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MAGNETIZATION REVERSAL IN SINGLE MOLECULE MAGNETS

by

Louisa Bokacheva

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TO MY PARENTS
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ABSTRACT

MAGNETIZATION REVERSAL IN SINGLE MOLECULE MAGNETS

I have studied the magnetization reversal in single molecule magnets (SMMs). SMMs are van der Waals crystals, consisting of identical molecules containing transition metal ions, with high spin and large uniaxial magnetic anisotropy. They can be considered as ensembles of identical, iso-oriented nanomagnets. At high temperature, these materials behave as superparamagnets and their magnetization reversal occurs by thermal activation. At low temperature they become blocked, and their magnetic relaxation occurs via thermally assisted tunneling or pure quantum tunneling through the anisotropy barrier.

We have conducted detailed experimental studies of the magnetization reversal in SMM material Mn$_{12}$-acetate (Mn$_{12}$) with $S=10$. Low temperature measurements were conducted using micro-Hall effect magnetometry. We performed hysteresis and relaxation studies as a function of temperature, transverse field, and magnetization state of the sample. We identified magnetic sublevels that dominate the tunneling at a given field, temperature and magnetization. We observed a crossover between thermally assisted and pure quantum tunneling. The form of this crossover depends on the magnitude and direction of the applied field. This crossover is abrupt (first-order) and occurs in a narrow temperature interval (<0.1 K), when an external field is parallel to the easy axis of the sample. We have shown that in this case there are competing
maxima in the relaxation rate versus energy, and the global maximum shifts abruptly from one energy to the other as a function of temperature. Strong longitudinal and transverse fields make the crossover more gradual (second-order), which occurs in an interval of 1 K.

We have demonstrated that a thermally independent quantum regime exists below the temperature of approximately 0.6 K. The existence of this regime was also supported by the results of the magnetization relaxation experiments. These results also show non-exponential form of relaxation, previously observed by other groups.

In order to understand the crossover, we have performed numerical simulations of a model Hamiltonian. The results of these calculations and their comparison of our experimental data suggest the presence of additional tunneling mechanisms in Mn$_{12}$. 
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INTRODUCTION

Mesoscopic physics has been an area of active research for the past two decades. It is an area that deals with the realm intermediate between microscopic objects (such as atoms and molecules), described by quantum mechanics, and that of bulk objects, containing large numbers of microscopic elements, described by classical laws. At the crossover region between these two limits, which spans an interval of sizes between 1 nm and 1 μm, an entirely new area of physics has emerged. Such discoveries, as quantum conductance, universal conductance fluctuations and the quantum Hall effect, have demonstrated that mesoscopic systems possess unique properties associated with their confined dimensions. Studies of these systems provide insights into the fundamental properties of matter at the border between the classical and quantum limits.

Mesoscopic systems have become available for experimental studies due to the advances in technology, which enabled the creation of artificial systems with reduced dimensionality. In fact mesoscopic systems have become the subject of applied interest, for example, as memory storage elements in computer technology. Current hard disk storage media consist of thin continuous magnetic films, on which information is stored as the orientation of the magnetization of individual magnetic domains, with each domain corresponding to one bit (either up or down).
Fig. 1 – Decrease of the number of spins per bit in the memory elements.

The size of the domains, and therefore, the storage density, is determined by the size of the heads used to read or write these domains. The storage density doubles every 2 years (empirical Moore's law), and according to IBM data [1] since 1991 this growth rate has increased even further, due to the improvements of read-write heads (Fig. 1).

The minimum size of the magnetic elements created using modern methods has a limit. At a size of about 10 nm thermal fluctuations can cause the magnetic bits to become unstable and randomly switch their magnetization direction (which is called
superparamagnetism). Even at zero temperature, quantum fluctuations can cause the magnetization to switch and thus are important to understanding the behavior of such a system. Avoiding the superparamagnetic limit presents a significant challenge for creating magnetic devices with smaller elements. Although the limits of existing methods for scaling down the magnetic elements are being constantly pushed further and further, an alternative approach is gaining momentum, namely using self-assembled systems with well-defined parameters created by chemical synthesis. Nanoparticles [2], metallic and semiconducting nanotubes [3], block co-polymers [4, 5], and single molecule magnets (SMMs) [6, 7], can serve as examples of the self-assembled systems. The size and properties of these systems are determined by their chemical composition and synthetic process. The size of an individual element within the systems is of the order of 5–10 nm. These systems open new perspectives not only in terms of interesting fundamental physics, but also some promising technological applications, such as ultra-high memory density and quantum computing.

Among these new systems, SMMs represent a new class of materials with unique magnetic properties. Their unusual features attracted physicists’ attention only about a decade after the first SMMs had been synthesized and characterized by chemists (in the early 1980s). These materials are Van der Waals crystals, which consist of molecules containing transition metal ions (Mn, Fe, Co) and organic ligands. All molecules within the crystal are characterized by the same set of well-defined parameters and are identical in their chemical composition, structure, spin,
anisotropy, and orientation. Within each molecule, strong exchange interactions (hundreds to thousands of degrees Kelvin) force the individual ionic spins to align rigidly resulting in a high total spin (currently from \( S = 5 - 16.5 \)), so that every molecule can be considered effectively as one 'giant' spin. Most known SMMs have a large uniaxial magnetic anisotropy (tens of degrees Kelvin). On the scale of the anisotropy energy, the interactions among the molecules are small, therefore the crystals of SMMs can be viewed as three-dimensional arrays of weakly interacting nanomagnets. These materials are superparamagnetic at high temperature, but become blocked at low temperatures. Their magnetization becomes hysteretic and the magnetic relaxation becomes slow on the experimental time scale.

These features make SMMs excellent model systems for the studies of the behavior of mesoscopic spins. Since these materials are monodisperse systems, at low temperature various effects associated with the quantized magnetic energy spectrum of an individual molecule can be observed in the response of the crystal, without being washed out by the distributions of molecular parameters. Due to the large anisotropy barriers, these effects can be observed within the temperature range accessible by modern low-temperature experimental techniques. SMMs are versatile systems, since their properties can be relatively easily controlled and modified during chemical synthesis. For example, by varying the type of the metallic ions one can create materials with different total spin and anisotropy, and the crystal symmetry can be changed by ligand exchange. SMMs are soluble in organic solvents, and their molecules maintain their chemical identity in solution, that opens a possibility of
studying the intermolecular interactions using solutions of different concentrations. By embedding the molecules in an organic matrix one may also create Langmuir-Blodgett films of SMMs, which might be important for applications. In other words, SMMs are remarkable systems, which enable the fundamental studies and suggest some potential technological advances.

Our research has been focused on the magnetic behavior of the SMM Mn$_{12}$-acetate. In the following chapters I will present the results of our experimental work, as well as the background information important to understanding the observed phenomena. Chapter 1 describes the basics of the chemical and magnetic structure of the two most studied SMMs, Mn$_{12}$ and Fe$_8$, and the physics of escape from a metastable state, which can be studied in SMMs. Chapter 2 contains an overview of the most important experimental and theoretical work conducted on SMMs. In Chapter 3 I will describe the experimental methods involved in our experiments, such as the micro-Hall effect magnetometry, sample preparation techniques, and the principles of operation of the cryogenic system. In Chapter 4 I will present the results of our experiments, and Chapter 5 contains the results of the numerical simulations of the SMM model Hamiltonian.
CHAPTER 1
SINGLE MOLECULE MAGNETS

1.1 Chemical structure and spin configuration of Mn₁₂ and Fe₈.

1.1.1 Mn₁₂

Mn₁₂-acetate (Mn₁₂) is an abbreviated name of a mixed valence dodecanuclear manganese cluster with the formula [Mn₁₂O₁₂(CH₂COO)₁₆(H₂O)₄] 2CH₃COOH 4H₂O, and molar mass 2060 g/mol. The chemical name of the compound is tetra-aqua-(μ₃-dodeca-oxo)-(μ₂-hexadeca-acetato)-dodeca-manganese acetic acid solvate tetrahydrate.

This material has been synthesized by Lis [8] in 1980. The cluster contains 12 manganese ions in two different oxidation states, 4 Mn⁴⁺ and 8 Mn³⁺ ions (see Fig. 1.1). The four Mn⁴⁺ ions form a tetrahedron in the core of the molecule, surrounded by a ring of eight Mn³⁺ ions. Manganese ions within the core are linked together by single oxygen atoms (μ₃-O) and connected to the peripheral ions by sixteen double oxygen bridges (μ₂-OOCCH₃) with four terminal H₂O groups attached to each of the four Mn ions. The molecule is almost planar and has a crystal imposed S₄ symmetry [9]. Individual clusters form a van der Waals crystal with tetragonal lattice and the following cell dimensions: (a = b = 17.319 Å, c = 12.388 Å, V = 3863 Å³ [8]) (see Fig. 1.2). Mn₁₂ crystal also contains disordered acetic acid molecules and waters of crystallization.
Fig. 1.1 – Mn$_{12}$ molecule. Arrows indicate the spins of Mn ions.

Fig. 1.2 – Mn$_{12}$ unit cell.
Unpaired electrons in the 3d shells of manganese ions form high-spin states according to Hund rules: 3 electrons with their spins aligned give rise to the spin $S = 3/2$ of Mn$^{4+}$ ion, and 4 electrons in Mn$^{3+}$ have a total spin $S = 2$. The strength of the exchange interactions between manganese ions is characterized by the following constants: $J_1 \sim -215$ K, $J_2 \sim J_3 \sim -85$ K (antiferromagnetic), $|J_4| < 45$ K (ferro- or antiferromagnetic) [9], see Fig. 1.3. The strongest interaction $J_1$ is between the ions
linked by the double oxygen bonds. Note that the three interactions $J_1$, $J_2$ and $J_3$ are antiferromagnetic, that leads to the spin frustration of $S_1$. The dominating interaction $J_1$ forces the spins in the core to be antiparallel to the spins of the ions in the outer ring. At sufficiently low temperatures (below 60 K), the ground state of the cluster is ferromagnetic with the total spin $S = 10$: $S = -3/2 \times 4 + 2 \times 8 = 10$.

1.1.2 Fe$_8$

Fe$_8$ ($\{[(tacn)_6Fe_8(\mu_3-O)_{12}(\mu_2-OH)_{12}]Br_7(H_2O)\}Br\cdot8H_2O$) (Fig. 1.4) consists of 8 Fe$^{3+}$ ions linked together by oxygen bridges and 6 tacn rings (tacn stands for 1,4,7-triazacyclononane, C$_6$H$_{15}$N$_3$), connected to the 6 peripheral Fe ions. The iron ions are arranged in a so called 'butterfly configuration' (see Fig. 1.5). All ions are in the same spin state $S = 5/2$. 

9
Fig 1.4 – Fe₈ molecule.
The exchange interactions are shown in Figure 1.5 and have the following values: $J_1 \sim -25 - 35$ K, $J_2 \sim -130 - 170$ K, $J_3 \sim J_4 \sim -20 - 50$ K (all antiferromagnetic). As in the case of Mn$_{12}$, the strongest interactions are transmitted via the double oxygen bond $\mu_3$-O. Spin frustration forces the two Fe ions in the body of a 'butterfly' be anti-aligned to the other of the ions. The total spin ground state of the cluster is therefore $S = 10$, as in the case of Mn$_{12}$: $S = 5/2 \times (6 - 2) = 10$. The molecule does not have any precise symmetry. The complex crystallizes in a triclinic lattice with the following parameters: triclinic P1, $a = 10.522(7)$ Å, $b = 14.05(1)$ Å,
\[ c = 15.00(1) \ \text{Å}, \ \alpha = 89.90(6)^\circ, \ \beta = 109.65(5)^\circ, \ \gamma = 109.27(6)^\circ, \ \text{and} \ V = 1956 \ \text{Å}^3 \]

(measured at \( T = -30^\circ \text{C} \)) [10].

1.2 Magnetic energy of the spin \( S = 10 \) system with uniaxial anisotropy.

Both \( \text{Mn}_{12} \) and \( \text{Fe}_8 \) are \( S = 10 \) systems and have a strong uniaxial magnetic anisotropy. It means that in the crystal there is a chosen direction, called the easy axis, with which the magnetization of the crystal tends to align to create the lowest energy state. Without an external magnetic field, the states with magnetic moments 'up' and 'down' relative to the easy axis have the lowest and equal energies. The form of the anisotropy is determined by the symmetry of the crystal, since the mechanism that causes the anisotropy is the interaction between the spins of the ions and the strongly non-uniform electrostatic crystalline field of the environment due to the other ions.

