitions to long-range ordered magnetic states, such as that occur in ferromagnets below their Curie temperature, $T_c$. In ferromagnetic materials, such as iron, exchange interaction between magnetic moment leads to the onset of long range magnetic order. The magnetic moments can also interact via long range dipolar interaction that affect physical property of magnetic materials. However, dipolar interactions are much weaker than quantum mechanical exchange interactions and hence play a minor role in determining the intrinsic properties of magnetic materials. In systems where exchange interactions are negligible, dipolar interactions can lead to long range order and such systems have been extensively explored theoretically [65] but only a few systems are realized experimentally [66] due to weak nature of the interaction. The exact ground state configuration of dipolar long-range order depends on the lattice symmetry and parameters. For a simple cubic lattice structure, an antiferromagnetic ground state is favored, whereas face
centered and body centered lattices favor ferromagnetic ground state. The ratio of lattice parameters (c/a) determines the ground state for tetragonal and hexagonal lattices [41].

Recent interest in dipolar ferromagnetism has focused on quantum systems, where quantum fluctuations of the spins compete with the dipolar long range order. Long ranged order also competes with thermal fluctuations and with the randomness that is present in any real material, all of which act to suppress $T_c$. A fundamental model used to study the interplay between these effects is the transverse field Ising model in a random magnetic field. The transverse field promotes quantum spin-fluctuations, while the random-field disrupts the long range order by randomly favouring different orientations of the spins on different sites [45, 48, 67]. The essential feature of the random-field is that it couples linearly to the order parameter, locally favoring one orientation over the other.

Despite the interest in the physics of random field models, there have been few experimental studies because of the difficulty of producing a magnetic field that varies randomly from site to site. The only ferromagnetic material found to date that shows characteristics of random-fields is the rare earth dipolar ferromagnet LiHo$_x$Y$_{1-x}$F$_4$ [51]. In the undoped material (x = 1), $T_c$ is found to decrease gradually with increasing applied transverse field, $H_\perp$, as $(1 - H_\perp^2)$, consistent with mean field theory (MFT). By contrast, dilution of the magnetic Ho ions with non-magnetic Y ions reveals a fundamentally different behavior. In particular, the material with x = 0.44 exhibits a much stronger, approximately linear, decrease of $T_c$ with $H_\perp$. This has been attributed to the fact that a transverse field applied to a site-diluted ferromagnet leads to a random longitudinal field [68]. However, several factors have made it difficult to obtain unambiguous results in the case of
LiHo$_{x}$Y$_{1-x}$F$_{4}$. The two most important are that dilution leads to randomness in the interactions themselves, thus changing the physics, and that the hyperfine fields are large and comparable to the dipole fields, further complicating the analysis [69, 70].

Finite temperature transitions to dipolar ferromagnetism have been demonstrated in several single molecule magnets (SMMs) [27, 34, 38–41]. In particular, recent neutron scattering experiments of Luis et al. [39] as well as Monte Carlo simulations [41], and calculations based on the mean-field approximation (MFA) [27] have reported a transition to dipolar ferromagnetism in Mn$_{12}$-acetate. In this chapter, I will present the study of the dipolar long-range order in two closely related SMMs, Mn$_{12}$-acetate and Mn$_{12}$-ac-MeOH. We deduce the nature of interaction from our experimental measurements of the temperature dependence of the magnetic susceptibility of Mn$_{12}$-acetate as a function of transverse field. Our experimental findings lead to the proposal that the Mn$_{12}$-acetate single crystal is a random-field Ising ferromagnet due to isomer disorder. To test this idea, we performed measurements on Mn$_{12}$-ac-MeOH, a new variant of Mn$_{12}$-acetate that does not have isomer disorder. Our findings on Mn$_{12}$-ac-MeOH are consistent with the MFA calculation for a pure transverse-field Ising ferromagnet, thus supporting our hypothesis that solvent disorder in Mn$_{12}$-acetate induces the random-field effect.

3.1 Experiments on Mn$_{12}$-acetate

Mn$_{12}$-acetate has been modeled as an Ising dipolar system. Each Mn$_{12}$ molecule behaves as a nanomagnet with spin $S = 10$ oriented along the crystallographic $c$ axis due to strong anisotropy $DS_{z}^{2} \approx 60$ K [7]. The spins crystallize in a body cen-
tered tetragonal lattice and the distance between them is sufficiently large that the intercluster exchange is negligible compared to the dipolar interaction. Hysteretic behavior due to slow relaxation is observed below a blocking temperature $T_B \approx 3$ K, as described in Chapter 1. The application of transverse magnetic field $H_\perp$ induces quantum tunneling between opposite spin orientations, accelerating the relaxation process towards thermal equilibrium. However, in transverse fields as high as 4 T used in our experiments, spin reversal by resonant quantum tunneling is extremely slow at low temperature, impeding a direct study of the ordered phase. Our approach is, therefore, to study the magnetic behavior above the transition temperature. Specifically, we measure the longitudinal magnetic susceptibility in the presence of $H_\perp$, and deduce the nature of the magnetic interactions from the temperature dependence of the susceptibility.

3.1.1 Blocking Temperature

Blocking of the system precludes measurements of equilibrium properties at temperatures where magnetic ordering is predicted. Hence, to measure the susceptibility, we need to make sure that the sample has achieved equilibrium before we can obtain a valid measurement. The factors that determine whether the measurement is taken at equilibrium are the longitudinal field sweep rate, $\alpha$, the temperature $T$ and the transverse field $H_\perp$. However, $T$ and $H_\perp$ are also parameters affecting the susceptibility; this leaves $\alpha$ as the only control parameter that can be adjusted to reach equilibrium. At lower temperature, for a given $H_\perp$, the relaxation time gets longer; hence, we need to keep $\alpha$ small enough so that the experimental time scale stays larger than the relaxation rate. In order to establish the range of experimental conditions in which it is possible to measure the equilibrium susceptibility we
first determine the blocking temperature $T_B$ as a function of transverse field.

Typical magnetization data for Mn$_{12}$-acetate is shown in Fig. 3.1 for different transverse fields at $T = 2.0$ K and longitudinal field sweep rate of $6.7 \times 10^{-3}$ T/s. The magnetization exhibits hysteresis due to slow relaxation and the steps characteristic of resonant tunneling [7]. The hysteresis can be eliminated by applying a transverse field or by sweeping the longitudinal field sufficiently slowly. The effect of transverse field is clearly demonstrated in Fig. 3.1: as the transverse field increases, relaxation processes accelerate and equilibrium is ultimately reached; the magnetization then exhibits reversible behavior.

The hysteresis can also be eliminated by sweeping the longitudinal field sufficiently slowly. The effect of reducing the sweep rate $\alpha$ is demonstrated in the two insets of Fig. 3.2 which show the hysteresis loops obtained for two different
Figure 3.2: Blocking temperature. Inset: Magnetization as a function of the longitudinal field swept at the indicated rates for $H_\perp = 2 \, \text{T}$ at $T = 2.15 \, \text{K}$ and $T = 2.40 \, \text{K}$. Main panel: Blocking temperature as a function of transverse field.

longitudinal magnetic field sweep rates in a narrow range $\pm 0.01 \, \text{T}$ about $H_z = 0$, measured in the presence of a constant transverse field $H_\perp = 2 \, \text{T}$ at $T = 2.15 \, \text{K}$ and $T = 2.40 \, \text{K}$. The point $H_z = 0 \, \text{T}$ was determined by symmetry from full magnetization curves taken between $-0.75 \, \text{T}$ and $0.75 \, \text{T}$ (see Figure 3.1). At 2.15 K, hysteresis is observed at sweep rate of $\alpha = 6.7 \times 10^{-5} \, \text{T/s}$, indicating that the system is below the blocking temperature; at a slower sweep rate, $\alpha = 1.0 \times 10^{-5} \, \text{T/s}$ the hysteresis loop is closed, indicating the system is above the blocking temperature. However at 2.40 K, the magnetization is reversible and there is no hysteresis for both sweep rates and equilibrium is reached. From the opening and closing of the hysteresis loop, we deduce the field dependence of $T_B$. 

\[ T_B (\text{K}) = 3.2 \left(1-\frac{H_\perp}{10}\right)^2 \]
The main panel of Figure 3.2 plots $T_b$ as a function of applied transverse field. As expected the applied transverse field $H_\perp$ accelerates the relaxation of the magnetization towards equilibrium and thereby lowers the blocking temperature, $T_b$. Note that a reduction in $T_b$ is also expected from a classical model of single domain uniaxial nanomagnets—the classical version of Mn$_{12}$-acetate—where $T_b = (1 - h)^2$, $h = H_\perp / H_A$, $H_\perp$ is the externally applied transverse field and $H_A$ is the anisotropy field ($H_A = 2DS/g\mu_B \approx 10$ T) [71]. The solid line in Figure 3.2 is a fit of the measured $T_b$ to the predicted quadratic dependence on field. However, we find that above $H_\perp = 4.5$ T, at our base temperature of 0.5 K, the system is not blocked and $T_b$ deviates from the classical expectations. This is associated with the onset of pure (i.e. temperature independent) quantum tunneling [72].

### 3.1.2 Longitudinal Susceptibility

Figure 3.3 shows the measured equilibrium longitudinal susceptibility of a Mn$_{12}$-acetate single crystal versus temperature and applied transverse field. Care was taken to ensure that the susceptibility and magnetization reported and discussed are equilibrium values and the measurements were performed at temperatures above $T_b(H_\perp, \alpha)$. The longitudinal magnetic susceptibility, $\chi \equiv \partial M_z / \partial H_z |_{H_z=0}$, was deduced from the slope of the reversible $M_z$ versus $H_z$ at $H_z = 0$, as illustrated in the insets of Figure 3.2.

The solid symbols in Fig. 3.3 show the inverse of the longitudinal susceptibility as a function of temperature for transverse fields between zero and 5 T. For zero transverse field $\chi^{-1}$ obeys the Curie-Weiss law expected from mean-field theory (MFT), $\chi^{-1} \sim (T - T_{cw})$. The solid black line is a fit of the data in zero transverse field to Curie-Weiss theory; the intercept $T_{cw} \sim 0.9$ K implies a transition at
Figure 3.3: Temperature and transverse field $H_\perp$ dependence of the inverse susceptibility of Mn$_{12}$-acetate.
this temperature from paramagnetism (PM) to ferromagnetism (FM), consistent with the result of Luis et al. [34]. As $H_\perp$ is increased from zero, there is a systematic increase in the inverse susceptibility, accompanied by a progressively larger deviation from the straight-line behavior found at $H_\perp = 0$ T.

![Figure 3.4](image)

Figure 3.4: The Curie-Weiss and the ferromagnetic transition temperatures as a function of transverse field. The intercepts $T_{cw}$ (blue squares) are obtained from the straight-line portion of the data curves in Figure 3.3. The green and red solid lines are mean-field transition temperatures, $T_c$, calculated for the pure and random case, respectively.