Since the exchange interactions between the metallic ions within one molecule are so strong compared to other interactions within the crystal, each molecule can be regarded as a single effective spin \( S = 10 \). Let the easy axis of the system be parallel to the \( z \)-axis. The anisotropy splits the spin \( S = 10 \) multiplet into a set of \( S \) doubly degenerate levels characterized by the eigenvalues \( m \) of the operator \( S_z \). The two lowest states are those with \( m = \pm 10 \) [9, 11]. At non-zero temperature the number of spins in different \( m \) states is given by the Boltzmann distribution and is proportional to \( \exp(-E_m/T) \).
The magnetic energy of such a system in an external field is described by a spin Hamiltonian, similar to that of a ferromagnetic particle. In the first order expansion in powers of the spin operators this Hamiltonian can be written as follows:

\[ \mathcal{H} = -D S_z^2 - g \mu_B H S, \tag{1.1} \]

where the first term is the energy of the state with a spin projection \( S_z \) in the presence of the anisotropy barrier characterized by the constant \( D \), and the second is the Zeeman term describing the interaction of the spin \( S \) with an external field \( H \) (\( g \) is a \( g \)-factor, \( \mu_B \) is the Bohr magneton). The parameter \( D \) has been determined by the spectroscopic techniques, such as inelastic neutron scattering and EPR, and was found to be \( D = 0.548 \text{ K} \) in Mn\(_{12} \) [12] and \( D = 0.275 \text{ K} \) in Fe\(_8 \) [13]. For a spin \( S = 10 \) system, the Hamiltonian is a \( 21 \times 21 \) matrix. Semiclassically the energy of the system can be represented by a double-well potential: the magnetic sublevels with positive and negative \( m \) occupy two different wells separated by an anisotropy barrier (see Fig. 1.6). The semiclassical energy is in this case expressed as \( -Dm^2 \cos^2 \varphi \), where \( \varphi \) is the angle that the spin with \( z \)-projection \( m \) makes with the easy axis.
The Hamiltonian may also contain other terms, such as terms due to a transverse anisotropy, or higher order uniaxial anisotropy terms, and contributions due to dipolar interactions, hyperfine fields, etc. The form of the anisotropy terms is determined by the symmetry of the crystal and is therefore different for the two materials. It has been shown that in Mn$_{12}$ terms of higher order are present [14], such as a uniaxial anisotropy term proportional to $S_z^4$ and the transverse anisotropy term, proportional to $(S_z^4 + S_z^{-4})$, which are the lowest order terms allowed by the tetragonal symmetry of the crystal. The resulting Hamiltonian can be therefore written as

$$\mathcal{H} = -DS_z^2 - BS_z^4 + C(S_z^4 + S_z^{-4}) - g\mu_B HS + \mathcal{H}' ,$$

(1.2)
where \( B = 1.17(2) \times 10^{-3} \) K, \( C = 2.24 \times 10^{-5} \) K [12], and \( \mathcal{H}' \) contains all other terms, for example, those describing interactions.

In Fe₈ the transverse terms appear in a lower order due to its lower (triclinic) symmetry, so that its Hamiltonian has the form

\[
\mathcal{H} = -DS_z^2 + E(S_x^2 - S_y^2) - g\mu_B HS + \mathcal{H}',
\]

(1.3)

where \( E = 0.046 \) K [13]. With this choice of axes and \( E > 0 \), the \( x \)-axis is called the hard axis, and \( y \)-axis – the medium axis.

1.3 Uniaxial \( S = 10 \) system in an external magnetic field.

Consider now the behavior of the spin \( S = 10 \) system in an external magnetic field. A three-dimensional field vector can be decomposed into two components: the longitudinal field, parallel to the easy axis of the crystal, and the transverse field, in a plane perpendicular to the easy axis (the hard plane, \( xy \)-plane). First, let only a longitudinal field be applied in a negative \( z \)-direction. This field removes the degeneracy between the states with positive and negative spin states \( \pm m \), making those states preferable (lower energy) whose magnetic moments are aligned with the field, i.e., states with \( m > 0 \) (note that in our case the magnetic moment is due to the electronic spin, therefore the magnetic moment is opposite to the spin direction)). In terms of the double potential in Fig. 1.6, without the applied field, the two wells are symmetric, but the longitudinal field tilts the barrier making the left well the ground state. If we initially prepare our system in this state \(( m > 0 \) \) and then reverse the field
direction, the left well will become metastable, and the lowest level in the right well will be a new ground state. The system will try to align its magnetic moment with the field, that is escape from the metastable state and achieve a new equilibrium state. The escape from the metastable state is the main focus of our research, and this process will be described in more detail in the next section.

The energy of the magnetic sublevels of Mn$_{12}$ calculated according to Eq. (1.2) as a function of the field $H_z$ in positive $z$-direction (Zeeman diagram) is shown on Fig. 1.7. Note that in zero field the transverse anisotropy term $C(S_u^+ + S_u^-)$ removes the degeneracy between the levels whose magnetic quantum numbers differ by $\Delta m = \pm 4$. This splitting is small and on Fig. 1.7 it is noticeable only between the levels with $m = +2$ and $m = -2$. At $H_z \neq 0$ the levels cross at certain values of the external field, which we will call resonance fields.
Fig. 1.7 – Zeeman diagram of Mn_{12}. Energy is plotted relative to the lowest level in the metastable well.

The behavior of the two levels close to this resonance point is determined by the symmetry breaking perturbations in the Hamiltonian, i.e., the terms that do not commute with $S_z$ and produce non-diagonal matrix elements. Near the crossing such a perturbation removes the degeneracy between the two levels, so that they form an anticrossing with a gap between them called the tunnel splitting $\Delta$ (see Fig. 1.8). If this splitting is non-vanishing and small compared to the spacing between the levels, a tunneling transition between the two levels on the opposite sides of the anisotropy barrier is possible.
Magnetic field $H_z$

Fig. 1.8 – Anticrossing of two energy levels.

These transitions occur when two levels are brought close to the resonance by the external field. If we neglect the transverse anisotropy term in Eq. (1.2), the longitudinal ($z$-axis) field at which the levels $m_{esc}$ and $m'$ become degenerate is:

$$H(n, m_{esc}) = nH_0(1 + B/D[m_{esc}^2 + (m_{esc} - n)^2])$$  \hspace{1cm} (1.4)

where $n = m_{esc} + m'$ is an index of the crossing describing the bias field, and $H_0 = D/g_z\mu_B$ is a constant (0.42 T). The transverse anisotropy does not significantly change the resonance fields, as we have checked by direct numerical diagonalization.
of the Hamiltonian (1.2). Note that the presence of the $B$-term prevents all the crossings with the same $n$-index, but different $m$-values, from occurring at the same value of the field. Instead, larger field is necessary to bring lower lying sublevels into the resonance. As we will show later, this fact is crucial for our experiments, since it allows us to determine which levels in the metastable well give the dominant contribution to the tunneling at a given set of external conditions, such as longitudinal and transverse magnetic field and temperature.

The effect of the transverse magnetic field of the form $H_z S_z$ is two-fold: First, it creates the symmetry-breaking terms, which do not commute with $S_z$ and therefore may produce tunneling. Second, it lowers the barrier and promotes the tunneling from the levels closer to the top of the barrier. In subsequent chapters, we will study the effect of the transverse field in more detail.

Other mechanisms, producing terms that do not commute with $S_z$, are the interactions between the clusters (dipolar interactions) and between the electronic spins and the nuclear spins within one molecule (hyperfine interactions). In Mn$_{12}$ the dipolar interactions are estimated to be on the order of 0.02 T, and the nuclear fields 0.01 T. In Fe$_8$, the dipolar interactions are about 0.05 T [15]. The hyperfine interactions due to the iron atoms are virtually absent (iron has only one isotope $^{57}$Fe with a non-zero spin and small natural abundance of about 2%). However hyperfine fields may arise from other nuclei in the cluster. The molecule of Fe$_8$ contains more than 100 hydrogen, 18 nitrogen and 8 bromine atoms, with a non-zero magnetic
moment, so that the resulting hyperfine fields can be estimated to be on the order of $10^{-4} \text{T}$ [7]. Despite being small compared to the anisotropy energy, the dipolar and hyperfine interactions, however, may play an important role in the spin tunneling processes, as it has been suggested by some experimental and theoretical results, which will be discussed in the next chapter.

1.4 Escape from a metastable state

Let us consider the escape from a metastable state in more detail. This is a general phenomenon that occurs in such systems as nuclei subject to $\alpha$-decay, SQUIDs, or magnetic particles. In our case we consider the decay of a metastable state of a uniaxial nanomagnet in an external field.
Let the system be prepared in a well-defined magnetization state as described in the previous section, i.e. with its magnetic moment anti-parallel to the $z$-axis. Then the field is reversed, and the system switches into the state with magnetic moment pointing in the positive $z$-direction (see Fig. 1.9). The probability for the system to
remain in the metastable well and not switch (persistence probability) \( P(t) \) decreases exponentially with time:

\[
P(t) = \exp(-\Gamma t),
\]

(1.5)

where \( \Gamma \) is the relaxation rate. The system can escape to the ground state by three different paths acting in parallel: thermal activation over the barrier (TH), thermally assisted tunneling (TAT), or pure quantum tunneling (QT) across the barrier, see Fig. 9, so that the total rate is a sum of the three of these contributions:

\[
\Gamma_{\text{total}} = \Gamma_{\text{TH}} + \Gamma_{\text{TAT}} + \Gamma_{\text{QT}}.
\]

(1.6)

These paths dominate at different temperatures and other external conditions. Thermal activation over the barrier (superparamagnetism) dominates at high temperatures and is described by the Arrhenius law:

\[
\Gamma_{\text{TH}} = A_{\text{TH}} \exp(-U/T),
\]

(1.7)

where \( A_{\text{TH}} \) is an amplitude, \( U \) is the height of the barrier, and \( T \) is the temperature. At lower temperatures, when the thermal energy is not sufficient for the system to jump over the barrier, the magnetic moment can first be thermally excited into a state closer to the top of the anisotropy barrier and then tunnel there, where the barrier is thinner. Such process is called thermally assisted tunneling and its rate can be described by the following expression:

\[
\Gamma_{\text{TAT}} = \sum_{excited} A_{\text{TAT}(E)} \exp(-E/T) \exp(-B(E)),
\]

(1.8)
where the summation is over all thermally excited states, $A_{\text{TAT}}(E)$ is an energy-dependent amplitude for the state with the energy $E$, $S(E)$ is an imaginary time action, which describes the probability of tunneling at this energy.

Thermally assisted tunneling is a result of the competition of the two processes: thermal population of the level described by the Boltzmann factor $\exp(-E/T)$, which decreases exponentially towards the top of the barrier, and the quantum mechanical probability of tunneling $\exp(-S(E))$, which increases exponentially with energy. Since these two functions are strongly dependent on the energy of the magnetic level, their product, $\Gamma_{\text{TAT}}$, will have a maximum in a very narrow interval of energy, or in our case, for only one or two magnetic sublevels.

Pure quantum tunneling rate $\Gamma_{\text{QT}}$ occurs at lowest temperatures, when only the lowest state in the metastable well has significant population. QT is independent of temperature and is determined only by the characteristics of the barrier:

$$\Gamma_{\text{QT}} = A_{\text{QT}} \exp(-S(0)), \quad (1.9)$$

where $A_{\text{QT}}$ is a prefactor, and $S(0)$ describes the probability of tunneling at the lowest state in metastable well at $E = 0$. 

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Our goal is to study how the system goes from classical thermal activation over the anisotropy barrier to the pure quantum tunneling, a process that we call the crossover between different regimes of tunneling. Let us clarify what is meant by the term ‘crossover’. Consider the plot on Fig. 1.10, which shows the natural logarithm of the relaxation rate as a function of temperature. At low temperatures pure QT dominates and therefore $\ln \Gamma_{QT}$ is constant, at high temperatures thermal activation and TAT prevails, therefore $\ln \Gamma_{TH}$ grows with temperature. This means that at some
temperature $T_0$, these rates must become approximately equal: $\Gamma_{QT} \sim \Gamma_{TH}$ (up to an exponential), $T_0 \sim U/B(0)$, and the behavior of the relaxation rate should change dramatically. We call this change from strongly temperature dependent regime to the temperature independent regime, “the crossover from TAT to QT”. The form of the crossover depends on the anharmonic terms in the expression describing the anisotropy barrier.

According to the theory by Larkin and Ovchinnikov [16], [17], for such barriers as $U(x) = -x^2 + x^4$, or $-x^2 + x^3$, the relaxation rate changes smoothly as a function of temperature, and the energy of the escape levels, also changes gradually from the top of the barrier to the bottom of the well as the temperature is reduced. On the other hand, if the form of the potential is $U(x) = -x^2 - x^4$, the relaxation rate may have a cusp. In this case escape levels shift abruptly from the top of the barrier to the lowest state in the metastable well in a very narrow temperature interval. Larkin and Ovchinnikov used the term ‘first-second order transition’ to describe this phenomenon, which created a certain amount of confusion, since the analogy with phase transitions is only formal. To avoid this confusion, we will use the term ‘crossover’ and label the two types of crossovers as ‘abrupt’ and ‘gradual’. Abrupt crossover occurs in a narrow temperature interval, and gradual crossover occurs in a much broader temperature interval.