Figure 3.4 shows approximate values of the intercept $T_{cw}$ (blue squares) obtained from fitting the high-temperature region of the experimental data of Figure 3.3 to the Curie-Weiss law. The fit does not include data at high transverse field and low temperatures (the upturns in Fig. 3.3). At small values of the transverse field the intercepts $T_{cw}$ derived from extrapolation of the high temperature data provides a reasonably reliable estimate for the mean field transition temperature, but the extrapolations are less reliable as the transverse field is increased. Yet,
the conclusion from Fig. 3.4 is clear: the application of transverse field leads to a strong, approximately linear reduction in $T_{cw}$. The plots also shows the mean-field calculations of paramagnetic-ferromagnetic transition temperature, $T_c$, i.e. the temperature where $\chi$ diverges ($\chi^{-1} = 0$). The theoretical model used for the calculation will be discussed in the following section. The calculated values of $T_c$ for the pure and random cases are denoted in Figure 3.4 by the solid green and red lines, respectively. From the figure it is clear that the experimental $T_{cw}$ does not follow the green curve–pure system calculations of $T_c$.

3.2 Theoretical Model

In this section I will introduce the refined version of the theoretical model of Mn$_{12}$-acetate developed by Millis et al.[28]. The model uses mean-field theory (MFT) to calculate the transition temperature $T_c$ and inverse magnetic susceptibility as $\chi^{-1} = \chi_{mol}^{-1} - J$, with $\chi_{mol}^{-1}$ obtained from an exact solution of the single molecule Hamiltonian $H_{mol}$ and the intersite dipolar interaction $J$ obtained on the lattice appropriate to Mn$_{12}$-acetate.

3.2.1 Transverse-Field Ising Ferromagnet Model (TFIFM)

The Hamiltonian that describes the application of transverse field to the easy axis of single crystal of Mn$_{12}$-acetate can be expressed as the sum of two terms, namely, a term that describes a single molecule of Mn$_{12}$-acetate and a dipolar interaction term: $H = H_{mol} + H_{dipole}$. The single molecule Hamiltonian is

$$H_{mol} = -DS_z^2 - BS_z^4 + C (S_+^4 + S_-^4) + g\mu_B \vec{H}_\perp \cdot \vec{S}_\perp + g\mu_B H_z S_z.$$  (3.1)
Here $S_z, \vec{S}_\perp = (S_x, S_y, 0)$ and $S_\pm$ are matrices from the $S = 10$ representation of $SU(2)$ and $D = 0.548$ K, $B = 0.0012$ K, $C = 1.44 \times 10^{-5}$ K and $g\mu_B = 1.34$ K/T. Ref [28] employed a simplified version of Eq. 3.1 with $B = C = 0$ and $D$ renormalized to reproduce the ground state tunnel splitting. The differences in $\mathcal{H}_{mol}$ are the source of the minor differences between the results presented here and those of Ref. [28]. We find that $C$ may be set to zero or doubled without changing the results. The solution of Eq. 3.1 is obtained by diagonalizing the Hamiltonian, $\mathcal{H}_{mol}$, which is just a $21 \times 21$ matrix. The uniaxial anisotropy term favors the states with with $S_z = \pm 10$ and the gap to the next lowest-lying pair is about 12 K in zero transverse field. As a result, the Hamiltonian can be treated as an effective two-level system at low temperatures.

![Figure 3.5: Canting angle as a function of applied transverse field.](image)

The effect of the transverse field is characterized by a mean canting angle $\theta_c$ such that $\langle S_x \rangle (H_\perp) = S \sin \theta_c$. The computed $\theta_c$ from $\mathcal{H}_{mol}$ for the Mn$_{12}$-acetate parameters is shown in Fig 3.5. The two allowed values of $\langle S_z(H) \rangle$ are

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\[ \pm \sqrt{S^2 - S_z^2} = \pm S \cos \theta_c. \] Thus, we can represent the system in two state Ising Hamiltonian by introducing the Ising variables \( s_i \) on each site \( i \) so that

\[ \vec{S}(R_i) = S (s_i \cos \theta_c \hat{z} + \sin \theta_c \hat{x}). \] (3.2)

Hence, we can write the projection of the single molecule Hamiltonian \( \mathcal{H}_{mol} \) to the two lowest-lying states as

\[ \mathcal{H}(s_i) = \Delta(H_\perp) \sigma_x - h_z \sigma_z, \] (3.3)

where, \( \sigma_i \) are Pauli operators, \( h_i = g \mu_B H_i \), and \( \Delta(H_\perp) \) is the tunnel splitting parameter from the energy difference \( E_{12} \) of the two lowest-lying levels of \( \mathcal{H}_{mol} \). \( \Delta \) as a function of transverse field is plotted in Figure 3.6.

The dipole interaction between \( R \) and \( R' \) (\( \vec{R} = 0.5(\pm a \hat{x}, \pm b \hat{y}, \pm c \hat{z}) \), where \( a, b \) and \( c \) are lattice parameters) label sites of body centered tetragonal lattice is

\[ \mathcal{H}_{dipole} = -\frac{(g \mu_B)^2}{2} \sum_{R} \vec{S}_R \cdot \sum_{R' \neq 0} 3\vec{R} \left( \vec{S}_{R+R'} \cdot \vec{R}' \right) - \vec{S}_{R+R'} |\vec{R}'|^2 |\vec{R}|^5. \] (3.4)

The strength of the dipolar interaction between the molecules is set by

\[ E_{dip} \equiv \frac{(g \mu_B)^2 S^2}{V_{cell}} = \frac{(g \mu_B)^2 S^2}{a^2 c} \sim 0.078 K. \] (3.5)

Since this interaction scale is much less than the splitting induced by the uniaxial anisotropy, considering just the lowest-lying states of Eq. 3.1 above is justified.
3.2.1.1 Transition Temperature

In mean-field theory (MFT) we assume that each site is an independent spin prob-
lem and represent the total Hamiltonian as follows:

$$\mathcal{H}_{MF}(R) = \Delta \sigma_x - h(R)_{tot} \sigma_z. \quad (3.6)$$

The above Hamiltonian describes the transverse-field Ising ferromagnet model (TFIFM), which is a fundamental model used to study the interplay between the long range order and spin fluctuations. The first term is the transverse field effect that induces quantum spin fluctuations, and the second term represents the effective field term, which is the sum of the externally applied field, and a contribution coming from the polarizations of the other spins, where

$$h(R)_{tot} = h_z(R) + h_{eff}(< s >)_{R' \neq R} \quad (h = g\mu_bH) \quad (3.7)$$

and, $h_{eff}$ is the effective dipolar interaction and is related to the interaction $J$ as

$$h_{eff} = J < s >. \quad (3.8)$$

The expectation value of the Ising spin operator on site $R$ is calculated using Eq. 3.6 to get

$$< s_R > = \frac{h_{tot}(R)}{\sqrt{h_{tot}^2(R) + \Delta^2}} \tanh \frac{\sqrt{h_{tot}^2(R) + \Delta^2}}{T} \quad (3.9)$$

For a uniform ferromagnetic state in Mn$_{12}$-acetate, Ref. [28] finds that the
interaction is

\[ J = E_{\text{dip}} \left( 2J_{SR} \left( \frac{c}{a} \right) + \frac{8\pi}{3} - 2\Lambda \right). \]  

(3.10)

Here \( J_{SR} \) is the short range part of the dipolar interaction that depends on the details of the crystal structure and is a function of the \( c/a \) ratio for the body centered tetragonal lattice. For Mn\(_{12}\)-acetate with \( c/a = 0.7 \), Millis et al. \[28\] calculated \( J_{SR}(0.7) \approx 1.23 \). The second term is the long ranged part of the dipole interaction and justifies the use of a mean-field theory. It does not depend on the details of the crystal structure or the sample shape. \( \Lambda \) is the demagnetization factor, which is positive but tends to zero for a prolate crystal highly elongated in the \( z \) direction. The effective dipolar interaction as a function of transverse field for Mn\(_{12}\)-acetate is presented in Fig. 3.6.

Fig. 3.6 shows different energies in Mn\(_{12}\)-acetate as a function of transverse magnetic field. The black solid line is the tunneling energy \( \Delta \) of two lowest levels.
induced by the transverse field. The exact form of $\Delta$ was given in Eq. 1.10 in Section 1.1.2. The purple dashed dotted line shows the ferromagnetic effective dipolar constant $J$ as a function of the transverse field. Fig. 3.6 shows that as we increase the transverse field it increases the quantum fluctuations (given by $\Delta$) and decreases the effective dipolar interaction between spins. So there is a competition between the quantum spin fluctuations and interaction. The system reaches the quantum critical point when this interaction energy is equal to the tuneling energy and the long-range ferromagnetic order is completely destroyed.

In MFT, the ferromagnetic phase boundary is found by linearizing Eq. 3.9 in $s$ and satisfying Eq. 3.8 for a given temperature, $T_c$. The result of MFT gives

$$1 = \frac{J}{\Delta} \tanh \frac{\Delta}{T_c},$$  

(3.11)

where at $J = \Delta$, mean-field transition temperature vanishes and gives the quantum critical point that can be read from Fig. 3.6 (around 7 T).

### 3.2.1.2 Longitudinal Susceptibility

We calculate the susceptibility by writing the mean field equations for very small applied field $h_z$,

$$<s> = \chi_{mol} h_{tot} = \chi_{mol}(h_z + J <s>),$$  

(3.12)

$$\frac{<s>}{h_z} = \frac{\chi_{mol}}{1 - \chi_{mol} J},$$  

(3.13)

$$\chi^{-1} = \chi_{mol}^{-1} - J,$$  

(3.14)
where, $\chi_{mol}$ is the differential susceptibility between spin expectation value $<s>$ computed at two infinitesimally different values of $h_z$. From Ref. [28], the high temperature limit of susceptibility is:

$$\chi^{-1}(H, T) = C \left( \frac{T}{\cos^2 \theta_c} + \frac{\Delta^2}{3T \cos^2 \theta_c} - J \right),$$  \hspace{1cm} (3.15)

where, $C$ is given by the sample volume ($C \approx \frac{V}{(g \mu_B)^2}$).

In our experiments, when there is no applied transverse field, $H_\perp = 0$, there is no tunnel splitting and spin canting ($\Delta = 0$ and $\theta_c = 0$), and we get

$$\chi^{-1}(H_\perp = 0, T) = C (T - J),$$  \hspace{1cm} (3.16)

the Curie-Weiss law with a transition temperature, $T_c = J \sim 1$ K.

In Fig. 3.3, the solid lines are the longitudinal susceptibility calculated using Eq. 3.15. We observe that the susceptibility of Mn$_{12}$-acetate in zero transverse field obeys the Curie-Weiss law and the susceptibility in the small transverse fields is well described by mean-field theory calculations performed above. However, it is clear that the TFIFM fails to describe the data obtained in the presence of a large transverse field, indicating the presence of physics not included in the model. We argue that the additional physics is a random-field effect arising from structural disorder in Mn$_{12}$-acetate crystals.

### 3.2.2 Randomness in Mn$_{12}$-acetate

The large change in the susceptibility in relatively small transverse fields and the rapid suppression of ferromagnetism in Mn$_{12}$-acetate shown in Fig. 3.3 indicates
that the TFIFM fails to describe the data. We propose that there is an addi-
tional random-field effect arising from structural disorder in Mn$_{12}$-acetate crystals
that competes with the dipolar interactions. As described earlier in Section 1.1.4,
different isomers of the host acetate material have been shown to cause the spin
quantization axis of some of the Mn$_{12}$-acetate molecules to tilt away from the crys-
tal z-axis by a small monomer-dependent angle ($\theta \approx \pm 1^\circ$) [1, 26, 32, 33, 73, 74].
As illustrated schematically in Fig. 3.7, in the absence of an applied magnetic field
these small tilts of the magnetic easy axis of individual molecules have negligible
effect on the magnetic properties. However, a field applied transverse to the easy
(Ising) axis has a nonvanishing projection along the tilted local spin quantization
axis (see Fig. 3.8). This additional field becomes comparable in magnitude to
the dipolar field itself for transverse field magnitudes of order 4 T [28, 35]. The
distribution of the isomers in the crystal is assumed to be random and thus, the
transverse field introduces random longitudinal fields that further supress the long
range order.