The theory of an abrupt crossover has been developed by Chudnovsky and Garanin [18], who considered mapping of the spin system onto a particle in an
inverted potential. This theory was formulated for a large spin case, however we will show that its predictions are relevant for a small spin system, such as $S = 10$. According to the model developed for the uniaxial system subject to a transverse field described by the Hamiltonian

$$\mathcal{H} = -D S_z^2 - g \mu_B H_z S_z,$$

(1.10)

the quasiclassical transition rate is

$$\Gamma \sim \int dE W(E) \exp(- (E - E_{\text{min}}) / T),$$

(1.11)

where $W(E)$ is the probability of tunneling at the energy $E$, and $E_{\text{min}}$ is the bottom of the potential. This probability is expressed via the imaginary-time action $S(E)$:

$$W(E) \sim \exp(- S(E)), $$

(1.12)

Then the rate $\Gamma$ can be written as

$$\Gamma \sim \exp(- F_{\text{min}} / T),$$

(1.13)

where $F_{\text{min}}$ is the minimum of the effective "free energy"

$$F \equiv E + TS(E) - E_{\text{min}}.$$

(1.14)

In order to determine $S(E)$, the authors of [18] used the method of mapping of the spin problem onto a particle problem [19], [20]. The spin Hamiltonian is then rewritten for the particle oscillating in the inverted potential, for which the imaginary time action can be written. The period of these oscillations is given by

$$\tau(E) = - \frac{dS(E)}{dE} = \frac{1}{T},$$

(1.15)
at the minimum of the free energy given by Eq. (1.14). This expression determines the trajectory of the particle that dominates the transition rate at a temperature $T$. The dependence of the period $\tau(E)$ on $E$ determines the type of the crossover from quantum tunneling to thermal activation. If $\tau(E)$ monotonically increases with the decreasing energy, the transition is of the second order, i.e. the dominant energy at which the system crosses the barrier changes smoothly (Fig. 1.11(a)). If the dependence of $\tau(E)$ is nonmonotonic, the transition is abrupt, or first-order, and the dominant energy of the barrier crossing will change abruptly in this case (Fig. 1.11(b)). It has been demonstrated that both kinds of the crossovers can occur in the spin system, depending on the strength of the transverse field. The theory of the crossover has been developed for the case of the biaxial system and spin system in arbitrarily directed field [21]. These models are particularly interesting from an experimental point of view, since in our experiments we can vary the perturbations of the system, such as the transverse field, and therefore switch between the two types of the crossover from TAT to the QT. In the subsequent chapters I will present the experimental data showing both types of the crossovers, in agreement with the predictions of this theory.
Fig. 1.11 – Gradual (a) and abrupt (b) crossovers.
CHAPTER 2
LITERATURE REVIEW

Chemists have synthesized a large variety of high-nuclearity clusters containing 3d metals (vanadium to copper) using small metalloorganic complexes as building blocks. A few of these materials behave as SMMs and have magnetic anisotropies that are sufficiently high to enable experimental studies in accessible temperature range. Despite the progress in synthetic methods, creating clusters with both high spin and high magnetic anisotropy is still a challenging task.

SMMs containing manganese or iron ions have been studied most extensively, and recently the first cobalt cluster has been reported [22]. The chemistry of manganese compounds offers the greatest flexibility for synthetic variations of these materials. For example, Mn$_{12}$-acetate ($S = 10$) is a representative of a large family of Mn$_{12}$ materials with different organic ligands (acetate, benzoate, propionate), crystal symmetry and ground state spins. Among other manganese compounds, of a special interest are clusters with half integer spin, such as Mn$_4$ ($S = 9/2$) [23] and [Mn$_{12}$O$_{12}$(O$_2$CET)$_{16}$]$^-$ [24], in which the effects due to the Kramers degeneracy may be studied.

Some initial attempts to make ordered Langmuir-Blodgett films of Mn$_{12}$-acetate and Mn$_{12}$-benzoate embedded in behenic acid matrix have been reported [25]. Although it was clear that the complete ordering of the molecules in these films was
not achieved, this is an important result, which may lead to potential applications of magnetic molecules as memory units.

Iron-based clusters are more difficult to synthesize and modify, yet there is a whole spectrum of these molecules too. The highest spin iron-based molecule is Fe_{19} \( S = 33/2 \), anisotropy energy \( E_A = 15.7 \) K. This cluster has been only recently separated as a pure material free from Fe_{17} species, which usually co-crystallizes with Fe_{19} in the same lattice cell [26]. Cyclic iron clusters (ferric wheels) with the number of iron ions from 6 to 18, in which antiferromagnetic interactions between ions result in a low total spin \( S = 0 \), have been characterized and are yet to be studied in greater detail [27-29].

An additional interest towards manganese and especially iron containing clusters is due to their structural and magnetic similarity to some biological molecules, such as ferritin. Ferritin is the second most important iron-storage protein in living organisms after hemoglobin. This large molecule (8-12 nm in diameter) consists of a core, containing Fe_{2}O_{3} (Fe^{3+} oxide) particle, surrounding by an organic shell (apoferitin). The number of Fe ions is usually between 2000 and 4500. Despite the huge difference in size, the magnetic behavior of ferritin resembles that of SMMS: at low temperature its magnetization becomes hysteretic and shows evidence of quantum tunneling, similar to that in SMMS [30-32].

SMM materials are usually characterized by variety of spectroscopic techniques. Their crystal structure and unit cell parameters are determined by X-ray diffraction. Important information about Mn_{12} and Fe_{8}, such as the total spin, magnetic
energy level structure and the parameters of their effective spin Hamiltonian, has been obtained from the EPR and inelastic neutron scattering experiments [12, 14, 33-36]. Hill and collaborators [33] used a novel experimental method – multifrequency, high-sensitivity EPR with frequency range between 35 and 115 GHz that enables measurements on sub-millimeter size crystals [37, 38]. The resonance cavities used in these experiments have the Q-factors, which are orders of magnitude higher than conventional ones and range from $5 \cdot 10^3$ to $2 \cdot 10^4$. EPR transitions between the levels at the top of the anisotropy barrier occur in the interval $0 - 5$ T, where steps in hysteresis occur.

SMMs have become the subject of many experimental and theoretical studies since the discovery of the regular series of steps and plateaus in magnetic hysteresis of first Mn$_{12}$ and then Fe$_8$ [39-45]. Magnetization curves of these materials have parts with steep slope corresponding to enhanced relaxation, followed by parts with almost zero slope, where the relaxation is suppressed. The steps occur in groups and their number and field positions are temperature dependent. At lower temperatures, steps occur at higher external field values.

The steps in hysteresis were ascribed to resonant tunneling between magnetic sublevels on the opposite sides of the anisotropy barrier [44, 45]. The relaxation of the magnetization is enhanced significantly when levels are brought close to the resonance by magnetic field. At other field values, when the levels are not aligned, the relaxation is suppressed. An alternative approach has been formulated by Garg [46], who suggested that the maxima in the relaxation rate are due only to spin-phonon
interactions. The coupling of phonons to degenerate magnetic levels at the top of the barrier produces a Jahn-Teller-like distortion, which lowers the barrier height and thus increases the relaxation rate. Although ample experimental evidence in favor of resonant tunneling in SMMs has been obtained since the publication of Ref. [46], the tunneling mechanisms still lack consistent description, and spin-phonon must be considered, as they may play an important role in the tunneling process [47-49].

The temperature dependence of the steps has been explained in terms of the thermally assisted tunneling (TAT) or pure quantum tunneling (QT). As the temperature decreases, the thermal population of the excited levels is reduced, and these states contribute less and less to the tunneling, therefore larger magnetic field is necessary to bring lower lying magnetic sublevels into resonance. Consequently, the steps in hysteresis curves shift to higher bias field values, and steps with larger indices $n$ become observable. At low temperature, tunneling from the lowest level in the metastable well dominates, and the position and amplitude of the steps become independent of temperature, denoted the pure quantum tunneling regime (QT). The QT regime has been observed in Fe$_8$ [50] below approximately 0.4 K. Prior to our studies QT has never been reported in Mn$_{12}$, which was mostly studied in the range from 3 K down to 1.6 K, i.e., at temperatures much higher than that of the crossover to QT, which occurs at about 1 K.

The question of whether hysteresis in these materials may be caused by collective effects, and especially by dipolar ordering [51], can be addressed by experiments on dilute solutions of SMMs. In Ref. [52] studies of the relaxation of the
field-cooled frozen solution of Mn$_{12}$ in CH$_3$CN, CH$_2$Cl$_2$ and toluene were presented. Below 3 K, the relaxation time of the solution is comparable to that of a crystalline sample of Mn$_{12}$, i.e. is slow, characteristic to the blocked regime. Studying the relaxation as a function of applied field at $T = 2.55$ K, Caneschi et al. [53] showed that the relaxation time of a zero-field cooled solution and a non-oriented powder follow the same dependence and are non-monotonic functions of the field. In another set of experiments, magnetic circular dichroism was measured on a very dilute solution of Mn$_{12}$ [54]. The magnetization of the sample was completely reversible at 4.2 K, but became hysteretic at 1.7 K. These experiments provide evidence that in Mn$_{12}$ the slow relaxation below the blocking temperature cannot be attributed to the 3D ordering of the molecules.

Another interesting problem is associated with an unusual form of magnetic relaxation in SMMs. It has been observed that the relaxation curves $M(t)$ of Mn$_{12}$ [55] and Fe$_8$ [42] follow the stretched exponential law:

$$M(t) = M_0 \exp(-t/\tau)^\beta,$$  

(2.1)

with an exponent $\beta \sim 0.5$, and is faster than exponential in its initial stage. The relaxation in SMMs cannot be fit by either a single exponential law (which should be the case for a system with a single barrier) or logarithmic law, usual in systems with distributed parameters. Although in Mn$_{12}$ this effect may be possibly due to the presence of the fast-relaxing minor species, Fe$_8$ has a uniform composition, yet it also shows the same form of relaxation. The nature of this non-exponential relaxation is still not completely understood [56-58], as well as the tunneling mechanisms in
SMMs. Possible mechanisms may include transverse anisotropy, dipolar fields, hyperfine fields, and Dzyaloshinskii-Moria fields, however there is no definitive evidence in favor of either of these mechanisms.

The problem of what causes the tunneling in SMMs is particularly interesting because of the following feature. The measured resonance width for SMMs is on the order of $0.1 - 0.5 \text{ K}$. The tunnel splitting between $m = +10$ and $m = -10$ spin states, $\Delta_{10}$ is estimated to be less than $10^{-8} \text{ K}$ in both Mn$_{12}$ and Fe$_8$. The distribution of static hyperfine and dipolar fields tunes almost all molecules off the resonance, so that they are not able to tunnel. According to the model of Prokof'ev and Stamp [59], the initial relaxation is due to the evolution of the dipolar fields of the clusters. Tunneling is possible because of the fluctuating hyperfine and dipolar fields that broaden the resonance condition. In an ellipsoidal sample with a uniform demagnetization field, initially fully magnetized, the distribution of the dipolar fields is extremely narrow (delta-function smeared by the finite size effects). When the sample is allowed to relax, the molecules that are brought into the resonance by rapidly fluctuating hyperfine fields switch altering the distribution of the dipolar fields. This distribution quickly broadens, bringing into the resonance new molecules. The magnetization relaxation is therefore initially very fast, followed by a slower decay. For an initially saturated sample, the initial relaxation is described by the square root of time law

$$M(t) \approx 1 - \sqrt{t/\tau},$$

(2.2)
where $M(t)$ is the normalized magnetization, and $\tau$ is the relaxation time, which depends on the sample shape. This model is better suited for Fe$_8$, where the field distribution is almost entirely due to the distribution of dipolar fields. Some experimental evidence supporting this mechanism has been found in Fe$_8$ [15]. It is still unclear however, why the non-exponential dependence of $M(t)$ has been observed in relaxation from all initial magnetization states, including demagnetized ones.

The idea of the initial square root relaxation was used to probe the distribution of the dipolar fields within the crystal of Fe$_8$ [60-62]. In order to study the effects of the dipolar and hyperfine fields, a “hole digging” method was used also based on the measurements of the initial square root of time relaxation of Fe$_8$ [15, 63]. The sample is first quickly quenched from the temperature above the blocking temperature (2 K) in an external field, so that the high temperature spin distribution was “frozen in”. Then a measurement field is applied and the decay of the magnetization is recorded as a function of time. The slope of the function $M(t)$ plotted as a function of the square root of time gives the value of $\Gamma_{\text{sqr}} = 1/\tau$ in Eq. (2.2). To observe the evolution of the energy states, the sample is first field-cooled, then allowed to relax during ‘tunneling time’ $t_\tau$ at ‘tunneling field’ $H_\tau$. During this time, a small fraction of molecules in resonance tunnel and switch their magnetization, therefore modifying the original distribution. The field is then ramped to the ‘measurement field’, at which the short-time relaxation is measured. Repetition of this procedure at many measurement fields gives a dependence of $\Gamma_{\text{sqr}}(H, H_\tau, t_\tau)$ and allows one to probe the distribution of the
molecular state. This dependence shows a narrow dip, due to ‘a hole’ that has been dug in the original distribution, when the spins population was depleted due to the switching near the tunneling field. The linewidth of the hole measured in $^{57}$Fe-enriched samples of Fe$_8$ was related to the hyperfine line broadening.

Another fascinating discovery has been made in Fe$_8$, where the quantum phase oscillations were observed [50]. The tunnel splittings of Fe$_8$ show clear periodic minima as a function of the field applied along the hard direction (x-axis) and have odd/even parity for different longitudinal field resonances. At larger transverse fields, or at non-zero angles between to the field and the hard axis, the oscillations are smeared and eventually suppressed.