3.2.3 Random-Field Ising Ferromagnet Model (RFIFM)

We can account for the random-field by adding a transverse-field dependent ran-
dom field term $H^\text{ran,i}_{mol}$ to Eq. 3.1, where

$$H^\text{ran,i}_{mol} = \theta_i \cos(\phi_i + \phi_H) g \mu_B H \perp S_z + E_i (S^2_x - S^2_y). \quad (3.17)$$

In terms of the Ising variables we can add site dependent random-field to $h_{tot}$ in
Eq. 3.7 to get the Hamiltonian that describes the random-field Ising ferromagnet
Figure 3.7: Effect of easy axis tilts on the transition temperature. In zero field a perfectly ordered crystal and a crystal in which there are easy axis tilts (e.g., the red spins) will order at nearly the same temperature (the small tilts do not greatly modify the interaction between spins, which depends on the longitudinal component of the magnetic moment). In an applied transverse field, the spins of misaligned molecules experience a field along their Ising axis. When this field is comparable to the exchange field these spins are frozen (red spins) and do not order. This leads to an effective dilution of the spins, a decrease in the susceptibility and a reduction in the transition temperature. It also increases the random-field on the other sites in the crystal.

model (RFIFM):

\[ \mathcal{H}_{RFIFM} = \Delta \sigma_x - h_{\text{tot}} \sigma_z = \Delta \sigma_x - h_z \sigma_z - J < s > \sigma_z - h_{\text{ran},i} \sigma_z, \quad \text{(3.18)} \]

where, in the small polar tilt limit, \( h_{\text{ran},i} = \theta_i \cos(\phi_i + \phi_H) g \mu_B H_{\perp} \) is the site-dependent field that arises from the misorientation of the Mn\(_{12}\)-acetate spin quantization (spin-\(z\)) axis with respect to the crystallographic \(z\) axis [1]. The misorientation is characterized by a small polar tilt \( \theta \) and an azimuthal angle \( \phi \), which is
measured with respect to the direction $\phi_H$ defined by the transverse field as shown in Figure 3.8. Setting $\theta$ and $\phi$ to be zero would result in vanishing $h_{ran,i}$ term and TFIFM model.

### 3.2.3.1 Transition Temperature

Calculations of the transition temperature for RFIFM follows the same steps as in TFIFM with the new $h_{tot}$ in Eq. 3.7 that includes random-field. Fig. 3.6 plots the energy scale of the random-field as a function of the transverse field for tilt angle $\theta \approx 1^\circ$. We can clearly see that the random-field energy becomes comparable to the dipolar interaction energy while the tunnel splitting $\Delta$ is still very small. Millis et al. [28] calculate the ferromagnetic phase boundary by linearizing Eq. 3.9 in $s$ and satisfying Eq. 3.8 for a given temperature, $T_c$ with modified $h_{tot}$ and neglecting $\Delta$. 

Figure 3.8: In an applied transverse field, the spins of misaligned molecules experience a field along their Ising axis.
They find the transition temperature satisfies the following equation:

\[ 1 = \left\langle \frac{J}{T_c \cosh^2 \left[ \frac{|h_{ran,i}|}{T_c} \right]} \right\rangle. \tag{3.19} \]

Here, the angle brackets denote the average over different random-field sites. In the above equation, when \( T \) becomes smaller than \( h_{ran,i} \), the \( \cosh^{-2} \) term becomes negligible. This leads to the random-field sites dropping out of the mean-field equation. As the random-field increases, more and more random-field sites drop out of the mean-field equation at any given temperature and this leads to decrease in transition temperature. For a continuous random-field distribution, the transition temperature decreases further and we reach the quantum critical point at which \( T_c \) vanishes.

### 3.2.3.2 Longitudinal Susceptibility

The magnetic susceptibility is calculated using the steps followed in the TFIFM with additional random-field term. From Ref. [28], we get:

\[ \chi^{-1}(T, H_T, z) = C \left( \frac{T^2 + \frac{1}{3} \Delta^2 (H_\perp) + \left\langle h_{ran,i}^2 \right\rangle}{T \cos^2 \theta_c} - J \right). \tag{3.20} \]

Here, \( \left\langle h_{ran,i}^2 \right\rangle \) is the mean square amplitude of the random-field distribution. Calculations were performed using the monomer distribution proposed by Cornia et al. [1, 75] which involves twelve inequivalent sites randomly distributed through the crystal. For temperatures greater than 2 K, the only important feature of the random-field is the mean square amplitude of the tilt angle and changing the form of the distribution but keeping the amplitude of the tilt fixed leaves the results invariant. For lower temperatures, specific properties of the distribution become
important, in particular the fraction of sites with vanishing random-field. In the Cornia model the angles $\phi_i = n\pi/4$ with $n = 0, 1, 2...7$ and the fraction of sites with very small random-field may be controlled by varying $\phi_H$, the angle of the applied transverse field.

### 3.3 Theoretical Results and Comparision to Mn$_{12}$-acetate Data

In this section, I present the calculations of the inverse susceptibility performed with the theoretical models presented above. Then we make a comparision between the experimental data of Mn$_{12}$-acetate and theoretical calculations and discuss the physics behind the experimental data.

The solid lines shown in Fig. 3.9 are the result of calculations for the pure system without randomness. As $H_\perp$ is increased, the slope of the calculated traces increases, reflecting spin canting induced by the magnetic field. Also, due to the increase in quantum tunneling, the estimated ferromagnetic transition temperature (the extrapolated value where $\chi^{-1}$ vanishes) decreases and the calculated traces develop a weak curvature at low temperatures. The pure-system calculation and the data agree well only at small transverse fields.

The dashed lines in Fig. 3.9 show the results of calculations that include the randomness associated with isomer tilts. Here we have assumed that all the sites have a tilt and the mean square tilt angle is $1.2^\circ$, larger than the $0.5^\circ$ calculated by Park et al. [1] but in good accord with the values determined using EPR [33] (which finds tilts up to $1.7^\circ$). Although not in complete agreement with the data, the theory with randomness accounts for all the major features of the observed
Figure 3.9: Temperature and field dependence of the inverse susceptibility of Mn\textsubscript{12}-acetate. The inverse susceptibility of a single crystal of Mn\textsubscript{12}-acetate as a function of temperature in different transverse fields $H_\perp = 0, 1, 2, 3, 4$ and 5 T, as labeled. The solid lines are the result of mean field calculations without randomness. The dashed lines are obtained for the distributions of the random-field in which all the sites have a tilt with a mean square tilt angle of 1.2°.
\( \chi^{-1}(T) \) in transverse fields.

To better understand the effects of random-field, from Eq. 3.20 we calculate the normalized change of the inverse susceptibility, \( \Delta \chi^{-1}(H_{\perp}) \),

\[
\Delta \chi^{-1}(H_{\perp}) = \frac{\chi^{-1}(H_{\perp}) - \chi^{-1}(0)}{\chi^{-1}(0)}.
\]  

The subtraction, \( \Delta \chi^{-1}(H_{\perp}) = \chi^{-1}(H_{\perp}) - \chi^{-1}(0) \), eliminates the intermolecular dipolar interaction term \((J)\), and the normalization removes the dependence on sample volume, \(C\). Therefore, \( \Delta \chi^{-1} \) shows the effect of the transverse field and random-field.

Figure 3.10 compares the measured and calculated field dependence of \( \Delta \chi^{-1} \) at a fixed temperature (3.16 K). The quadratic field dependence at low fields follows from general principles. The magnitude is seen to be inconsistent with the pure-system calculation (solid line) and consistent with the random-field calculation (dotted line), further supporting our proposal. The dashed red line was calculated for a mean tilt angle of 1.2°. The dashed green and blue lines, calculated for 0.6° and 1.7° respectively, define the range of mean tilt angles that are consistent with the experimental data. We therefore conclude that MFT with randomness included accounts also for the field dependence of \( \chi^{-1} \).

It is important to note that in the experimentally accessible temperature range the results are insensitive to the details of the distribution, depending only on the mean square tilt angle; however, at low temperature the random-field effect is strongly dependent on the distribution as demonstrated by Fig. 3.11. Fig. 3.11 shows calculations of \( \Delta \chi^{-1} \) for 5 T obtained using two different distribution of the random-field with the same mean square tilt angle of 1.2°. The solid line shows
Figure 3.10: The difference $\Delta \chi^{-1}$ versus $H_{\perp}^2$. The dashed lines in the inset are calculated for mean square tilt angles of 0.6° and 1.7°. The red dotted line and solid black lines are calculated for the same parameters as in the main panel for random and pure case respectively. The solid line is the behavior expected for a system without randomness.

Cornia model [1, 75], with 1/4 of the sites not tilted and the dashed line shows the distribution with some random-field effect (20%) on 1/4 sites that are not tilted in Cornia model. The solid and dashed lines overlap in most of the temperature range.

At high temperatures ($T > 1$ K) the dependence on random-field comes from strength of the random-field on level spacings that depends on the tilt angle $\theta$. The angle $\theta$ is same in both distribution so they overlap above 2 K. Deviation from Curie-Weiss behavior is due to the distribution of random-field. The downturn in
solid line starting around 1 K comes because in the calculation 1/4 of the sites have no random-field, which leads to a Curie law with coefficient 1/4 of the pure system one and to a $\chi^{-1} \sim T$. Hence, the Curie-Weiss behavior exists over a limited range, cut off on the high temperature by the effect of random-field on transitions to higher levels and the lower temperature by the downturn, which depends critically on the details of the random-field. When we change the distribution of the random-field such that all the sites feel some random-field by giving some distribution of tilts then there is no Curie-Weiss law for any sites and we see an upturn in the

Figure 3.11: Different random-field distribution. The solid and dashed lines are obtained for different distributions of the random field with the same mean square tilt angle of 1.2°: the solid lines are for the distribution obtained using density functional theory where 25% of the sites are not tilted [1]; the dashed curves are for the case in which all the sites have a tilt.
susceptibility calculation (dashed line).

Hence, it is clear from the figure that the behavior of $\chi^{-1}(T)$ at lower temperatures does depend on the detailed distribution of tilts. This can be further shown by rotating the applied field in the plane perpendicular to the mean quantization axis, $\phi_H$. As shown in the inset of Fig. 3.12, the change in $\phi_H$ changes the isomer distribution and thereby changes the random-field distribution. As shown in the main panel of Fig. 3.12, this change in random-field distribution only changes the low temperature susceptibility.

3.4 Experiments on Mn$_{12}$-ac-MeOH

In this section, I present the results of an investigation of Mn$_{12}$-ac-MeOH. As discussed in Section 1.1.4 the two systems differ only in the isomer disorder introduced by the solvent molecules in Mn$_{12}$-acetate. Hence, a comparison of their magnetic response provides quantitative information about the effect of random fields. We find that the behavior of Mn$_{12}$-ac-MeOH is consistent with Eq. 3.6 that does not include any disorder effects. Therefore, the new “pure” MeOH variant represents a model-system for the study of intrinsic transverse-field Ising ferromagnetism model. However, there are deviations from simple theoretical expectations for both Mn$_{12}$ variants below about 2 K that are not currently understood and require further study.

3.4.1 Longitudinal Magnetization

In the main panel of Fig. 3.13 the field dependence of the magnetization of Mn$_{12}$-ac-MeOH (Sample C) in the absence of transverse magnetic field is shown for
temperatures below 1 K. The steps in the magnetization occur due to faster spin-reversal due to resonant tunneling of magnetization when energy-levels on opposite spin-projections coincide at specific magnetic fields [7]. In Mn$_{12}$-ac-MeOH the resonant fields at which the steps occur are the same as in Mn$_{12}$-acetate, which indicates that the two systems have similar spin energy-level structures. The magnetization exhibits hysteresis due to slow relaxation below a blocking temperature, $T_B$, that depends on the rate at which the magnetic field is swept. Equilibrium
Figure 3.13: Normalized magnetization of Mn$_{12}$-ac-MeOH as a function of longitudinal magnetic field, $H_z$, in zero transverse field at several temperatures below 1 K. The sweep rate of $H_z$ in the main panel and the top inset is 1.67 mT/s. Top Inset: Magnetization vs $H_z$ at $T = 0.53$ K for different $H_\perp$. Bottom Inset: Schematic diagram of the sample, the Hall sensor and magnetic fields.

can be established in Mn$_{12}$-ac-MeOH following the same method described in Sec. 3.1.1 by increasing the temperature, decreasing the sweep rate and applying the transverse magnetic field. The latter is demonstrated in the top inset of Fig. 3.13 which shows the low-field magnetization in transverse field at 0.53 K. While hysteresis is evident for $H_\perp = 3.75$ T (green stars), the system is in equilibrium at the higher field of $H_\perp = 5.5$ T (blue solid dots).
3.4.2 Longitudinal Susceptibility

Figure 3.14: Temperature and transverse field $H_\perp$ dependence of the inverse susceptibility of Mn$_{12}$-ac-MeOH.

Figure 3.14 shows the measured equilibrium longitudinal susceptibility of a Mn$_{12}$-ac-MeOH single crystal versus temperature and for various fixed transverse magnetic fields between 0 and 6 T. The longitudinal magnetic susceptibility, $\chi$, was deduced from the slope of the reversible $M_z$ versus $H_z$ at $H_z = 0$ described in Sec 3.1.2. For zero transverse field $\chi^{-1}$ obeys the Curie-Weiss law, $\chi^{-1} \sim (T - T_{cw})$, expected from mean-field theory (MFT). The intercept $T_{cw}$ implies a transition at this temperature from paramagnetism (PM) to ferromagnetism (FM). As we apply the transverse field, there is a systematic increase in the inverse susceptibility, accompanied by a progressively larger deviation from the straight-line behavior.
found at $H_\perp = 0$ due to canting of spins in the transverse field.

3.5 Comparison between Mn$_{12}$-acetate and Mn$_{12}$-ac-MeOH

Figure 3.15 presents the measured equilibrium longitudinal susceptibility of Mn$_{12}$-ac-MeOH and Mn$_{12}$-acetate. Figures 3.15(a) and 3.15(c) show the inverse susceptibility of a Mn$_{12}$-ac-MeOH (Sample C) and Figures 3.15(b) and 3.15(d) show the inverse susceptibility of a Mn$_{12}$-acetate crystal as a function of temperature for various applied transverse fields. As demonstrated by the data at small transverse fields in Fig. 3.15 (c) and (d), the response of $\chi$ to transverse field is distinctly different for the two systems. The slopes of the $\chi^{-1}$ vs. $T$ curves increase rapidly with the transverse field for Mn$_{12}$-ac-MeOH; however, in Mn$_{12}$-acetate, the curves remain approximately parallel with little change of slope and the apparent Weiss temperature decrease rapidly with the increasing transverse field [35].

The solid lines shown in Fig. 3.15 (a) and (c) are the result of calculations for TFIFM (setting $\theta$ and $\phi$ to be zero, i.e. eliminating $\langle h_i^2 \rangle$ in Eq. 3.20). As $H_\perp$ is increased, the slope of the calculated traces increases, reflecting spin canting induced by the magnetic field. Also, due to the increase in quantum tunneling, the estimated ferromagnetic transition temperature (the extrapolated value where $\chi^{-1}$ vanishes) decreases and the calculated traces develop a weak curvature at low temperatures. The TFIFM calculation and the Mn$_{12}$-ac-MeOH data agree well.

The solid lines shown in Fig. 3.15 (b) and (d) show the results of calculations that include the randomness associated with isomer tilts. As noted earlier, we have assumed that all the sites have a tilt and the mean square tilt angle is $1.8^\circ$. 
Figure 3.15: (a) Inverse susceptibility as a function of temperature for Mn$_{12}$-ac-MeOH (Sample C) in various transverse fields up to 6 T. (b) Inverse susceptibility as a function of temperature of Mn$_{12}$-acetate (Sample E) for various transverse fields up to 5 T. (c) and (d) Inverse susceptibility in low transverse field up to 3 T for Mn$_{12}$-ac-MeOH and Mn$_{12}$-acetate, respectively. The solid lines are theoretical curves based on Eq. 3.20.
larger than the 0.5° calculated by Park et al. [1] but in good accord with the values determined using EPR [33] (which finds tilts up to 1.7°). The theory with randomness accounts for all the major features of the observed $\chi^{-1}(T)$ in Mn$_{12}$-acetate in the transverse fields.

For both systems with and without randomness, a transverse field leads to a canting of the spins away from the z-axis, as illustrated in Fig. 3.7, and enhances quantum fluctuations of the spin. The strength of intermolecular dipole interaction, which is associated with the z-component of spin, gets reduced due to canting. A transverse field much smaller than the anisotropy field $H_A \approx 10$ T produces very little spin canting ($\tan \theta_c = H_\perp/H_A$) and thereby a negligible change in the interaction strength. As a result, the susceptibility and the ordering temperature are virtually unchanged in the system without randomness for transverse fields below 3 T. Only when the tunnel splitting, $\Delta$, of the lowest spin states is comparable to the intermolecular dipole interactions, do the quantum fluctuations become important and the FM order is very strongly suppressed (when the transverse field $H_\perp$ approaches the anisotropy field $H_A$, the energy eigenstates are going from the eigenstates of $S_z$ to eigenstates in the direction of the field $S_x$). This occurs at $\sim 7$ T for both Mn$_{12}$-ac-MeOH and Mn$_{12}$-acetate [27, 28]. As discussed earlier, due to the tilts present in the disordered system, transverse field gives rise to the random-fields comparable in magnitude to the intermolecular dipole field (approximately 50 mT [76], corresponding to 3 T for a tilt angle of 1°). In such cases, the tilted spins can no longer participate in the FM order and there is an effective dilution of the spins which causes a rapid reduction of the susceptibility and of the ordering temperature as seen in the disordered system of Mn$_{12}$-acetate [28].

We further demonstrate the different response to the magnetic field in Fig. 3.16.
Figure 3.16: (Color on line) The change in inverse susceptibility, $\Delta \chi^{-1}$, normalized to the susceptibility at zero field versus $H^2_{\perp}$ for Mn$_{12}$-ac-MeOH (green dots) and Mn$_{12}$-acetate (red squares) at $T = 3.2$ K. The red dashed line is calculated using RFIFM for the root mean square tilt angle of 1.8°. The solid green line shows the result for TFIFM.

by plotting the normalized change of the inverse susceptibility, $\Delta \chi^{-1}$ (Eq 3.21), as a function of $H^2_{\perp}$ for three Mn$_{12}$-ac-MeOH samples (green dots) and three Mn$_{12}$-acetate (red squares) at $T = 3.2$ K. Figure 3.16 clearly shows that the effect of the transverse field is much larger for Mn$_{12}$-acetate consistent with the discussion above regarding the additional effect of transverse field in the system. In the same figure we plot the normalized change of the inverse susceptibility calculated for the TFIFM with no tilt angle (green solid line) and for the RFIFM with the
mean square tilt angle of 1.8° (red dashed line) for the random-field distribution proposed by Park et al. [1]. The excellent agreement between calculation and data for the MeOH material at $H_\perp < 4$ T at 3.2 K is an indication that this system is a realization of the dipolar Ising model in a transverse field. A good fit obtained for the Mn$_{12}$-acetate crystal data with the calculations using root mean square tilt angles of 1.8° suggest that the material is a realization of dipolar random-field Ising model in a transverse field.

The $\chi^{-1}(T)$ data between 2 and 6 K in Fig. 3.15 are consistent with theory for both samples, where a particularly good fit is obtained for fields below 3 T. However the plots in Fig. 3.15 reveal a discrepancy at low temperatures and high transverse fields ($H_\perp > 4$ T). While the theoretically calculated lines intersect the temperature axis at $T_{cw}(H_\perp)$ implying the approach to a ferromagnetic phase, the measured susceptibility deviates from this simple behavior, flattening as the temperature decreases toward the presumed transition. The behavior observed at these low temperatures and high fields is not understood, and may imply that a transition to a new phase is prohibited for reasons that are unclear.

Figure 3.17 shows approximate values of the the Curie-Weiss intercepts $T_{cw}$ of Mn$_{12}$-ac-MeOH (black diamonds) and Mn$_{12}$-acetate (blue squares) obtained from fitting the high-temperature region of the experimental curves shown in Figure 3.15 (a) and 3.15 (b) to the Curie-Weiss law. The fit does not include data at low temperature and higher fields where, as discussed above, $\chi^{-1}$ deviates from the Curie-Weiss behavior. The initial suppression of $T_{cw}$ in Mn$_{12}$-ac-MeOH for transverse fields $H_\perp < 5$ T is expected due to spin canting, which reduces the net moment in the axial direction; the more rapid suppression at higher fields derives from the tunneling term, $\Delta$. A substantially more rapid suppression of $T_{cw}$ with
$H_\perp$ is evident for Mn$_{12}$-acetate. As discussed, the results for Mn$_{12}$-acetate are consistent with a modified theory that includes the effects of random fields arising from the tilt angles. We also plot the calculated mean-field PM-FM transition temperature $T_c$ (where $\chi$ diverges). The calculated values of $T_c$ for the TFIFM (Equation 3.11) and RFIFM (Equation 3.19) are denoted in Fig. 3.17 by the solid green and red lines, respectively. For the theoretical calculation, the dipolar part of the interaction was obtained using the measured lattice parameters and crystal structure of Mn$_{12}$-acetate (very similar values of Mn$_{12}$-ac-MeOH) and the spin canting and tunnel splitting were obtained as described in Ref. [28].

3.6 Summary

In summary, these studies demonstrate that the temperature dependence of the susceptibility and the dependence of the (extrapolated) Weiss temperature on applied transverse field are different for the two very closely related materials, Mn$_{12}$-acetate and Mn$_{12}$-ac-MeOH. In both materials, the susceptibility is found to obey a Curie-Weiss law with a positive Weiss temperature, implying a transition to long-range ferromagnetic order at low temperatures in agreement with earlier findings in Mn$_{12}$-acetate. A magnetic field applied transverse to the easy-axis of the crystal reduces the Weiss temperature, suppressing the long-range ferromagnetic order. However, the temperature intercept is reduced far more rapidly in Mn$_{12}$-acetate than Mn$_{12}$-ac-MeOH. We have attributed this to the presence of a random-field in the former and its absence in the latter.