This phenomenon has been explained semiclassically within the Feynman path integral formalism [64-66]. According to this picture, the minima of the tunneling rate are due to destructive interference between two symmetric spin reversal paths in the plane perpendicular to the hard axis (yz-plane) shown on Fig. 2.1.
Fig. 2.1 – Schematic view of the symmetric spin tunneling paths in a biaxial spin system. The paths are in the $yz$-plane between almost degenerate minima A and B on a unit sphere. External field $H_t$ is applied in the $xy$-plane at an angle $\varphi$ with respect to the hard axis.

For integer spin $S$, there is a destructive interference between the two tunneling paths when this area is equal to $k\pi/S$ for odd $k$. For transitions in non-zero longitudinal field from $m = -S$ to $m = S - n$ with odd $n$, the interference condition is
the same as for half integer spin, i.e. there is destructive interference at even \( k \).
Therefore the tunnel splittings at non-zero longitudinal field show the parity effect. Increasing transverse field changes the area within the spin trajectory, thus changing the phase of the two paths and creating conditions for constructive and destructive interference (Berry phase). As a result, the corresponding tunneling rate also shows a non-monotonic, oscillating behavior. If the magnetic field is applied at an angle to the hard axis, the degeneracy between the two relaxation paths in the \( yz \)-plane is destroyed and the oscillations disappear.

Quantized energy structure and the possibility of controlling the splittings between the levels by external field make SMMs very appealing candidates for the observation of quantum coherence, i.e. oscillations of the probability of finding the system in either of two nearly degenerate states. Such experiments are particularly challenging because the interaction with the environment quickly destroys the phase coherence between the states. Few attempts have been made to observe the coherence in SMMs [37, 67, 68]. A technique similar to that employed in high-frequency EPR experiments was used in attempts to observe coherent oscillations in single crystals and oriented powders of Fe\(_8\) [37]. Oriented powdered samples were obtained by solidifying of the epoxy matrix containing microcrystallites of Fe\(_8\) in a high field (5.5 T, 12 h, room temperature). The sample was placed into a split-ring resonator with a high Q-factor (\( Q = 3100 \)) and resonance frequency \( f = 680\,\text{MHz} \). Constant magnetic field was applied perpendicular to the easy axis of the crystallites, and the ac magnetic field was applied parallel to it. The resonator was in contact with the mixing
chamber of a dilution refrigerator and the experiments were conducted in the millikelvin temperature range. To avoid heating of the sample, low-repetition rate \((10^{-3} - 10^{-2} \text{ Hz})\) electromagnetic pulses were used to measure the resonance line of the resonator. By measuring the line broadening and the resonance frequency shift, imaginary part \(\chi''\) and real part \(\chi'\) of the magnetic ac-susceptibility were determined. The imaginary part \(\chi''\) as a function of the transverse field showed two peaks, at \(H_1 = 2.25 \text{ T}\) and \(H_2 = 3.60 \text{ T}\). The height of the peaks did not change significantly below 200 mK, but decreased at higher temperatures. The peaks were observed at the same field positions when the dc field was applied parallel to the easy axis, although they were far less pronounced.

The appearance of the peaks was attributed to the quantum splitting \(\Delta\) of the ground state due to the transverse field. The splitting depends on both the magnitude of this field and its direction with respect to the hard axis. The peaks appear when the field is directed parallel and perpendicular to the hard axis and a resonance condition is fulfilled

\[
\Delta(\varphi = \pi / 2, H_1) = \sigma, \\
\Delta(\varphi = 0, H_2) = \sigma,
\]

(2.3)

where \(\sigma = 2\pi f\), and \(f\) is the frequency of the ac field. The positions of the two peaks in \(\chi''\) yielded the following values for the anisotropy parameters of Fe$_8$ crystal:

\(D = 0.275 \pm 0.005 \text{ K}\) and \(E = 0.092 \pm 0.005 \text{ K}\), in very good agreement with the published EPR and neutron scattering data. The splitting \(\Delta\) separates the states...
correspond to the symmetric ground state \( |G\rangle \) and the antisymmetric excited state \( |E\rangle \), which could be written as superpositions of the eigenstates \( |m\rangle \) of \( S_z \):

\[
|G\rangle = \sum_{m=-10}^{m=10} A_m |m\rangle, \quad |E\rangle = \sum_{m=-10}^{m=10} B_m |m\rangle, \tag{2.3}
\]

where \( A_m = A_{-m} \) and \( B_m = B_{-m} \). These results, however, may be also due to a regular absorption of the energy of the ac field between the lowest sublevels, similar to that observed in the EPR experiments. In order to observe coherent oscillations, the two states must be separated by a tunnel splitting \( \Delta \), and the frequency of these oscillations \( f = \Delta/(2\pi\hbar) \) should be greater than the decoherence rate due to the interactions with the environment, such as the nuclear spins or phonons. In the above experiments, it has been assumed that at millikelvin temperatures and megahertz frequencies, this condition is satisfied, although little is known about the decoherence factors in \( \text{Fe}_8 \). Also, the experiments were performed on powdered samples, where the distribution of the orientations of the magnetic axes of the crystallites leads to a distribution of the tunnel splittings. In \( \text{Mn}_{12} \) a single peak in the imaginary part of the ac-susceptibility has been observed [68], and its interpretation was debated [69, 70].

Further studies are necessary to provide persuasive evidence of the quantum coherence in SMMs.

These experiments show that SMMs open remarkable opportunities for the studies of interesting phenomena, which would be very difficult to observe in other systems. Successful experiments on SMMs require a combination of few factors: good
chemical base, allowing easy access to high quality samples, well-suited measurement technique, such as micro-SQUIDs, Hall probes, or cantilever magnetometry, cryogenic and magnetic field equipment which performs well at low temperatures and high fields.
CHAPTER 3
EXPERIMENTAL TECHNIQUE

3.1 Experimental setup

Our experiments have been performed using a micro-Hall effect magnetometer as a probe of the sample's magnetization. The schematic of the setup is shown on Figure 3.1. The main parts of the set-up are the micro-Hall device with the sample, a high field superconducting magnetic system, a low-temperature insert, measurement equipment, such as a lock-in amplifier, digital voltmeters, current source, and a computer controlling the experiment.

A micro-Hall effect device with a single crystal on it is mounted on a low-temperature insert (Heliox\textsuperscript{VL}, Oxford Instruments). The temperature of the sample is monitored by a calibrated Cernox\textsuperscript{TM} thermometer placed next to the sample. Heliox\textsuperscript{VL} is a commercial low-temperature $^3\text{He}^4\text{He}$ system with a base temperature of 0.3 K. With the heat load in our experiment we have been able to achieve temperatures as low as 0.5 K. Control units monitor and adjust the insert temperature. An important feature of our set-up is a custom made rotator added to the insert, which allows one to change the orientation of the sample with respect to the applied magnetic field \textit{in situ}, i.e., at low temperature. The ability to vary the angle between the easy axis of the crystal and the magnetic field is crucial for our studies of the effects of the transverse field.
Fig. 3.1 – Schematic of experimental setup.

Once the desired orientation is achieved, the rotator can be disengaged from the low temperature part of the system and the sample, in order to avoid thermal coupling to the upper, high temperature parts of the insert. The orientation of the Hall magnetometer with the sample on it is monitored by a second Hall bar, oriented in a plane perpendicular to that of the first magnetometer.
The insert with the sample is placed in the center of a superconducting magnet, which sits in a cryostat filled with liquid helium. A computer running LabView software controls the field strength by communicating with the magnet’s power supply and enables automatic data acquisition from the digital measurement equipment. The computer is connected with the measurement equipment (such as HP digital voltmeters) via the GPIB interface. Oxford Instruments control units are equipped with a low-noise optical RS 232 interface in order to avoid coupling the noise from the digital equipment to the measurement circuit.

A low-noise current source supplies a low-frequency (typically below 25 Hz) alternating current to the magnetometer device, whose Hall voltage signal is registered by an analog lock-in amplifier. The measurement frequency is chosen based on a spectral analysis of the voltage noise from the Hall device in such a way as to minimize the coupling with the parasitic AC signals (such as 60 Hz radiation and the like). The voltage signal is then passed to an HP digital voltmeter connected to the computer. Another current source supplies current to the calibrated resistive thermometer, whose readings are also registered by an HP voltmeter.

In the subsequent sections I will describe the basics of the micro-Hall effect magnetometry and the parameters that characterize the quality of a Hall device (Section 3.2), the fabrication process of these devices (3.3), the principles of operation of the low-temperature \(^3\text{He}^4\text{He}\) insert Heliox\(^{l}\) (3.4) and the procedures used to prepare single-crystals of Mn\(_{12}\) and Fe\(_8\) (3.5).
3.2 Principles of the Hall-effect magnetometry

Hall-effect magnetometry is a method of measuring a sample magnetization based on the Hall effect [72, 73]. A Hall effect sensor is a four-terminal solid-state electronic device, shown schematically on Figure 3.2.

![Diagram of a Hall plate]

**Fig. 3.2 – Schematic of a Hall plate.**

It is a plate of conducting material with four contacts. A current $I$ flows through the two contacts called the current contacts. The second pair of contacts, called the voltage contacts, is placed at the equipotential surfaces on the other two sides of the plate. When a magnetic field $B$ is applied perpendicularly to the plate, a Hall voltage $V_H$ appears between the voltage contacts. The Hall voltage appears due to the Lorentz force $F$ acting on the charge carriers:
\[ F = eE + ev \times B, \]

where \( e \) is the charge, \( E \) is the electric field that produces the current, and \( v \) is the velocity of the carriers. The Hall voltage is proportional to the component of the magnetic induction \( B \) perpendicular to the plate and to the current \( I \):

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

Here \( R_H \) is the Hall coefficient of the material, \( G \) is a geometrical factor of the Hall plate, and \( t \) is the plate thickness [72].

The quality of a Hall-effect device as a magnetic sensor is characterized by the following parameters: sensitivity, linearity, offset, noise and stability of the sensor's properties. These parameters are influenced by the properties of the material used for the Hall probe, such as the concentration of the carriers, their type and mobility, defects and strain in the material, as well as the size and the geometry of the device.

The absolute sensitivity \( S_\Lambda \) of a Hall-effect device is defined as a ratio of the Hall voltage to the magnetic field normal to the Hall structure [73]:

\[ S_\Lambda = \left| \frac{V_H}{B} \right|. \]

The supply-current related sensitivity \( S_I \) is defined as a ratio of the absolute sensitivity to the bias current \( I \):

\[ S_I = \frac{S_\Lambda}{I} = \left| \frac{V_H}{I B} \right|. \]

Using Eq. (3.2), we get:
\[ S_1 = \frac{R_H}{l} G. \] (3.5)

For a Hall plate with only one type of carriers

\[ S_1 = G \frac{r_H}{\text{ent}}, \] (3.6)

where \( n \) is the charge density and \( r_H \) is the Hall scattering factor, \( \mu_H = r_H \mu \) \((r_H \geq 1)\).

This expression shows that a thin film with a low concentration of carriers (for example, a low-doped semiconductor film) is a good starting material for a Hall sensor.

Another important factor that affects the sensitivity of the Hall probes, is the carrier mobility. The carrier velocity is due to the thermal motion and drift in the electric field \( E \). To a first approximation, the thermal contribution can be neglected, then for a given electric field, the drift velocity of the carriers is proportional to their drift mobility \( \mu \):

\[ v = \mu E. \] (3.7)

Consequently, for the higher mobility material and given applied electric field, the Lorentz force Hall voltage is greater and it causes a higher. The angle between the electric field and the current is given by

\[ \theta_H = \arctan(\mu_B), \] (3.8)

called the Hall angle. For a given applied longitudinal voltage, the Hall voltage is proportional to the mobility of the carriers. As an example, the mobility of the carriers in thin films of semiconductors, such as InSb, can be as high as \( 6 \cdot 10^4 \) cm\(^2\)/(Vs) at
300 K. However, one significant disadvantage of InSb is a small band gap ($E_g \approx 0.36 \text{ eV}$), which leads to a strong temperature dependence of its properties, and therefore limits the temperature range of the operation of a Hall sensor. Wide band gap materials, such as GaAs ($E_g \approx 1.43 \text{ eV}$) can be used to avoid this limitation.

A further increase of the carrier mobility can be achieved using semiconductor heterostructures with a two-dimensional layer of carriers at the interface between two materials with different band gaps, for example two-dimensional electron or hole gas (2DEG or 2DHG) at the interface of GaAs/AlGaAs heterostructure shown on Figure 3.3(a). In such a structure, 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 and form a heterostructure, their equilibrium Fermi levels must coincide and therefore their bands must bend at the interface. The band bending causes the electrons to move from the broad band gap $N$-side to the narrow 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 width of this potential well is small, so that 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 lattice scattering, which
decreases dramatically at lower temperatures. If the thickness of the $N$-type material is reduced below the depletion layer width, it will be completely depleted of its low-mobility electrons. The electric conduction parallel to the interface will be due to the high mobility electrons in 2DEG. In GaAs/AlGaAs heterostructure the low temperature mobility of electrons can reach $2 \cdot 10^6 \text{ cm}^2/(\text{Vs})$. The Hall probes used in our experiments were manufactured from a two-dimensional hole gas material with low temperature mobility of about $10^5 \text{ cm}^2/(\text{Vs})$ with a density of $3 \cdot 10^{11} \text{ cm}^{-2}$. 
Fig. 3.3 – Schematic (a) and band diagram (b) of a GaAs/AlGaAs heterostructure
A response of a Hall device with a two-dimensional gas of carriers can become strongly nonlinear at low temperatures and high magnetic fields due to the Schubnikow-de Haas oscillations and the quantum Hall effect. These oscillations of the resistivity and plateaus (or steps) in the Hall voltage of the 2D gas are due to the periodic field dependence of the Fermi level, caused by the transfer of the electrons to lower Landau levels with increasing magnetic field. To avoid the appearance of these oscillations in a Hall device at low fields, materials with two-dimensional hole gas are used, despite the fact that the mobility of the holes is usually lower than the electron mobility. In a 2DHG the spacing between the Landau levels grows slower with the field, because of the higher effective mass of the holes than the electrons:

$$\Delta E = \hbar \omega_c = \frac{e \hbar}{m^*} B,$$

(3.9)

where $\omega_c$ is the cyclotron frequency, and $m^*$ is the effective mass. Therefore the onset of Schubnikow-de Haas oscillations in a 2DHG will occur at higher fields, than in a 2DEG.

Linearity of a Hall probe is a characteristic of its response as a function of the magnetic field. A deviation of the Hall voltage from a linear dependence on the magnetic field, i.e., nonlinearity, can be defined as

$$N = \frac{V_H - V_H^*}{V_H^*},$$

(3.10)

where $V_H$ is the measured Hall voltage and $V_H^*$ is the best linear fit to the measured values [74]. Nonlinearity appears due to the dependence of the Hall coefficient $R_H$
(material nonlinearity), geometrical factor $G$ (geometrical nonlinearity), and/or thickness $t$ (junction field-effect nonlinearity) on the magnetic field. There is also nonlinearity arising from the magnetoresistance of the Hall plate material.

The material nonlinearity is caused by the field dependence of the Hall coefficient:

$$ R_H = \frac{r_H}{ne} . $$

The Hall scattering factor $r_H$ depends on the magnetic field. At strong fields, i.e., when $\mu_H B >> 1$, $r_H$ approaches unity. In the experimentally relevant limit of the weak field, $\mu_H B << 1$, $r_H$ can be expressed as

$$ r_H (B) = r_0 (1 - \alpha \mu_H^2 B^2) , $$

where $r_0 = r(B = 0)$, and $\alpha$ is a numerical coefficient, strongly depending on the scattering mechanism. Therefore the material nonlinearity has a quadratic dependence on the magnetic field

$$ NL_m = -\alpha \mu_H^2 B^2 . $$

Geometrical nonlinearity is caused by the asymmetry of the sensor geometry and appears as a magnetic field dependence of the geometrical factor $G$. This dependence has a general form [74]:

$$ G(\lambda, \theta_H) \approx 1 - g(\lambda) \frac{\theta_H}{\tan \theta_H} , $$

where $g(\lambda)$ is a function of the ratio of the total contact length to the length of the boundary $\lambda$. 

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Expanding in Eq. (3.17) the dependence on the Hall angle \( \theta_H \), we get:

\[
G(\lambda, \theta_H) = 1 - g(\lambda)(1 - \frac{1}{3} \theta_H^3) \equiv G_0 (1 + \beta \mu_H^2 B^2),
\]

where \( G_0 = (1 - g(\lambda)) \), and \( \beta = (1 - G_0)/3G_0 \). Thus we find that the geometrical nonlinearity is also proportional to the square of the magnetic field:

\[
NL = \beta \mu_H^2 B^2.
\]

Note that the material and the geometrical nonlinearities have opposite signs. It opens a possibility to compensate the material nonlinearity by choosing an appropriate geometry of the Hall probes. It has been shown that the optimum geometry for a Hall device is a cross-shaped plate. Semiconductor Hall sensors are often fabricated as mesa structures with series of crosses, lithographically defined on a thin film.

Magnetoresistance nonlinearity arises from the magnetic field dependence of the conductivity tensor of the sensor material. In an experiment involving a Hall device, the measured quantity is the resistivity, therefore it is convenient to write the relation between the electric field and the current using the resistivity tensor \( \rho \):

\[
E = \rho j = \begin{pmatrix}
\frac{1}{\sigma} & -\frac{\mu B}{\sigma} \\
\frac{\mu B}{\sigma} & \frac{1}{\sigma}
\end{pmatrix} j.
\]

If the conductivity \( \sigma \) is field dependent, the off-diagonal elements, which represent the Hall resistivity, will also show the field dependence and cause a non-linear response:

\[
E_H = \frac{\mu_H B}{\sigma_0} j + \mu_H B \frac{\sigma'}{\sigma_0^2} j,
\]

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assuming that the conductivity can be written as \( \sigma = \sigma_0 (1 - \sigma' / \sigma_0) \), where only \( \sigma' \) depends on the magnetic field. The field dependence of \( \mu_B B \sigma' / \sigma_0 \) is odd.

In order to understand the contributions from different sources to the nonlinearity of a Hall effect sensor, we can parametrize the voltage signal as follows. If the measured voltage is

\[
V = V_{\text{NL}} + V_H, \quad (3.19)
\]

where \( V_{\text{NL}} \) is a nonlinearity from all sources with a quadratic field dependence, and \( V_H \) is a Hall signal, which may include a contribution due to magnetoresistance. After subtracting the linear background, which can be determined by fitting the data in the low field interval to a linear function, the remaining signal consists of an odd part due to the magnetoresistance, and an even part, \( V_{\text{NL}} \). Measurements of \( R_{xx} \) provide information about the sources of the magnetoresistance nonlinearity.

The offset voltage of a Hall device is a quasistatic output voltage that appears in the absence of the magnetic field. The offset is caused by the imperfections of the geometry, variations in doping density, surface quality, contact resistance, and a mechanical stress in combination with the piezoresistance effect. The offset can be characterized by the offset-equivalent magnetic induction \( B_{\text{off}} \):

\[
B_{\text{off}} = \frac{V_{\text{off}}}{V} \frac{1}{S_v} \approx \frac{1}{\mu_B} \frac{V_{\text{off}}}{V}, \quad (3.20)
\]
where $V_{\text{off}}$ is the offset voltage and $(w/l)G$ is taken to be approximately equal to unity. It is clear that using high mobility materials for Hall devices is also beneficial for lowering the offset.

![Sample with Hall crosses](image)

**Fig. 3.4** – Schematic of a micro-Hall effect magnetometer

Micro-Hall effect magnetometry is used to measure the magnetization of small magnetic samples [75-84]. A sample is attached on the surface of a magnetometer, biased by a current $I$, and is placed in an external magnetic field. The magnetization of the sample creates the magnetic induction $B$ outside of the sample. At the edges of the sample, a component of this magnetic induction normal to the magnetometer plate creates a Hall voltage proportional to the sample's magnetization $M$ (see Figure 3.4). The response function (the Hall voltage as a function of the position within the device area) of a cross-shaped sensor is peaked near the center of the cross, called the active
area. Ideally the size of the active area must match the size of the sample: if the sample is much smaller than the typical size of the active area, the Hall response for such sample will vanish, since the magnetic induction contributions directed into the plate and out of the plate will cancel each other. For a very large sample, the coupling of its field is limited by the size of the active area, and the Hall response does not further increase with sample size. The optimum case is achieved when the sample is approximately of the same size as the active area. To improve the coupling with the Hall structure, the sample’s edge must be placed as close as possible to the active area. If for certain applications a higher spatial resolution is required, the geometry of the Hall sensor can be altered. It has been shown that in an asymmetric Hall probe with one narrow voltage strip, the response function is peaked more sharply than in a symmetric cross [85].

In high-sensitivity experiments it is convenient to apply the external magnetic field parallel to the plane of the Hall probe, so that only the sample field has a component normal to the sensor surface. A small part of the Hall probe response due to the inevitable misalignment of the structure with respect to the external field may be eliminated by adjusting the orientation of the structure in situ, or by subtracting a linear background from the total measured signal.
Fig. 3.5 – Schematic of a bridge circuit with the external field perpendicular to the plane of the Hall device.

If it is impossible to avoid coupling of the external field into the device structure, a gradiometer geometry can be used [86]. A gradiometer is a device with two closely spaced Hall crosses, one containing the sample and one reference cross. The difference between the sample cross signal and that of the reference cross can be measured with a bridge circuit (see Figure 3.5). When the bridge is balanced, the output voltage is proportional to the sample’s magnetic induction.
Fig. 3.6 – Photograph of Mn$_{12}$ single crystal on a Hall bar.

Figure 3.6 shows a photograph of a micro-Hall effect device with Mn$_{12}$ crystal on it. The structure is patterned as a series of 3 Hall crosses: 1 pair of current leads and 3 pairs of voltage contacts. The width of the lines on this device is 10 $\mu$m. A single crystal of Mn$_{12}$ is placed onto the surface of the device with its shorter edge close to the active area. The dimensions of the crystal are approximately $500 \times 50 \times 50 \mu$m$^3$. 

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The longest dimension of the crystal is parallel to its magnetic easy axis and is placed along the symmetry axis of the central Hall cross. This figure shows a very large crystal, used on early stages of our work, which could not be better aligned with the axis of the probe. Later we chose to use smaller crystals, approximately 200 μm long, which also allowed us to solve a problem of thermal avalanches, when heat generated during rapid magnetization relaxation caused the sample to unblock and switch by thermal activation over the anisotropy barrier (superparamagnetic regime). Another advantage of using small crystals is a weaker torque that they experience in an external field, and therefore a lower chance that the crystal falls off the Hall probe. The shortest edge of the crystal is positioned very close to the active area of the device. Current is passed through the pair current leads. An external magnetic field is applied in the plane of the Hall probe.

Figure 3.7 shows a plot of the Hall voltage of a 2DHG Hall sensor used in our experiments as a function of an external field. This plot shows that the Hall signal is linear and has small offset. This plot shows that the Hall signal is linear and has small offset. The quality of the fit is characterized by a linear correlation coefficient $R$:

$$R = \sqrt{1 - \frac{\chi^2}{\sum \sigma_i (y_i - \bar{y})^2}}.$$  \hspace{1cm} (3.21)

where $\chi^2 = \sum_i \left[ \frac{y_i - f(x_i)}{\sigma_i} \right]^2$, $\sigma_i$ is weight, $y_i$ is the actual value, and $\bar{y}$ is the mean of actual values, $f(x_i)$ is a curve fit function of calculated values $x_i$. 

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Fig. 3.7 – Hall signal of a magnetometer device measured at $T = 0.6 \, \text{K}$. 

$V_{H} = 0.443 + 18.177H_{z}$; 
(\(R=0.9998\))
-4T < H_z < 3T:

\[ V_{H}^z(H_z) = 0.701 + 1.263H_z - 0.009H_z^2 \]

\[ (R=0.999991) \]

**Fig. 3.8** – Hall signal of a Mn_{12} single crystal and a Hall effect magnetometer.

Inset shows the sample signal after subtraction of a linear background.

Figure 3.8 illustrates our data processing procedure. The Hall voltage on this plot is due to the sample (step-like structure) and a background from the Hall bar. The Hall bar background can be fit with a linear function and subtracted from the total voltage, leaving only the component of the signal due to the sample (Fig. 3.8 (inset)).
Among the advantages of micro-Hall effect magnetometers are their large temperature and magnetic field operating range, high sensitivity, linearity, ease of manufacturing and versatility of applications. For our experiments, micro-Hall devices are particularly convenient, since they can be manufactured with a variety of linewidths, matching the active area of the probe to the size of a microscopic crystal.

The parameters that we can control in our experiments are external field strength, its orientation with respect to the easy axis of the sample, field sweeping rate, and the temperature of the sample. Measuring the response of the sample for a given set of these parameters, we can characterize the magnetic behavior of our sample. Hall probes can be calibrated using a sample with well-known parameters, and the magnetization can then be measured quantitatively. It is important to stress that absolute measurements of magnetization depend on sample geometry, and thus are prone to systematic errors. However, relative magnetization can be obtained quantitatively.

For our experiments it is very important to measure and control the temperature of the sample very accurately, and to avoid self-heating of the sample when its magnetization changes rapidly in the field. A small calibrated thermometer was placed onto the magnetometer close to the sample to measure its temperature. To ensure good thermal contact between the sample and the magnetometer, the crystals of SMMs were attached to the surface of the magnetometer with vacuum grease.
3.3 Fabrication of micro-Hall effect devices

Our micro-Hall effect magnetometers were fabricated by photolithography from the two-dimensional hole gas (2DHG) heterostructure GaAs/AlGaAs. The important parameters of the materials are its low density \( n \approx 3 \cdot 10^{11} \text{ cm}^{-2} \) and high mobility of the carriers \( \mu \approx 10^3 \text{ cm}^2/(\text{V-s}) \). The Hall coefficient of such a structure can be as high as \( R_H = 2000 \, \Omega/T \).

The main steps of the fabrication process of a micro-Hall device are shown on Figure 3.9. These steps include defining the mesa structure, deposition of contacts (second exposure, metal deposition and lift-off), and thermal annealing of contacts.