In Mn$_{12}$-acetate, isomer disorder tilts the individual spins away from the global easy-axis, thereby creating a random-field in the presence of a transverse field.
In addition to the reduction of the Weiss temperature associated with thermal fluctuations and quantum spin fluctuations, this random-field further suppresses the long-range order. In our experiment, we observed that the dependence of $T_{cw}$ on $H_\perp$ is much stronger than the mean-field expectation for a pure transverse field Ising ferromagnet model system.

To confirm the validity of our proposal that the rapid suppression in Mn$_{12}$-acetate is indeed due to random fields associated with isomer disorder, we did a comparison experiment in Mn$_{12}$-ac-MeOH, which is known to be a much cleaner system without isomer disorder. The result of the comparison experiment shows that the results on Mn$_{12}$-ac-MeOH are indeed consistent with that expected for a pure transverse field Ising ferromagnet. Given that the most important difference between the two systems is the isomer disorder, we conclude that the difference in their magnetic behavior originates from the isomer disorder in a way described by the random-field model.
Figure 3.17: The Curie-Weiss and the ferromagnetic transition temperatures as a function of transverse field. The intercepts $T_{cw}$ of Mn$_{12}$-ac-MeOH (black diamonds) and Mn$_{12}$-acetate (blue squares) are obtained from the straight-line portion of the data curves in Figure 3.15 (a) and 3.15 (b). The green and red solid lines are mean-field transition temperatures, $T_c$, calculated for the pure and random case, respectively. $T_c$ for RFIFM is calculated using the Cornia distribution and the parameters ($\theta = 1.8^\circ$ and $\phi = 0$) are the same as those used to fit the data in Figure 3.15.
Chapter 4

Magnetic Deflagration

Raising the temperature of a flammable substance can ignite combustion, an exothermic reaction between a substance and an oxidizer that results in a chemically modified substance [77]. Deflagration is a self-sustained combustion that propagates at subsonic speed via thermal conduction; a locally burning substance increases the temperature of an adjacent unburnt substance and ignites it. Deflagration is governed by local reactions and diffusion; reaction-diffusion systems are ubiquitous in nature—from cell growth to epidemics. The study of these nonlinear dynamical systems reveals rich phenomenology—including traveling waves, dissipative solitons [78], and self-organized patterns [79, 80]. Mathematical understanding of such systems relies on studying their instabilities and physical understanding requires control of the two competing processes: local reactions where the substance is transformed, and diffusion that causes interaction over a surface in space.

Deflagration is characterized by a propagating flame that separates locally burnt and unburnt substance. The speed and width of the flame are determined by the distance the heat diffuses during the characteristic timescale of the reaction.
The flame may die out if the smallest sample dimension is larger than the width of the flame. In this situation, the heat may escape through the sample boundary rather than move inside the material.

In magnetic materials, magnetic deflagration has been observed as an abrupt and complete magnetization jumps [52–55, 81, 82]. As discussed in Section 1.1.2, at low temperature \((k_B T \ll U)\) the spins in Mn\(_{12}\)-acetate do not have enough energy to jump over the double well potential energy barrier and hysteresis will be observed in the magnetization curve due to blocking of the spins in one well. As shown by the red curve in Figure 4.1, the hysteresis curves have step-like behavior at resonance fields due to quantum tunneling of magnetization [7]. When the spins
that are in a metastable state slowly relax to a lower energy state, they release heat typically in the form of phonons. In some circumstances, the heat released cannot be compensated by thermal diffusion, resulting in an instability that gives rise to a front of rapidly reversing spins traveling through the sample at constant speed. When this happens, the whole magnetization is reversed in one step in a very short time with a relatively small reversing magnetic field as shown by the black curve in Figure 4.1 [56].

In magnetic deflagration the released heat is the Zeeman energy that comes from the interaction of an external magnetic field $H_z$ with the spins of the system. The rate at which the released heat is transferred to unburnt region is controlled by the activation energy (energy barrier $U$), thermal diffusivity, $\kappa$ and population of flammable spins, $n_i$. The main difference between chemical combustion and magnetic deflagration is the non-destructive nature of the process in the latter. Unlike in chemical reactions, the burnt spins (stable state) can be made flammable spins (metastable state) by reversing the applied bias field. Due to this nature, magnetic deflagration allows comprehensive studies of combustion. Also, the appearance of maxima due to resonant quantum tunneling in the deflagration speed in Mn$_{12}$-acetate is a quantum feature that is not present in classical burning.

Prior to the discovery of steps in the hysteresis loops of Mn$_{12}$-acetate due to resonant tunneling by Friedman et al. [7], Paulsen and Park [56] reported that Mn$_{12}$-acetate sometimes exhibit a sharp single-step reversal of the magnetization during a field-swept measurement. They estimated the duration of the reversal was at most 10 ms for the samples with 2 mm length and deduced the reversal to be at least 0.2 m/s and compared the finding to the spin-phonon relaxation time of $\tau_0 = 10^{-6}$ s. From the measured specific heat [22, 23] and the Zeeman
energy calculation, the rise in sample temperature was estimated to be 12 K at 1 T. However, the nature of the sharp spin-reversal was unclear.

From spatial and time-resolved measurements on Mn$_{12}$-ac crystals, Suzuki et al. [52] were able to detect the deflagration front as it propagates through the crystal. Using surface acoustic waves, Hernández-Mínguez et al. [53, 83] were able to ignite deflagration at a fixed applied bias field and show that the speed of the reversal-front is enhanced at the resonant fields ($kH_r, H_r = D/g\mu_B = 0.45$ T, \(k=1,2,\ldots\)) due to quantum tunneling of magnetization. All these previous studies of magnetic deflagration on Mn$_{12}$-acetate have extensively focused on the effect of a large longitudinal magnetic field ($H_z \geq H_r$) applied along the magnetic easy axis of the sample.

In this chapter I present magnetic deflagration studies on Mn$_{12}$-acetate in the presence of an applied transverse and longitudinal (easy axis) bias field. Application of a transverse field, $H_\perp$, increases the tunnel splitting, which increases the magnetic relaxation and allows us to explore deflagration, for the first time, at small bias fields ($H_z < H_r$). Using both transverse and bias magnetic fields, we independently control both activation and Zeeman energies (see Fig. 4.2a) and therefore the initiation and the speed of deflagration. This control of deflagration onset and speed is generally not possible in conventional combustion experiments.

4.1 Experiment

In this section I present the local time-resolved measurements of the speed and width of deflagration fronts in single crystals of Mn$_{12}$-acetate. Using a trigger heat pulse and transverse and longitudinal magnetic fields, we investigate and
control the crossover between thermally driven magnetic relaxation and magnetic deflagration in single crystals of Mn$_{12}$-acetate. We find incomplete spin-reversal to a non-equilibrium state, determined by the blocking temperature due to the applied fields. We also find that the speed of the spin-reversal front is well controlled with the applied magnetic fields. The speed data also shows clear effect of intermolecular dipolar fields on the spin-reversal propagation. Our results can be understood within a model that considers the heat energy supplied, heat propagation and the Zeeman energy released in the spin flips.

4.1.1 Experimental Procedure

Magnetic measurements were performed on three Mn$_{12}$-acetate single crystals of dimensions $\sim 0.3 \times 0.3 \times 2.1$ mm$^3$, $0.35 \times 0.35 \times 1.75$ mm$^3$ and $0.4 \times 0.4 \times 1.6$ mm$^3$ (samples I, II, and III, respectively). The samples were mounted on a one-dimensional array of Hall sensors (active area $20 \times 100$ $\mu$m$^2$ with $200$ $\mu$m separation).
(see Fig. 4.2(b) and discussion in Section 2.2.1). The three samples show essentially the same behavior; here we show data for sample III. Care was taken to align the sample and the Hall array (placed in the $yz$ plane) relative to each other and relative to the magnet axes, as shown in Fig. 4.2(b). The Hall sensors detect the stray field $B_x$ (see the inset of Fig. 4.3(b)), which is maximum at the reversal front. Measurements were taken at 0.4 K in a $^3$He refrigerator in a three-dimensional vector superconducting magnet capable of producing bipolar bias fields up to 1 T and bipolar transverse fields up to 5 T. A 6 V, 30 ms pulse was applied to a thin film heater ($R \approx 1.32 \, \text{k}\Omega$ at 0.4 K) placed at one end of the sample to trigger spin reversal. A dc current of 20 $\mu$A was supplied to the array of Hall sensors and the signal from each sensor was amplified by a factor of 1000, filtered, and recorded by a data acquisition card.

At base temperature (0.4 K), the crystal was prepared in a fully magnetized state so that all the spins were aligned in one direction. A fixed transverse field $H_\perp$ was applied and the bias field $H_z$ was swept to the desired field and held. At this low temperature the spins are essentially blocked by the strong magnetic anisotropy of Mn$_{12}$-acetate, and relax slowly toward equilibrium. In this nonequilibrium state, we supplied a voltage pulse to the heater to increase the temperature at one end of the crystal to initiate spin reversal. The same pulse was used to trigger the data acquisition card to record the magnetization signals of different Hall sensors during 1 s. The procedure was repeated for several values of bias fields for a particular transverse field. The set of measurements taken with the system initially prepared in the spin down state is called sweep up; the other case we call sweep down.
4.1.2 Hall Sensors Signals

Figure 4.3 shows the time evolution of the Hall sensor signals when a heat pulse is applied at $t = 0$ to sample III with the magnetization prepared as described above. Two cases are considered: a zero bias field ($H_z = 0$ T, Fig. 4.3(a)), and a large bias field ($H_z = 0.61$ T, Fig. 4.3(b)) for the same transverse field $H_\perp = 1.5$ T. A propagating spin-reversal region is observed in both cases; the change in magnetization always starts at the heater end and propagates towards the other.
end (from the 1\textsuperscript{st} to the 6\textsuperscript{th} sensor, see Fig. 4.2(b)). As shown in Fig. 4.3, a peak in the signal corresponding to the enhancement of the local stray field ($B_x$) travels in the $z$ direction as the spin reversal propagates along the easy axis, ultimately reversing the magnetization of the entire crystal.

While the curves in Fig. 4.3(a) and Fig. 4.3(b) appear similar, closer inspection shows that the reversal processes at low and high bias are distinctly different. At zero (or low) bias, the time interval between adjacent peaks is relatively long and increases as the spin-reversal propagates, indicating that the spin reversal is slowing down: the time to completion is on the order of 80 ms, and the peaks are fairly broad and broaden further as the reversal proceeds. Here the spin reversal propagates slowly and its speed decreases because the magnetization relaxes toward equilibrium following the heat pulse; its progress through the crystal is governed by thermal diffusivity.

By contrast, in the case of high bias shown in Fig. 4.3(b), the time between adjacent peaks is constant and on the order of 100 $\mu$s, corresponding to a constant speed of $v \sim 2$ m/s, consistent with the data measured by Suzuki et al. [52]; the total time for reversal of the full magnetization of the crystal is of the order of 1 ms; and the peaks in Fig. 4.3(b) are substantially sharper and do not broaden as they travel. The constant speed in the case of a large $H_z$ is a signature of magnetic deflagration, a self-sustained process driven by the Zeeman energy released by the spins as they reverse.