In the first step a thoroughly cleaned wafer is coated with a photoresist and exposed by UV light through a contact mask with the pattern of the Hall probe. The resist is then removed from the exposed areas with developer. Next, the structure is etched in an acid mixture (or Nanostrip – a stabilized Piranha solution, a mixture of sulfuric acid \( \text{H}_2\text{SO}_4 \), hydrogen peroxide \( \text{H}_2\text{O}_2 \), and water) at a rate of approximately 20 Å/s. The etchant removes parts of the material, which are not covered with the resist, leaving a mesa structure approximately 50-60 nm high. The height of the mesa is determined by the depth of the two-dimensional gas layer in the starting material, which is usually about 40-50 nm. The remaining resist is removed with acetone after the etching process is complete.
Fig. 3.9 – Main steps of lithographic process: 1) first exposure, 2) chemical etching, 3) second exposure, 4) metal (contact) layer deposition 5) lift-off, 6) end result.
The resulting structure with a Hall cross or crosses defined on it is ready for the second step of the lithographic process necessary to fabricate metal contact pads.

The structure is then covered with a new layer of photoresist and exposed through a mask with the contact pads pattern. The device is then developed, and the photoresist is stripped from the parts where the contact pads must be located. The three layer metal contacts are then fabricated by thermal or e-beam deposition. In our case, the following combination was used: Ge (20 nm), Ni (15 nm), Au (175 nm). In the next step, lift-off is performed: the resist under the metal layer is dissolved in acetone, and the metal remains only in the contact pads openings. To ensure that the contacts are electrically connected with the two-dimensional gas of carriers, the contacts must be carefully annealed so that the metal diffuses into the semiconductor heterostructure. The Hall device must be tested at low temperature in order to determine its connectivity and noise level.
3.4 Low-temperature $^3\text{He}/^4\text{He}$ system

The principle of operation of a $^3\text{He}/^4\text{He}$ system is as follows. A closed volume with $^3\text{He}$ gas is cooled below the liquefaction temperature (1.6 K). The gas condenses, forms a liquid, which is collected in a reservoir. The vapor pressure above the liquid is reduced by pumping on the $^3\text{He}$ gas thus lowering the temperature of the reservoir far below the liquefaction temperature. $^4\text{He}$ is used to cool the volume containing the $^3\text{He}$ gas. An isolated chamber filled with $^4\text{He}$ liquid is placed in thermal contact with the $^3\text{He}$ volume. $^4\text{He}$ gas is pumped out of the chamber in the same way as $^3\text{He}$, and the temperature of this chamber drops below 1.6 K, cooling at the same time the volume occupied with $^3\text{He}$.

In a $^3\text{He}/^4\text{He}$ system the two forms of helium never come into a direct contact and circulate separately. The two major types of $^3\text{He}/^4\text{He}$ low-temperature systems are continuous mode and single-shot mode systems. In continuous mode systems, $^3\text{He}$ is being condensed continuously while being pumped on, while in the single-shot systems it is condensed once and then the collected liquid is used until all of it is pumped out, after which the condensation of $^3\text{He}$ must be done again.

In our setup we used a single-shot Heliox$^{\text{VL}}$ insert (Oxford Instruments). The advantages of this system are operation in a broad temperature range (between 0.3 and 300 K), temperature stability, long hold time at low temperatures, automatic operation capability, ease of use, and efficiency due to closed-cycle of $^3\text{He}$. 
The schematic diagram of the Heliox\textsuperscript{y}L insert is shown on Figure 3.10. The main parts of the insert are carbon sorption pump (sorb), 1 K pot, and \textsuperscript{3}He pot. The sample is mounted on a holder close to the base of \textsuperscript{3}He pot. It is enclosed by a metal cylinder, which is sealed and evacuated before the insert is placed into a main reservoir with liquid \textsuperscript{4}He. The sample sits in vacuum and never comes in contact with the cryogens. The sorb and 1 K pot are equipped with heat exchangers. The temperature control unit allows one to monitor and control the temperature of the sorb, 1 K pot and \textsuperscript{3}He pot by applying power to local heaters mounted on these parts. Auxiliary gas-handling system is used for pumping \textsuperscript{4}He gas out of the heat exchangers of the sorb and 1K pot.

The Heliox insert operates in two different regimes. In the low-temperature regime, below approximately 1.2 K, the sorb is first heated to $T = 45$ K, so that it releases \textsuperscript{3}He gas into the internal space of the insert. 1 K pot is maintained at a low temperature by pumping on its heat exchanger ($T_{1k} < 1.5$ K). \textsuperscript{3}He passes through a cold 1 K pot and condenses into a liquid, which runs down in the \textsuperscript{3}He pot. After a condensation time (approximately 25 minutes), the sorb heater is turned off and pumping on the 1 K pot is reduced to a minimum. As the sorb cools down, it reabsorbs the \textsuperscript{3}He gas. Reduced vapor pressure lowers the temperature of \textsuperscript{3}He reservoir until it reaches its minimum, called the base temperature.
Fig. 3.10 – Schematic of a $^3$He/$^4$He low-temperature system.
In our setup the sample is not mounted directly on $^3$He pot. Instead the heat is
carried away from the sample by copper wires used for electrical connection of the
sample holder. These wires are tightly wound around He$^3$ pot and are affixed to it with
low-temperature varnish for a better thermal contact. In the high-temperature mode,
the heat is applied directly to the $^3$He pot.

The base temperature and the hold time are determined by the experimental
load and condensation time. In our experiments we have been able to achieve a
minimum temperature of approximately 0.5 K and maximum hold time of up to 12
hours, which enabled the automated measurements.

3.5 Sample preparation and characterization

3.5.1 Mn$_{12}$ synthesis

Mn$_{12}$ ([Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$]-2CH$_3$COOH-4H$_2$O) single crystals were
synthesized at the Department of Chemistry, New York University, following
the procedure described by Lis [8] from commercially available ingredients.

4 g of powdered manganese acetate tetrahydrate (Mn(CH$_3$COO)$_2$ ·H$_2$O) and
40 ml of 60 % acetic acid CH$_3$COOH (24 ml of pure acid and 16 ml of water) were
gently heated until dissolution of the powder. 1 g of potassium permanganate
(KMnO$_4$) in the form of very fine powder was gradually added to this mixture with
careful stirring. We have observed that the yield of the reaction, as well as the size of
Mn_{12} crystals, increase if potassium permanganate is finely ground and completely dissolves without leaving residue.

According to the original recipe, this reaction mixture should be slowly heated to 60° C, then allowed to sit at room temperature in air for two days, after which the crystals were collected. In our case, the crystals started to form immediately after potassium permanganate was dissolved. We observed that heating to 60° C led to disappearance of Mn_{12} crystals and the formation of a thick brown precipitate. Leaving the mixture to sit for longer than 1 hour had the same effect. Therefore, after continuous stirring of the mixture for about 15 minutes, we collected the crystals by filtering the solution through a Buchner funnel. Then the crystals were washed thoroughly with acetone and THF to remove the acetic acid excess, which may cause decomposition of the material [9].

The filtered crystals are reddish-black, needle-shaped with well-defined shiny facets. The yield of the reaction varied from 50 % to 80%. We were able to obtain crystals up to 2 mm long. For our measurements, the optimal length of a crystal is approximately 200-300 μm. Crystals were stored in sealed vials in air and proved to be stable over long periods of time (few months).

Individual single crystals of Mn_{12} were characterized by X-ray microdiffraction at the X-ray laboratory of University of Delaware, by Dr. Roger Sommer. XRD verified that the chemical structure and composition of the material is identical to those described in Ref. [8, 9] and provided the following crystallographic
parameters: space group tetragonal I (4), unit cell dimensions \(a = b = 17.189 \text{ Å}, \ c = 12.307 \text{ Å}\), unit cell volume \(V = 3636 \text{ Å}^3\). These measurements were performed at the temperature of \(T = -100^\circ\), which accounts for slightly smaller unit cell dimensions and volume than those reported in [8] \((a = b = 17.319 \text{ Å}, \ c = 12.388 \text{ Å}, \ V = 3863 \text{ Å}^3)\).

3.5.2 Fe\(_8\) synthesis

Synthesis of Fe\(_8\) has been carried out in two stages. First, a precursor (tacn)FeCl\(_3\) was prepared as described in [87]: 12 ml of an ethanolic 1 M solution of 1,4,7-triazacyclononane (tacn, \(\text{C}_6\text{H}_{15}\text{N}_3\)- commercially available ligand) was added to a solution of 3.5 g FeCl\(_3\)·6H\(_2\)O in ethanol (100 ml). Due to high reactivity of the tacn ligand, this stage was carried out under the nitrogen atmosphere. The resulting yellow powder of (tacn)FeCl\(_3\) was filtered and washed with ethanol. In the second stage [10], 0.25 g (tacn)FeCl\(_3\) was dissolved in 20 ml H\(_2\)O and 2 ml pyridine at room temperature. After 15 minutes of stirring, 5 g of NaBr was added to the mixture, which was then allowed to sit at room temperature. Translucent brownish-red crystals of Fe\(_8\) formed after waiting from 2 to 5 days, depending on the temperature and flow of air above the reaction mixture.

Initially, the crystals precipitated only on the walls and on the bottom of the beaker and were very small (less than 100 \(\mu\)m). In order to increase the size of the crystals, we used a sharp glass needle with its tip submerged in the solution. Remarkably, introduction of such a crystallization center influenced the size of all the
crystals in a batch. A big crystal (up to 3 mm long, apparently with many defects) formed on the glass tip, while all the other crystals were also much bigger than without the tip and formed everywhere within the beaker, some of them floating in the solution.

Further experiments proved that the synthesis of Fe₈ is very sensitive to the conditions of crystallization and the speed of evaporation of the solvent. For example, crystals which precipitated in a shallow dish are more likely to have a flat platelet shape than those which form in a taller beaker. Thus the conditions of crystallization allow to vary the size, shape, and the preferential growth direction of the crystals.

The resulting material was characterized by single-crystal high-precision XRD at the X-ray laboratory of Hunter College, City University of New York, by Dr. Louis Todaro. These measurements were performed at room temperature. The composition of the material was found to be identical to the one reported by the original authors of the compound [10]: \(((C₆H₁₅N₃)₈Fe₈(μ₂-O)₂(μ₂-OH)₁₂)Br₇(H₂O)\)Br·8H₂O. We obtained the following lattice parameters: triclinic P1, unit cell dimensions \(a = 10.589(3)\) Å, \(b = 14.068(2)\) Å, \(c = 15.014(2)\) Å, \(α = 89.61(1)^°\), \(β = 110.02(1)^°\), \(γ = 109.20(1)^°\), unit cell volume \(V = 1970\) Å³. Our data are in a good agreement with the XRD results reported in Ref. [10]: triclinic P1, \(a = 10.522(7)\) Å, \(b = 14.05(1)\) Å, \(c = 15.00(1)\) Å, \(α = 89.90(6)^°\), \(β = 109.65(5)^°\), \(γ = 109.27(6)^°\), \(V = 1956\) Å³ at \(T = -30^°\) C.
Fe$_8$ crystals deteriorate in air and especially when heated (for example, under a microscope light) due to the loss of solvent, therefore only fresh crystals should be used for measurements.

Both Mn$_{12}$ and Fe$_8$ were examined under the optical microscope, then high-quality crystals of suitable size were selected (100-500 μm long, 50-100 μm wide), manually placed on a micro-Hall effect magnetometer chip and covered with low-temperature vacuum grease to ensure thermalization. The size of the crystals was determined with the help of a calibrated microscope equipped with a CCD camera. The alignment of the easy axis of the crystal with the symmetry axis of the Hall probe was also done using a microscope image, which resulted in an error of no more than 5°.
CHAPTER 4
EXPERIMENTAL RESULTS

In this chapter I will present the results of our studies of the magnetization reversal processes in Mn$_{12}$, and in particular, the investigations of the crossover from classical activation over the anisotropy barrier to the thermally assisted and pure quantum tunneling. These regimes of the magnetization reversal of a SMM crystal can be tuned by external parameters, such as temperature and magnetic field. We are particularly interested in the role of a transverse field, since it breaks the underlying axial symmetry and leads to terms in the Hamiltonian important to tunneling transitions.

We performed systematic hysteresis and relaxation measurements of single crystals of Mn$_{12}$ as a function of temperature, field ramp rate, magnetization state of the sample, and transverse field. The transverse field was introduced by changing the angle between the easy axis of the crystal and the external field. In the hysteresis experiments (unless stated otherwise) the sample was first saturated with an applied field in the z-direction ($M_0 = -M_s$), then the field was ramped at a constant positive rate while the magnetization was measured. All magnetization data are in units of saturation magnetization $M_s$.

In the following sections I will present the results of our measurements in the high-temperature superparamagnetic regime, in the low-temperature blocked regime with the external field parallel to the easy axis of the crystal, and with the field
applied at an angle to the easy axis. I will discuss our results in light of the recent theory of the crossover from TAT to QT discussed in Chapter 1.