4.1.3 Final State

The main panel of Figure 4.4 shows the final magnetic state, $M_f$, of the sample after the spin reversal. The initial magnetic state is $M_i \sim -M_S$ for all $H_z$ values.
Figure 4.4: Main panel: The final state of magnetization after the spin-reversal. When the reversal is triggered, the final state is not a complete reversal for all the bias fields. As we increase the transverse field we observe that for the same bias field the jumps are larger. The zero magnetization value always occur at zero bias field for all transverse fields. Inset: The final magnetic state for the system prepared in two different initial magnetic states.

Application of the heat pulse to the out of equilibrium system changes the magnetization from $M_i$ to $M_f$. Above a certain applied bias magnetic field ($H_z = 0.27$ T for $H_\perp = 3$ T), a complete reversal of the magnetization is observed ($M_f = M_S$), which is consistent with the previous reported results [52–54, 56]. However, below this bias field, the spin reversal is incomplete (i.e. $M_f < M_S$). This corresponds to partial burning, where the propagating front leaves behind unburnt fuel. For all transverse fields when the longitudinal field is zero the magnetization in the
final state is zero, the equilibrium value. However, for a non-zero bias field, as we
increase the transverse field the jump in magnetization increases ($M_f$ increases),
which suggest that the final state is not a equilibrium state as equilibrium mag-
etization does not depend strongly on the transverse field. There will be small
effects of the transverse field on the equilibrium curves, but these effects should
go as $(H_\perp/H_A)^2$ (i.e. be very small). The black curve is the equilibrium curve at
2 K for a 3 T transverse field. At lower thermal bath (0.4 K), we expect the final magnetization value to be higher than the equilibrium value at 2 K. This shows
that the final state is not the equilibrium value at 0.4 K.

The inset of Figure 4.4 shows the final magnetic state, $M_f$, of the system prepared in two different initial magnetic state for a given transverse field of 3 T. The blue open dots represent the negative magnetized state ($M_i \sim -M_S$) in which all the spins are in metastable well. The solid red dot shows the final state for the system that is not magnetized ($M_i = 0$) and has equal population of spins in both stable and metastable state. In both cases, we observe that the final state after the spin reversal is the same. This shows that the final state has no memory effects; it is independent of the initial magnetic state of the system.

The final magnetic states are not the equilibrium states corresponding to the bath temperature (i.e. $T_{\text{bath}} = 0.4$ K) at the ignited magnetic fields. The equi-
librium state of the magnetization depends strongly on the bias field, $H_z$, and temperature, $T$, and not significantly on an applied transverse field, $H_\perp$. However, in our experiments, we observe that $M_f$ for a given $H_z$ increases with increasing transverse fields. The results can be understood when we take the spin relaxation into account. During the magnetic deflagration process the sample temperature increases above the blocking temperature (at the fast timescale of the reversal)
so the magnetization goes toward an equilibrium state given by the applied bias field and the particular temperature reached. After the deflagration propagates, the sample starts to cool down towards the bath temperature. As the sample is cooling down, the magnetization blocks at an temperature (much larger than the bath temperature) determined by a competition between the decay time of the sample temperature \( T = (T_f - T_{bath}) \exp(-t/\tau) \) and the rate of magnetization relaxation, \( \Gamma \). Both the longitudinal and the transverse fields affect the height of the barrier, \( U \). The applied transverse field reduces the blocking temperature (as shown in Fig. 3.2 of section 3.1.1) and allows the magnetization to proceed towards equilibrium during the cooling of the sample.

4.1.4 Front Speed

The speed of propagation of the spin-reversal fronts was determined from the time interval between maxima of the Hall sensors in the middle of the crystal (sensor 3 and 4) and their spatial separation. Note that while the same speed is obtained using any pair of Hall sensors for large bias field, the speed varies from point to point at low bias, and therefore between different Hall sensor pairs.

We first present the data obtained at zero transverse magnetic field in order to compare with previous reported data [52, 53, 83]. Figure 4.5 presents the dependence of the speed of the reversal front on \( H_z \) for both sweep up (blue) and sweep down (red) sets. As expected the observed speed is symmetric with \( H_z \) between sweep up and sweep down sets as the polarity of the initial magnetic state does not affect the speed. Since all the data we obtained exhibit this symmetry, I will present and discuss data obtained during the sweep up process.

The peak in the speed at \( H_z \sim 0.45 \) T shown in Figure 4.5 is a clear man-
Figure 4.5: The bias magnetic field dependence of the speed of reversal front at zero transverse field for both sweep up (solid red spheres) and down (open blue circles) sets. The inset shows a zoom around \( H_z = 0 \). The two sets are symmetric with \( H_z \) and at small \( H_z \) the speed tends to constant, whereas at large \( H_z \) the speed shows an exponential dependence on \( H_z \).

Manifestation of the important influence of quantum mechanics on the dynamics of the system. The maxima is due to quantum tunneling at the first resonant field [7, 15, 16] whenever spin states on opposite sides of the anisotropy barrier have nearly the same energy. As noted earlier, tunneling enhances relaxation and effectively reduces the anisotropy barrier and, as a result, the speed of the reversal front increases at the resonant field. A small peak can also be seen in the inset of Figure 4.5 at the zero bias resonance. Note that the zero-field resonance is slightly shifted (\( \sim 40 \) mT) due to internal dipolar fields [35, 76].
As shown in Figure 4.5 and Figure 4.6, the speed of the spin-reversal front changes abruptly at a bias field that depends on the transverse field. Both Hall sensor signals and the speed data suggest that there are two regimes of spin-reversal propagation and the crossover between these two regimes is surprisingly sharp. For a given transverse field $H_{\perp}$, below a crossover bias field $H_{\text{CO}}$ (for e.g., $H_{\text{CO}} = 0.25$ T for $H_{\perp} = 0$ T), the speed of propagation of the reversing spins is nearly independent of the bias field. However, above the crossover, the speed increases suddenly and depends strongly on the bias field. Figure 4.6(b), a magnification of Fig. 4.6(a)
where the vertical scale has been expanded by a factor of 100, demonstrates this even more clearly.

Fig. 4.6 shows the bias magnetic field dependence of the speed of the spin-reversal front at different transverse fields. As we increase $H_\perp$ we increase the tunnel splitting between levels, which results in a broadening of the resonance steps, as is clearly seen in the figure. Also, increasing the transverse field makes the crossover bias field smaller and also increases the speed of spin-reversal in the thermal regime. We could not investigate the speed of spin-reversal above the first resonance in a high transverse field as the metastable population decreased due to the increase in the tunnel splitting.

The smoothness and reproducibility of the data in Fig. 4.6 suggest that the appearance of instabilities leading to a magnetic deflagration when raising the temperature of the Mn$_{12}$-Ac crystal is a well controlled process. Once the crystal is in the Zeeman regime the speed of the magnetic deflagration can be controlled by the strength of the applied field. Additionally, equal propagation speeds are obtained for different combinations of applied fields, as seen in Fig. 4.6 and Fig. 4.8 where a particular speed can be seen to correspond to different magnetic field configurations. Larger bias fields would produce larger amounts of heat released and higher temperatures for the overall process, while large transverse fields that speed up the process by the same amount would heat the sample much less. This illustrates that the deflagration in Mn$_{12}$-acetate is strongly anisotropic with respect to the direction of the applied field. The anisotropic properties of magnetic deflagration have been investigated both experimentally [58, 84] and theoretically [85].

Figure 4.7 shows the speed of the spin-reversal front at different pulse duration for various fixed bias field. We observe that the speed at higher bias field of
Figure 4.7: The speed of propagation of the spin reversal as a function of pulse width duration for different $H_z$. In both regimes, we observe that the propagation of spin-reversal is independent of the applied pulse duration.

0.4 T is two orders of magnitude greater than the speed at small bias field 0.2 T (see inset of Figure 4.7). Furthermore, we observe that the speed is constant and almost independent of applied bias in both high and small bias fields. This shows that pulse is just required to initiate the spin-reversal. Once the spin reversal propagates, it's speed is independent of the pulse duration.

Figure 4.8 shows the transverse field dependence of the deflagration speed for various fixed applied bias fields. Here fixing the bias field fixes the energy released and allows us to study the dependence of the speed of the reversal front on the activation energy. We observe that the speed of the front increases exponentially
with the applied transverse field. This is explained by the exponential dependence of the speed on the activation energy. Fig. 4.8 shows that when the chemical energy is held fixed, we can increase the speed of combustion just by lowering the activation energy.

The magnetic flammability of the material can be varied by changing the initial magnetization. The main panel of Figure 4.9 shows the speed of the spin reversal front for different initial magnetic states that the system was prepared in. It shows that the speed of the front strongly depends on the fuel (the metastable state population). To prepare the initial states we first unblocked the system by
applying a large transverse field ($H \approx 5$ T) and applied the appropriate bias field to set the initial population. Then we removed the transverse field to block the system at the prepared magnetization. Next we applied the transverse and bias fields to make measurements. The green stars represent the system prepared in negative saturation state (all the spins are frozen in metastable state). The red dots shows the speed for the system prepared in zero magnetized state (equal population in both spin projections). The open blue circles show the system prepared in half positive magnetized state (one quarter spins in meta-stable state). From the figure we can clearly see that as we reduce the amount of fuel, the speed of the reversal front decreases. This is due to less total energy released as we decrease
the population of the metastable state. The inset of Figure 4.9 shows a zoom of
the main plot at low bias field. Note that when the system is prepared in fully
negative saturated or half saturated state, the speed is constant at low bias field
and then increases rapidly consistent with the result observed in Figure 4.5 and
Figure 4.6. However, for the system prepared in zero magnetized state (red solid
spheres), there is an equal population of spins in both potential wells. Hence, we
find that the speed is symmetric for positive and negative bias fields as there is a
same amount of fuel to burn in each case.

4.2 Theoretical Model

In this section I will present the theoretical model and the numerical calculations
that we performed to better understand our experimental results. The theoretical
model is based on previously developed theory of deflagration [60, 86].

The reaction-diffusion system that describes the time evolution of the magne-
tization \( m \) towards equilibrium \( m_{eq} \) entails two processes involving heat. The first
is the heat diffusion through the sample, \( C \dot{T} = \nabla \cdot k \nabla T \) where \( k \) is the thermal
conductivity and \( C \) the heat capacity. The other process is Zeeman energy released
by the spins when they make a transition from the metastable state to the mini-
mum energy stable state, \( \Delta E = 2g\mu_B H_z S \). When this crystal thermalizes there is
a change in temperature \( C \Delta T = \Delta E \). Therefore, the dynamical system of nonlin-
ear partial differential equations describing both temperature and magnetization

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evolution in the sample can be written down as follows

\[
\dot{m} = -\Gamma(m - m_{eq}), \quad (4.1)
\]
\[
\dot{T} = \dot{m} \Delta E/C + \nabla \cdot \kappa \nabla T. \quad (4.2)
\]

Here, \(T\) is the temperature, \(\kappa\) is the thermal diffusivity \((\kappa = k/C)\) and \(\Gamma\) is the relaxation rate, \(\Gamma = \Gamma_0 \exp \left[-U(h_{\perp}, h_z)/(k_B T)\right]\). For fields that are much smaller than the anisotropy field \(h_i = g\mu_B H_i/2DS \ll 1\) [14]:

\[
U(h_{\perp}, h_z) \approx DS^2(1 - h_z)^2 \left[1 - 2h_{\perp} \frac{(1 - h_z^2)^{1/2}}{(1 - h_z)^2}\right].
\]

### 4.2.1 Deflagration Ignition

For some applied fields and initial conditions, the thermal diffusivity cannot compensate for the increase in temperature due to the Zeeman energy released by the reversing spins; the sample temperature then rapidly increases and a magnetic deflagration develops. To study the ignition of magnetic deflagration, we study a small volume. We consider a system of spins blocked in a given metastable magnetic state, increase its temperature \(T_s\), (e.g., from \(T_s = 0.5\) to 6 K), and study the resulting temperature evolution. Let us consider here for simplicity the temperature evolution in the volume under consideration is independent of coordinates. Then, Eq. 4.2 can be written as:

\[
\dot{T} = \dot{m} \Delta E/C - 2\kappa(T - T_s)/R^2 = F(T, H), \quad (4.3)
\]
where, \( T \) is the temperature of the volume under study and \( 2R \) is the characteristic size of the volume. The negative term in Eq. 4.3 is linear with temperature while the reaction term (the first term) increases exponentially with temperature \( \dot{m} \propto \exp \left( -U/(k_B T) \right) \); there is thus a competition between these two terms and stationary solutions (\( \dot{T} = 0 \)) correspond to temperatures when the dissipation equals the released energy.

![Figure 4.10: Temperature dependence of the temperature evolution \( \dot{T} = F(T, H) \) for three different \( H \). The solid and open black circles indicate stable and unstable solutions for the case \( H = (1, 0.05) \) T. The arrows indicate the directions of the temperature evolution.](image)

When the temperature of the volume \( T \) approaches \( T_s \), the function \( F(T_s, H) \) is positive, indicating an increasing trend for the temperature as the flipping spins release heat. It is clear however that at high temperatures the function \( F(T, H) \)
is positive indicating a rapid uptrend of the temperature evolution. At low longitudinal fields, $H_z$, the function $F(T, H)$ has two zeros (i.e., two critical points of $\dot{T} = 0$); the first one, $T_1$, is stable ($\partial_T F(T, H) < 0$) and the second one, $T_2$, is unstable ($\partial_T F(T, H) > 0$). There is therefore an instability at $T = T_2$.

As shown in Fig. 4.10, some magnetic field configurations $[H = (H_\perp, H_z)]$ corresponding to small bias fields have stationary solutions (red dotted curve). As we vary $H$ (i.e., we vary the relaxation rate $\dot{m}$), the two critical points of $\dot{T} = 0$ move closer to each other and eventually merge (green dashed curve) and disappear. When there is no stationary solution for Eq. 4.3 (blue solid line), $\dot{T}$ is positive at all temperatures. As a result, the temperature derivative is always positive and the temperature would rise exponentially leading to an instability—a magnetic deflagration may develop. The condition for the crystal to lose stability at a given $T_s$ and $H$ is $\dot{T} > 0$ and its crossover points are found by solving

$$\dot{T} = 0, \quad \partial \dot{T} / \partial T = 0. \quad (4.4)$$

### 4.2.2 Deflagration Propagation

The deflagration front proceeds as a flame of a finite width $\delta$ and propagates at a constant speed $v$ along the crystal. The characteristic width of the flame is determined by the distance through which the heat diffuses during the time of the energy released [60]. So we get,

$$\delta \sim \sqrt{\kappa \tau} = \sqrt{\kappa \tau_0} \exp \left[ \frac{U(H)}{2k_B T_f} \right], \quad (4.5)$$
where $T_f$ is the corresponding temperature of the flame, which is given by

$$T_f = \frac{\Theta_D}{\pi} \left[ \frac{5n_i\Delta E}{3k_B\Theta_D} \right]^{1/4},$$

(4.6)

where $\Theta_D$ is the Debye temperature and $n_i$ is the initial population of metastable spins ($n_i = (M_s - m)/(2M_s)$, where $M_s$ is saturation magnetization).

The speed $v$ of the flame propagation is simply given by the width of the flame and the characteristic time of the energy released.

$$v \simeq \frac{\delta}{\tau} \simeq \sqrt{\frac{\kappa}{\tau}} = \left( \frac{\kappa}{\tau_0} \right)^{1/2} \exp \left[ -\frac{U}{2k_BT_f} \right]$$

(4.7)

The strongest dependence of $v$ on $H$ comes from the exponential, which contains the known dependence of the energy barrier on the magnetic field.

### 4.3 Comparison of Data and Theoretical Results

In this section I will present the theoretical calculations of the crossover fields and compare it to the experimental finding. We find that the simple theoretical picture that we developed in earlier section is able to capture our experimental finding.

#### 4.3.1 Crossover Fields

At a given transverse field, for $H_z < H_{CO}$, the energy released during the spin-reversing process is small (or even zero in the case of zero bias). The dynamics of the propagating front observed in this case (Fig. 4.3(a)) are determined by the diffusion of the heat supplied by the heater pulse; this corresponds to a thermal regime. Here the reaction term in Eq. 4.3 is negligible and the equation has a stable
solution at a temperature close to the sample temperature \((T_1)\). Neglecting the reaction term in the full set of Eqs. 4.2, it is clear that the heat diffuses and the magnetization locally follows the sample temperature.

For \(H_z \geq H_{\text{co}}\), the energy released by the reversing spins is large, the reaction term dominates over the diffusion term, and Eq. 4.3 displays an instability. In this Zeeman regime, the released energy drives the spin relaxation to a deflagration with steady propagation, where the speed of the propagating front of reversing spins strongly depends on both bias and transverse fields.

The sharp transition in propagation speed from thermal to Zeeman regimes as a function of the applied magnetic field is given by the condition in Eqs. 4.4. The transverse field varies the activation barrier and does not change the released energy; it affects only \(m\) in the reaction term. The applied bias field affects both magnetization dynamics and the energy released.

In Fig. 4.11, we plot the boundaries that separate the thermal regime from the Zeeman regime derived from Eqs. 4.4 together with the experimental points (blue dots) obtained from Fig. 4.6b. For fields above the boundary curve, the reaction term dominates and the crystal develops a magnetic deflagration; below the curves, thermal diffusion dominates and the spins evolve toward equilibrium through slow thermal relaxation. For the calculations we have taken as free parameters the temperature \(T_s\) we heat one end of the sample (\(T\) is the sample temperature), and the combination of thermal diffusivity and nucleation size \(\kappa/R^2\). Using a heat capacity close to the measured value \(C/k_B = 1\) (i.e. \(C = 8.3\) J/(mol K)) [23], and bounding \(2R\) by the smallest sample dimension of 400 \(\mu\)m, a good qualitative fit was obtained for \(T_s = 6\) K and \(\kappa = 1 \times 10^{-4}\) m\(^2\)/s, which agrees well with previously used values [87]. It is important to note that equally good fits can be
Figure 4.11: The boundary curves separating thermal and Zeeman regimes. The different curves denote different initial metastable spin populations $n_i = (M_s - m)/(2M_s)$, where $M_s$ is saturation magnetization. The blue dots are crossover fields derived from the data in Fig. 4.6b. Obtained using different combinations of parameters.

4.4 Summary

To summarize, we have measured the dynamics of spin-reversal fronts in Mn$_{12}$-acetate crystals in the presence of both bias and transverse magnetic fields. We have shown how these applied fields can be used to control an instability that separates slow magnetic relaxation from rapid, self-sustained magnetic deflagration.
We have also expanded the range of conditions under which magnetic deflagration has been observed, particularly to the case of small bias fields, which corresponds to small energy release in the deflagration process. This is a particularly interesting limit in which instabilities in the front are predicted to occur, such as pattern formation and oscillations of the propagating front [88]. In the presence of large transverse fields, where quantum tunneling dominates over thermal effects, the instabilities in the magnetization dynamics could lead to a deflagration-to-detonation transition [89, 90] and may result in supersonic fronts [91]. The present experiments thus provide opportunities to study—in a nondestructive manner—a large variety of instabilities in magnetic systems.
Chapter 5

Conclusions and Perspectives

In this thesis I report our study of collective effects in single molecule magnets. The first set of studies focused on magnetic ordering due to dipolar interaction between molecules in two single molecule magnets, Mn_{12}-acetate and Mn_{12}-ac-MeOH. In both materials, we found that in zero transverse field, the magnetic susceptibility obeys a Curie-Weiss law with a positive Weiss temperature, implying a transition to long-range ferromagnetic order at low temperatures. Application of a magnetic field applied transverse to the easy-axis of the crystal increases quantum spin fluctuations and quantum tunneling of the magnetization and suppresses the long-range ferromagnetic order. However, we have found that suppression of the Curie temperature by the transverse field in Mn_{12}-acetate is far more rapid than in Mn_{12}-ac-MeOH. Moreover, our magnetic susceptibility data of Mn_{12}-acetate does not agree with the results of the mean-field calculation of susceptibility for a transverse-field Ising ferromagnetic Model (TFIFM) system. We proposed that the known solvent disorder in Mn_{12}-acetate that results in an intrinsic distribution of small discrete tilts of the molecular magnetic easy axis from the global easy axis...
of the crystal ($\approx \pm 1^\circ$) gives rise to a distribution of random-fields that further suppresses long-range order. When we took the random-field into account and developed the theoretical model, we found that the susceptibility data of Mn$_{12}$-acetate follows the prediction of the mean-field calculation of susceptibility for a random-field Ising ferromagnetic model (RFIFM).

To confirm the validity of our proposal that the rapid suppression in Mn$_{12}$-acetate is indeed due to random-field associated with isomer disorder, we did a comparison experiment in the high symmetry Mn$_{12}$ variant, Mn$_{12}$-acetate-MeOH. The new system has the same spin structure and similar lattice constants but without the same solvent disorder as Mn$_{12}$-acetate. The susceptibility studies of Mn$_{12}$-ac-MeOH is indeed consistent with that expected for the transverse-field Ising ferromagnetic Model (TFIFM). An important implication of our studies is that long-range order in these two chemically very similar SMMs are described by distinct physical models.

The second set of experiments that was presented in this thesis focused on magnetic deflagration where the molecules in SMM interact through the lattice. We studied the dynamics of magnetic deflagration in Mn$_{12}$-acetate single crystal under the application of both a (small) longitudinal and a transverse magnetic field. The important energies in a magnetic deflagration—or a conventional combustion—are the activation energy and the released energy and there are two distinct processes: ignition (triggering) and propagation (the dynamics of a self-sustaining front). In Mn$_{12}$-acetate using both transverse and bias magnetic fields we independently control both activation and released energies and study both processes.

In our experiments, we applied a heat pulse to one end of Mn$_{12}$-acetate crystal prepared in a metastable spin configuration to initiate the spin-reversal. We found
that the energy released by reversing spins as they relax toward equilibrium can lead to a dynamical instability that ignites self-sustained rapid relaxation along a deflagration front that propagates at a constant subsonic speed. We observed spin reversal near zero field and found a sharp crossover from relaxation driven by heat diffusion to a self-sustained reversal front that propagates much like a domain wall in a ferromagnetic stripe.