4.1 Magnetization in superparamagnetic regime

Figure 4.1 shows the magnetization of Mn_{12} versus \( H_z / T \), a ratio of the longitudinal applied field and temperature, measured at \( T = 3.82 \, \text{K} \) and ramping rate of 0.2 T/min. Under these conditions the magnetization shows no hysteresis on a cycle of applied field. This is characteristic of an equilibrium magnetization curve, therefore the data can be understood using basic statistical mechanics. Magnetization of a paramagnetic system with \( 2S + 1 \) spin states is given by

\[
M / M_s = \frac{\sum m \exp(-E_m / kT)}{Z}
\]

where \( Z \) is the partition function, and \( E_m \) is the energy of the level, including the Zeeman energy. At low temperatures, when the thermal energy is small compared to the energy spacing between the lowest level in the metastable well and first excited level, i.e., \( |E_0 - E_{10}| >> kT \), we can assume that there is a significant population only in the lowest state, so that the system switches only between the two lowest states with their magnetic moments parallel and antiparallel to the \( z \)-axis. In Mn_{12} the level spacing between \( m = \pm 10 \) and \( m = \pm 9 \) states is approximately 12 K, therefore at the measurement temperature below 4 K this approximation is justified. In this case, Eq. (4.1) can be written as:
\[ \frac{M}{M_s} = \tanh(aSH_z/T), \] (4.2)

where \( a = g\mu_B/k \). Therefore, we can fit our experimental magnetization curve with a hyperbolic tangent curve and extract the value of the spin \( S \) from this fit. The value of the spin extracted from the curve fit \( S = 10.5 \pm 0.5 \), which is satisfactory taking into account the simplified picture used. The discrepancy may arise when excited levels contribute to the magnetization, besides the two lowest levels. Also, in order to obtain a reliable value of spin using this procedure, a set of systematic measurements in superparamagnetic regime is necessary. Such experiments were not our immediate goal, since the samples were characterized by other methods and our main interest was focused on the low-temperature behavior of Mn\(_{12}\).
Fig. 4.1 – Magnetization of Mn$_{12}$ single crystal as a function of applied field in superparamagnetic regime.
4.2 Hysteresis studies with the external field parallel to the easy axis ($\theta = 0'$)

4.2.1 Hysteresis $M(H)$ at different ramp rates

Below the blocking temperature, the magnetization of Mn$_{12}$ becomes hysteretic and shows evidence of quantum effects. Figure 4.2 shows a set of hysteresis curves $M(H)$ of Mn$_{12}$ measured at the same temperature, $T = 0.6$ K, and different magnetic field ramp rates, $R = 0.02$, 0.05, 0.1, 0.2, and 0.4 T/min. Each hysteresis curve shows a series of steps and plateaus separated by a field interval of approximately 0.45 T, in agreement with previously published results. The steps correspond to the enhanced magnetization relaxation due to the resonant tunneling between the magnetic sublevels on the two sides of the anisotropy barrier. The plateaus occur where the relaxation is suppressed when the levels are misaligned (Fig. 1.6). The steps occur at approximately the same field values for all ramp rates. At this low temperature only the lowest state in the metastable well $m_{\text{esc}} = 10$ is important to the magnetic relaxation, a we can identify the positions of the observed steps by the resonance field values $H(n,m_{\text{esc}} = 10)$, calculated according to Eq. (1.4), from low to high magnetic field. Four steps $n = 6, 7, 8, 9$ can be easily distinguished. The height of the steps, which occur at the same resonant field, is different for different ramp rates. Lower field steps are higher at lower ramp rates, and high field steps are larger for higher ramp rates. Compare, for example, the step at $H_z = 3.075$ T in all curves.
Hysteresis curves of Mn_{12} at different ramp rates:

\[ R = 0.02, 0.05, 0.1, 0.2, 0.4 \text{ T/min.} \]
For $R = 0.02 \ \text{T/min}$ at this step the magnetization changes by $\Delta M = 0.22M_s$, by $\Delta M = 0.13M_s$ at $R = 0.05 \ \text{T}$, and only by $0.05M_s$ at $R = 0.4 \ \text{T/min}$. The step that occurs at $H_z = 4.47 \ \text{T}$ is on the contrary higher for higher ramp rates: $0.09M_s$ at $0.02 \ \text{T/min}$, $0.20M_s$ at $0.05 \ \text{T/min}$, and $0.55M_s$ at $0.4 \ \text{T/min}$. This is a consequence of the dynamic nature of the hysteresis: the field ramp rate affects the time that the system spends in resonance when the energy levels are nearly degenerate. At higher ramp rates, the time spent in resonance is shorter, therefore the probability for the system not to switch is higher, and larger fraction of molecules remains in their former magnetization state until higher fields. At lower ramping rates, the relaxation takes place more actively at lower fields, and magnetization of most molecules has already been reversed when the field reaches high values. Note that because of this effect, the curve at $R = 0.02 \ \text{T/min}$ shows a low-field $n = 5$ step.

4.2.2 Hysteresis $M(H)$ and $dM/dH$ at different temperatures

As it was mentioned in Chapter 3, recent theoretical models suggest that different types of crossovers between thermal activation over the anisotropy barrier and quantum tunneling under the barrier are possible in the large spin limit [88]. The crossover can occur in a narrow temperature interval with the energy at which the system crosses the anisotropy barrier shifting abruptly with temperature (denoted a first-order crossover), or the crossover can occur in a broad interval of temperature
with this energy changing smoothly with temperature (second-order). In finite spin systems the crossover is always smeared, nevertheless, the two scenarios can be distinguished experimentally. In the first case, there are competing maxima in the relaxation rate versus energy and the global maximum shifts abruptly from one energy to the other as a function of temperature. In the second-order case there is a single maximum in the relaxation rate, which shifts continuously with temperature.

The "phase diagram" of the crossover for a uniaxial ferromagnetic particle, shown on Figure 4.3, depends on the form of the spin Hamiltonian, particularly the terms important for tunneling, such as terms due to a transverse field of the form $H_z S_z$. The magnitude and direction of the external field with respect to the easy axis of the particle determine the form of the crossover. For example, below the curve separating the regions where a metastable exists and where there is only a ground state (Stoner-Wohlfarth astroid) at a fixed longitudinal field and higher transverse field, the crossover must become more gradual. In our experiments, we have shown that the form of the crossover can be tuned by the magnitude and direction of the applied field. We have performed a series of hysteresis measurements for four different angles between the applied field and the easy axis of the crystal in order to probe different regions of the diagram on Fig. 4.3.
Fig. 4.3 – Phase diagram of the crossover from TAT to QT for a uniaxial ferromagnetic particle (from [88]). Dashed lines show the four angles studied in our experiments.
Fig. 4.4 – Hysteresis curves of Mn₁₂ for θ = 0° at different temperatures.

 Isothermal hysteresis curves at different temperatures between 0.67 K and 1.97 K for the field parallel to the easy axis are shown on Figure 4.4. These curves also show steps separated by regular field intervals. As the temperature decreases, the curves expand towards higher fields, lower field steps disappear and new steps
develop at higher fields. The amplitude and position of the steps are strongly temperature dependent and can be best studied using the field derivative of magnetization $dM/dH$ data, obtained from these hysteresis measurements [89, 90].

A plot of the field derivative of the magnetization $dM/dH$ versus the applied field at different temperatures for the field parallel to the easy axis is shown on Figure 4.5. At the lowest temperature $T = 0.67$ K, four steps labeled $n = 6, 7, 8$ and 9 can be seen. The position and structure of the peaks in $dM/dH$ show the magnetic fields at which there are maxima in the magnetization relaxation rate at a given temperature, applied field and magnetization. Due to the presence of the term $BS_z^4$ in the Hamiltonian Eq. (1.2), the crossings of the magnetic sublevels with the same longitudinal field index $n$ and different $m_{oc}$ occur at slightly different external field values (see Fig. 1.7). Therefore studying the positions and structure of the maxima in $dM/dH$ we can probe the energy levels that dominate the tunneling process at given conditions.

The dashed lines on Fig. 4.5 mark the positions of the observed peaks showing their shift with temperature. As mentioned before, not all peaks are present in the whole temperature range, such as $n = 5$, which disappears upon lowering the temperature, and high field peaks $n = 8$ and 9, which appear only at lower temperatures ($T = 1.44$ K and $T = 1.26$ K respectively).

The amplitude of $n = 5$ peak decreases with lowering temperature and its position shifts gradually from $H = 2.37$ T at $T = 1.68$ K to $H = 2.43$ T at $T = 1.35$ K
(by $0.14H_0$ over an interval of 0.33 K), which can be identified as the TAT regime.

The next peak, $n = 6$, also gradually shifts to higher field values from $H = 2.78$ T at 1.68 K to $H = 2.92$ T at 1.16 K (by $0.33H_0$).
Fig. 4.5 – Field derivative of magnetization \( \frac{dM}{dH} \) versus applied field

for \( \theta = 0^\circ \) at different temperatures.
The amplitude of this peak also decreases significantly, so on this plot it is barely visible at $T = 1.16\ K$. In a narrow interval of 0.09 K between $T = 1.16\ K$ and $T = 1.07\ K$, the $n = 6$ peak shifts by approximately $0.4H_0$ (0.17 T). Further we will show that this shift occurs even in a smaller temperature interval. At temperatures between $T = 1.07\ K$ to 0.67 K, this peak occurs at a constant field value $H = 3.08\ T$. We attribute this temperature independent regime to the pure QT. The three higher field peaks, $n = 7, 8$ and 9, show a similar behavior, i.e. gradual shift to higher fields followed by an abrupt shift over a narrow temperature interval of about 0.1 K. These maxima also show an interesting structure, which may provide an insight into the behavior of the levels dominating the tunneling near the crossover region.

Figure 4.6 shows a detail of $dM/dH$ plot for the hysteresis measured in narrow temperature intervals near the crossover temperature. We can examine the behavior of the maxima in $dM/dH$ in detail. This graph shows that in fact the crossover occurs in an interval of 0.05 K for the peaks $n = 7, 8$ and 9. The peaks show "fine structure", which indicates that indeed in this case there are competing maxima in relaxation rate from different magnetic sublevels.
Fig. 4.6 – Field derivative of magnetization $dM/dH$ at $\theta = 0^\circ$ in narrow temperature intervals near the crossover temperature.
4.3 Hysteresis $M(H)$ and $dM/dH$ data for the field at an angle with respect to the easy axis

We have collected similar sets of hysteresis data at four different angles between the applied magnetic field and the easy axis of the crystal, $\theta = 0^\circ, 10^\circ, 20^\circ, \text{and } 35^\circ$. Figure 4.7 shows a set of hysteresis curves for $\theta = 35^\circ$. Comparing this plot with the $\theta = 0^\circ$ data, we notice that in the presence of a larger transverse field, steps that occur at lower longitudinal field can be observed. For $\theta = 35^\circ$ we can observe the steps with indices $n = 3, 4, 5$, while for $\theta = 0^\circ$ we can see $n = 6 - 9$. This is consistent with the idea that the transverse field promotes tunneling.
Fig. 4.7 – Hysteresis curves at $\theta = 35^\circ$ at different temperatures.
The hysteresis $M(H)$ (Fig. 4.8) and $dM/dH$ data (Fig. 4.9) for $\theta = 10^\circ$ show that even a small transverse field has a considerable effect on the temperature behavior of the peaks [91]. First, for $\theta = 10^\circ$ 3 steps, $n = 5, 6$ and 7 are observed instead of four ($n = 6 - 9$) for $\theta = 0^\circ$. The three peaks observed at $\theta = 10^\circ$ do not follow all the same pattern. The lowest field peak shifts gradually from $H = 2.41$ T to $H = 2.48$ T (by $0.17H_o$) as the temperature decreases from 1.55 K to 1.23 K (TAT). As the temperature is reduced from 1.23 K to 1.15 K, this maximum is shifted abruptly to $H = 2.62$ T (i.e., by $0.34H_o$) and remains approximately at the same value upon further decrease of temperature to 0.62 K (QT). The middle peak also shifts gradually from 2.81 T to 2.94 T in the interval between 1.55 K to 1.10 K, but then it shifts abruptly between 1.10 K and 0.91 K, at lower temperature than the previous maximum. Below 0.91 K the position of this peak also remains constant. The peaks labeled $n = 5$ and $n = 6$ show an abrupt (first-order) crossover between TAT to QT, which occurs in an interval of approximately 0.1 K.

In contrast to $n = 5$ and $n = 6$ peaks, the $n = 7$ peak shifts to higher field (from 3.20 T to 3.52 T) step-wise in the whole studied temperature interval ($\sim 1$ K). We consider the crossover to QT for this peak as gradual (second-order).
Fig. 4.8 – Hysteresis curves at $\theta = 10^\circ$ at different temperatures.
Fig. 4.9 – Field derivative of magnetization at $\theta = 10^\circ$ and different temperatures.
Figure 4.9 shows a plot of the derivative of magnetization $dM/dH$ versus the longitudinal applied field at different temperatures for two orientations, 20° and 35°. To investigate the role of the transverse field in the tunneling processes, it is interesting to compare the behavior of the peak with the same longitudinal field index $n = 4$, observed at different angles [92].