Using both magnetic fields allowed us to explore and control the crossover between slow magnetic relaxation and rapid, self-sustained magnetic deflagration. Application of a transverse field, $H_\perp$, increases the tunnel splitting, which increases the magnetic relaxation and allows us to explore deflagration at small bias fields. We find that from our local time-resolved measurements of triggered spin-reversal in single crystals of Mn$_{12}$-acetate that the speed of spin-reversal front is well controlled with the applied magnetic fields. We show that the speed of reversal is independent of the pulse applied but strongly depends on the initial state of the magnetization. We find that the final state after the spin-reversal depends strongly on the transverse field and is independent of the initial magnetic state. We proposed a simple model based on a reaction-diffusion model and performed numerical simulations to explain the ignition of deflagration in Mn$_{12}$-acetate. Our model provides a good description of the experimental finding of a sharp crossover between slow magnetic relaxation and rapid, self-sustained magnetic deflagration.
5.1 Future Studies

5.1.1 Magnetic Ordering

The magnetic susceptibility of both Mn$_{12}$-acetate and Mn$_{12}$-ac-MeOH observed at low temperatures and high transverse magnetic fields (as shown by Fig. 3.9 and Fig. 3.14) is not well understood. While the theoretically calculated lines intersect the temperature axis at $T_{cw}(H_\perp)$ implying the approach to a ferromagnetic phase, the measured susceptibility deviates from this simple behavior, flattening as the temperature decreases toward the presumed transition. Such discrepancy may imply that a transition to a new phase is prohibited for reasons that are yet unclear. Further susceptibility studies down to very low temperature (mK range) at large transverse fields ($\sim 5$ T) may allow one to understand the discrepancy. Such investigations may further reveal interesting ground states (ferromagnetic, spin glass, or even antiferromagnetic) that may differ for the pure and random-field systems.

Further experiments could be performed to verify the RFIFM in Mn$_{12}$-acetate by experimentally verifying other theoretical predictions. One such prediction of the theory is that by changing the angle at which the transverse field is applied ($\phi_H$), the distribution of random-fields is changed. Changing the distribution of random fields is predicted to change the magnetic ordering and susceptibility. This would be a test of the isomer model for disorder that was used in the calculation. The change in distribution can be studied by observing the temperature dependence of the susceptibility at low temperature as shown in Fig. 3.12. In Fig. 5.1, I present our preliminary measurements of the susceptibility as we change the angle $\phi_H$. As we increase the angle, we do observe some differences in susceptibility; but,
the results are not yet conclusive. Further experiments at very low temperature (mK) may be able to verify the theoretical prediction of random-field model due to discrete distribution of easy axis tilts.

![Figure 5.1: The susceptibility dependence on the applied transverse field angle $\phi_H$.](image)

As discussed earlier, it is difficult to reach the ferromagnetic phase in both Mn$_{12}$-acetate and Mn$_{12}$-ac-MeOH due to very slow relaxation at low temperatures. In principle different variants of Mn$_{12}$ with different ligands, different unit cells, and with different degrees of the isomer disorder that gives rise to locally tilted axes could be synthesized that would allow one to expand the studies presented in the thesis. Synthesizing variants with lower anisotropy barriers and/or higher ordering temperatures would enable the study of the critical behavior as one ap-
proaches the ferromagnetic phase and to test whether the system follows TFIFM or RFIFM. As discussed below, it may also be possible to synthesize SMMs in which dipolar ferromagnetic and antiferromagnetic interactions are very close in energy, allowing study of the competition and interplay between ferromagnetic and antiferromagnetic alignment in the presence of randomness.

Mn$_{12}$ complexes have significantly different barriers to magnetization relaxation due to differences resulting from crystal space group symmetry and lattice solvent molecules on the resulting magnetic properties of molecular magnets. The energy barrier in Mn$_{12}$-acetate is around 65 K and other common variants of Mn$_{12}$-Ac, such as Mn$_{12}$-tBuAc and Mn$_{12}$-Ac-MeOH have similar energy barrier. In comparision, the 2 electron reduced form of [Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_{16}$(H$_2$O)$_4$], which has two forms, has barrier height of 18.5 K and 30.3 K. Another promising complex is the electron reduced form of [Mn$_{12}$O$_{12}$(O$_2$C$_6$F$_5$)$_{16}$(H$_2$O)$_4$] that has barrier height of 21 K to 49 K depending on the fast and slow relaxing compounds. These complexes with lower barrasser height have lower blocking temperatures ($T_B \sim 1.8$ K compared to $\sim 3$ K Mn$_{12}$-acetate) and with the application of the transverse field offer us the possibility of reaching the transition temperature and studying the nature of the intermolecular interactions [92–94].

The transition temperature depends on the strength of the dipolar interaction, which is set by the dipolar energy per unit [Mn$_{12}$] molecule $J$. I presented in the thesis that Mn$_{12}$-acetate with $J$ is 0.138 K orders around 0.8 K and Mn$_{12}$-ac-MeOH with similar lattice parameters and the same unit cell volume and also orders around 0.8 K. But, Mn$_{12}$-tBuAc has unit cell volume almost twice that of Mn$_{12}$-acetate and the ordering temperature is expected to be around 0.4 K ($J=0.08$ K). Most of the reduced version of Mn$_{12}$ have $J \approx 0.07$ K and are expected to
order around 0.3 to 0.4 K. The ordering temperature are still predicted to be lower than the blocking temperature in these systems. However, these systems could be studied in transverse field, which promote tunneling and increase the relaxation rate, to study whether they follow the transverse-field Ising model. Furthermore, synthesizing a variant with a small volume per Mn$_{12}$ unit would increase the dipolar energy and thus increase the transition temperature and allow one to observe the transition.

The nature of the interaction in a tetragonal crystal depends sensitively on the $c/a$ ratio and can change the ordering from ferromagnetic (FM) to antiferromagnetic (AFM). According to Millis et al. [28], for $c/a \lesssim 2.5$ FM is favored; for $c/a \gtrsim 2.5$, the $(\pi, \pi, 0)$ AFM has the lowest energy. For $c/a \lesssim 0.5$ FM and the $(\pi, \pi, 0)$ AFM become extremely close in energy. The $c/a$ ratio of Mn$_{12}$-acetate is 0.7 and most of the reduced version of Mn$_{12}$ have $c/a$ ratio of 0.8 to 1.4. Newer variants of Mn$_{12}$ could be synthesized with larger $c/a$ ratio. The proximity of these two states (FM and AFM) may be important in the study of randomness as the random-field might locally favor one particular configuration over another and change the nature of the interaction.

5.1.2 Magnetic Deflagration

In the magnetic deflagration studies while comparing our experimental results with theoretical models we estimated the thermal diffusivity and the temperature of the flame. Therefore, in future, experimental measurements of both separately could be performed. Experiment with precise measurement of the width of the flame is also required to compare the flame width to the theoretical prediction to verify the deflagration theory.
In our experiments we could not investigate the speed of spin-reversal above the first resonance in a high transverse field as we always observed “spontaneous” deflagration–deflagration that appeared without any triggering mechanism. The precise mechanism that gives rise to such deflagration is not well understood. There might be defect sites in the crystal due to which dipolar fields [95, 96] to the spins in neighboring sites is reduced. Thus, the spins around the defect sites may reverse easily as we approach the resonance field. This in turn provides heat to the neighbors and drives the self-sustained reversal. Experimental work is necessary to verify the picture.

There is also theoretical prediction that “cold deflagration” would occur in Mn$_{12}$-acetate at high transverse field (above 3.5 T) that may result in supersonic fronts [91]. The spin-reversal in such deflagration is not driven by heat transferred from reversing spins to the neighbors, but instead by multi-spin tunneling events that change the dipolar interactions on other spins. As a result, the speed of the propagation could be very fast and comparable to the speed of sound in the material. The cold deflagration could be observed near the first resonance field. We could prepare the system very close to the first resonance—within the dipolar window—and trigger the spin reversal with a field perturbation. This triggering mechanism could be made with a small superconducting coil placed next to the sample in a similar manner of placing a heater in our experiments. The field from the coil would change the local field in some part of the crystal and bring the spins in that area in-resonance and allow tunneling. The tunneling of these spins would change their dipolar fields that results in change in local fields that the neighbors feel and bring them in resonance and thus drive the rapid reversal of spins.
In summary, there is a great deal that can be still done and learned about collective effects in single molecule magnets. My work has shown that these are interesting systems to study random-field Ising ferromagnetic model, transverse-field Ising ferromagnetic model and reaction-diffusion processes. Therefore, single molecule magnets continue to be of broad interest to the study of Magnetism and Solid State Physics.
List of Publications and Presentations

Publications

• P. Subedi, S. Vélez, F. Macià, S. Li, M. P. Sarachik, J. Tejada, S. Mukherjee, G. Christou and A. D. Kent, “Quantum deflagration in Mn$_{12}$-acetate in the presence of a transverse field,” (in preparation)


• Bo Wen, P. Subedi, Lin Bo, Y. Yeshurun, M. P. Sarachik, A. D. Kent, A. J. Millis, C. Lampropoulos, and G. Christou, “Realization of random-field
Presentations

Invited Presentations and Seminars

- “Onset of a Propagating Self-Sustained Spin Reversal Front in a Magnetic System,” IBM T. J. Watson Research Center, June 10, 2013, Yorktown Heights, NY


- “Transverse field and random-field Ising ferromagnetism in Mn$_{12}$-acetates,” APS March Meeting, March 21, 2013, Baltimore, MD

- “Realization of random-field Ising ferromagnetism in a molecular magnet,” Condensed Matter Physics Seminar, Service de Physique de l’Etat Condense, CEA Saclay, Nov. 28, 2011, Saclay, France

- “Longitudinal susceptibility measurement of Mn$_{12}$-ac single crystals as a function of temperature and transverse magnetic field,” Third Workshop on Current Trends in Nanoscale and Molecular Magnetism, June 24, 2010, Orlando, FL

Contributed Presentations and Posters

- “Quantum deflagration in Mn$_{12}$-acetate in the presence of a transverse field,” International Conference on Molecular Magnetism 2012, Oct. 8,
2012, Orlando, FL (flash talk, poster prize)

• “Quantum deflagration in Mn$_{12}$-acetate in the presence of a transverse field,”
  APS March Meeting, February 29, 2012, Boston, MA (talk)

• “Realization of random-field Ising ferromagnetism in a molecular magnet,”

• “Realization of random-field Ising ferromagnetism in a molecular magnet,”
  Gotham Metro Condensed Matter Meeting, April 15, 2011, NYAS, New York, NY (poster)

• “Hall magnetometry measurements of the susceptibility of variants of Mn$_{12}$-ac,”
  APS March Meeting, March 23, 2011, Dallas, TX (talk)

• “Realization of random-field Ising ferromagnetism in a molecular magnet,”
  Cryoconference 2010, Sept. 12, 2010, Pavol Jozef Safarik University, Kosice, Slovakia (talk)

• “Susceptibility of single molecule magnet Mn$_{12}$-ac single crystals as a function of temperature and transverse field,”
  APS March Meeting, March 17, 2010, Portland, OR (talk)

• “Dipolar ordering in single molecular magnets,”
  Gotham Metro Condensed Matter Meeting, Nov. 21, 2009, NYAS, New York, NY (poster)
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