Consider the data for 20°, shown in Figure 4.9(a). As the temperature decreases from 1.34 K to 1.2 K, the maximum in $dM/dH$ (at $H = 1.97$ T) shifts to higher field values. At $T = 1.24$ K, two high-field shoulders appear, which can be interpreted as the "turning on" of relaxation from energy levels closer to the bottom of the potential well.

Between 1.34 K and 1.17 K, amplitude in the lower field peaks is reduced, and at $T = 1.17$ K the three peaks are of approximately equal height. However, when the temperature decreases by 0.03 K, the maximum shifts to the peak, which occurs at $H = 2.16$ T. On lowering the temperature from 1.14 K to 0.94 K, the amplitude of the low-field peaks decreases, which means that the tunneling from excited levels is "frozen out". At $T < 1$ K only one maximum at $H = 2.16$ T survives, and its amplitude and position remain independent of temperature down to 0.6 K, which we associate with pure QT.
Fig. 4.10 – Field derivative of magnetization vs $H_z$ at different temperatures for two orientations of the applied field and magnetic easy axis: (a) $\theta = 20^\circ$ (an abrupt crossover) and (b) $\theta = 35^\circ$, showing a smooth crossover to QT.
We can compare the positions of the peaks in this picture with the values of the resonant field, calculated according to Eq. (1.4). The high temperature regime corresponds to tunneling mostly from $m_{esc} = 8$, for which $H(4,8) = 1.97$ T. The peaks appearing at higher fields are due to tunneling from $m_{esc} = 9$, $H(4,9) = 2.06$ T, and $m_{esc} = 10$, $H(4,10) = 2.17$ T. In the pure quantum regime the ground state, $m_{esc} = 10$, dominates the tunneling. The crossover from $m_{esc} = 8$ (TAT) to $m_{esc} = 10$ (QT) occurs over an interval of less than 0.05 K.

In contrast with this abrupt crossover, for $\theta = 35^\circ$ the peak with the same index $n = 4$ shifts gradually to the higher field in the range of $1.35 - 0.75$ K, as shown on Fig. 4.9(b). Below approximately $0.75$ K, the peak remains at a constant field value of $2.11$ T, which indicates the transition to the quantum regime. In this case the three escape levels, $m_{esc} = 8, 9$ and $10$ are active over comparable temperature intervals, which are marked by small steps on the dashed line.

4.4 Peak positions data

In order to obtain a picture of the crossover from TAT to QT, we have analyzed the $dM/dH$ data for four studied angles $\theta = 0^\circ, 10^\circ, 20^\circ, \text{and } 35^\circ$ and determined the positions of all observed maxima. Peak position data as a function of temperature are summarized in Figure 4.11, which shows the values of the
longitudinal field, at which the maxima in $dM/dH$ occur, versus temperature for the four studied angles [91].

![Graph showing peak positions vs temperature for different angles]

**Fig. 4.11** – Peak positions (in the units of $B_0 = 0.42$ T) vs temperature for

$\theta = 0^\circ$ (squares), $\theta = 10^\circ$ (triangles down), $\theta = 20^\circ$ (triangles up), and $\theta = 35^\circ$ (circles). The bars on the left-hand side of the graph show the escape levels calculated using Eq. (1.4).
Fig. 4.12 – Hysteresis curves measured at $\theta = 35^\circ$ for three different initial magnetization states: $M_0 = 0, 0.54M_z, -M_z$. The inset shows the change in the $n = 3$ peak position versus magnetization at the step. Circles show data points from hysteresis measurements, and squares are from field sweeps across the peak.
The determination of the peak positions must take into account the internal magnetic fields in the crystal [92]. These depend on both the magnetization and the crystal shape (via the demagnetization factors). We have used the correction coefficient $\alpha$ to determine the shift due to the magnetization of the sample. Figure 4.12 illustrates the procedure that we used to determine this coefficient. The sample was prepared in three different initial magnetization states: $M_0 = 0, 0.54M_z, -M_z$, by field cooling, then the field was ramped at a constant rate (0.2 T/min) towards positive saturation. The inset of Figure 4.12 shows the field position of the $n = 3$ step versus sample magnetization at this step. The displayed data were obtained from hysteresis measurements as shown on Figure 4.12 and from measurements in which the field was swept back and forth across the step, with the sample magnetization varying on each crossing. The peak positions are seen to depend slightly on the sample magnetization due to the average internal dipolar fields. Assuming that the peak positions are a linear function of magnetization, $H_z = B_z - 4\pi\alpha M_z$, an average coefficient $\alpha$, determined from different peaks, is approximately 0.51. The maximum correction is $\Delta B_z = 8\pi\alpha M_z = 0.064$ T and is relatively small on the scale of the plot in Figure 4.11.

The bars on the left hand side of Figure 4.11 show the escape levels calculated by using Eq. (1.4), with parameters from spectroscopic data [14, 34]. Analyzing the Figure 4.11, we can make following observations. First, for larger angles, and therefore higher transverse field, peaks with lower indices (i.e. lower $H_2$) can be
observed in the experimental time window. The lowest step observed for $\theta = 0^\circ$ and $10^\circ$ is $n = 5$, for $\theta = 20^\circ$ it is $n = 4$, for $\theta = 35^\circ$ it is $n = 3$. This is consistent with the idea that the transverse field promotes tunneling and lowers the effective anisotropy barrier. We find that there is greater amplitude in lower lying peaks as the transverse field is increased. Second, two regimes can be distinguished: the high temperature regime, where the peaks gradually shift to higher fields with decreasing temperature, and the low temperature regime, where the peak positions are constant. We associate the first regime with the TAT and the second with pure QT. Third, the form of the crossover between these two regimes depends on the longitudinal field. For each sample orientation, peaks with lower indices (smaller $H_z$) show a more abrupt crossover between TAT and QT than peaks with higher indices (compare peaks $n = 6$ and $n = 7$ for $\theta = 0^\circ$ and $10^\circ$, or $n = 4$ and $5$ for $\theta = 20^\circ$, or $n = 3$ and $4$ for $\theta = 35^\circ$).

The positions of the maxima can be also represented a color scale plot of the $dM/dH$ for $\theta = 0^\circ$ on Figure 4.12 (without the internal field correction). The data on this plot was interpolated on a regular array of field/temperature points, which eliminates the error associated with determination of the maxima in $dM/dH$ manually. This plot also shows the presence of the minor species of Mn$_{12}$ ($B_z < 1.5$ T). In fact, the minor species exhibits the same type of behavior as the major species.
Fig. 4.13 – Color scale plot of normalized $dM/dH$ for $\theta = 0^\circ$. Color intensity corresponds to the amplitude of $dM/dH$. 
4.5 Minor loop experiments

It is important to note that in our hysteresis experiments, in which the field is increasing, relaxation will first occur from thermally excited states because these come into resonance first (Eq. (1.4)). Therefore our data on Figures 4.12 and 4.13 somewhat underestimate the crossover temperature [91].

To show this we have performed a series of minor loop hysteresis experiments near the crossover temperature. In these experiments the field was swept at a constant rate back and forth across an interval, where a peak in $dM/dH$ was observed. If the field is ramped towards positive saturation, relaxation from the excited levels is emphasized, if the direction of the sweep is towards lower magnetization, the ground state tunneling is favored.

The results of these experiments in which the field was swept across the $n = 6$ peak five times at $\theta = 10^\circ$ are shown in Figure 4.14. Figure 4.14(a) shows a typical hysteresis curve at $T = 1.01$ K. Figures 4.14(b-d) show plots of $dM/dH$ at three different temperatures. For $T = 1.01$ K (Fig. 4.14(b)) the maximum in $dM/dH$ for all sweeps occurs at 3.06 T, which corresponds to QT from $m_{esc} = 10$. At a higher temperature, $T = 1.12$ K (Fig. 4.14(c)) the maximum of the first sweep is at a lower field, $H = 2.93$ T, which can be identified as a thermal channel $m_{esc} = 9$. For the sweeps 2 - 5 the maximum occurs at the QT position (3.06 T), which suggests that at this temperature QT still dominates. At higher temperature (1.23 K, Fig. 4.14(d))
almost all relaxation occurs via a thermal channel at $H = 2.87 \ \text{T} \ (m_{\text{exc}} = 8)$, which shows that the crossover to TAT has already taken place.

These results show that regular hysteresis experiments emphasize the tunneling from the excited states, and therefore, that the crossover temperature determined from such experiments is underestimated.
Fig. 4.14 – Minor loop hysteresis experiments for $n = 6, \theta = 10^\circ$: (a) typical hysteresis curve for $T = 1.01$ K; (b) - (d) – normalized $d(M / M_s) / dH$ at $T = 1.01, 1.12$, and 1.23 K respectively.
4.6 Relaxation experiments

The crossover from TAT to QT is also evident in magnetization relaxation measurements [92]. In these experiments the sample was first saturated \( M = -M_r \), then the field was ramped (at 0.2 T/min) to a certain value and held constant for 1 hour, during which the magnetization was measured as a function of time. Figure 4.15 shows two sets of relaxation curves measured at \( \theta = 0^\circ \) (Fig. 4.15(a)) and \( \theta = 35^\circ \) (Fig. 4.15(b)) at the fields where peaks \( n = 6 \) and \( n = 4 \), respectively, occur at the lowest temperature. For \( n = 6, \theta = 0^\circ \) below approximately 1.1 K, the relaxation curves are spaced very closely, i.e., the relaxation rate almost does not change, while at higher temperature it changes significantly. This temperature corresponds to the crossover temperature seen in Fig. 4.11 – consistent with pure QT. In contrast, for the peak \( n = 4, \theta = 35^\circ \), the relaxation rate changes significantly as the temperature decreases in the entire studied range. Relaxation curves can be fit by a stretched exponential function \( m(t) = m_0 \exp(-t/\tau)\beta \), where \( \beta \approx 0.4 - 0.6 \). Five overlapping curves in Fig. 4.15(a) measured below 0.74 K (0.56, 0.58, 0.63, 0.68 and 0.74 K) can be fit with the stretched exponential function with the following parameters: \( m_0 = 0.94 \pm 0.01 \), \( \tau = (5.45 \pm 0.15) \times 10^4 \) s, \( \beta = 0.48 \pm 0.02 \). This form of relaxation has been observed previously in Fe$_8$ [42] and in Mn$_{12}$ [55], although it is not completely understood [56-58].
Fig. 4.15 – Relaxation of the reduced magnetization

\[ m(t) = \frac{[M_z - M(t)]}{2M_z} \text{ vs time at different temperatures for} \]

(a) \( n = 6, \theta = 0^\circ \) and (b) \( n = 4, \theta = 35^\circ \).
Figure 4.16 shows the parameters of the stretched exponential fits, time constant $\tau$ and exponent $\beta$ as functions of temperature, for the data shown on Figure 4.15(a). The time constant $\tau$ changes little below approximately 0.8 K, which is in agreement with the other crossover data. Exponent $\beta$ varies in the range between 0.52 and 0.67, which suggests a square root of time dependence of the initial relaxation.

**Fig. 4.16** – Stretched exponential fit parameters, exponent $\beta$ and time constant $\tau$ for the relaxation data on Fig. 4.15.
5.1 Description of the model

In order to understand the picture of tunneling in the studied spin \( S = 10 \) system, we have performed numerical simulations of the model Hamiltonian of \( \text{Mn}_{12} \) as a function of various parameters, such as the magnitude and direction of the applied field and transverse anisotropy. For these calculations we used a model Hamiltonian [93] in the form

\[
\mathcal{H} = -D S_z^2 - B S_z^2 + C(S_+^4 + S_-^4) - g \mu_B S_z H_z - g \mu_B S_z H_1 \cos \varphi - g \mu_B S_y H_1 \sin \varphi.
\] (5.1)

Here \( H_z \) is the longitudinal field, parallel to the easy axis of the crystal, and \( H_1 \) is the field in the plane perpendicular to the easy axis (transverse field), making an angle \( \varphi \) with the \( x \)-axis (see Fig. 5.1). In most cases we neglected the second order uniaxial term \( BS_z^4 \) and assumed that the \( g \)-factor is anisotropic. The system has a four-fold symmetry with its axis along the \( z \)-direction. In this case, the \( x \)- and \( y \)-axes are considered hard axes, and the lines at \( 45^\circ \) degrees to \( x \)- or \( y \)-axis are medium axes.
Fig. 5.1 – System with a four-fold symmetry axis along z direction (easy axis).

The longitudinal field $H_z$ is applied along the $z$-axis, and the transverse field $H_t$ makes an angle $\phi$ with the $x$-axis.

It is convenient to rewrite the Hamiltonian (5.1) in terms of the dimensionless variables:

$$H_r = -\frac{S_z^2}{S^2} + c(S_+^4 + S_-^4) - 2h_z \frac{S_z}{S} - 2h_t \frac{S_x}{S} \cos \phi - 2h_t \frac{S_y}{S} \sin \phi,$$

(5.2)

where $h_z = \frac{H_z}{H_a}$, $h_t = \frac{H_t}{H_a}$ are the longitudinal and transverse fields related to the anisotropy field $H_a = \frac{2DS}{g\mu_a}$, and $c = \frac{C}{DS^2}$. The longitudinal resonance fields, at which the magnetic sublevels cross (in the absence of the $B$-term), can be written as
\[ h_n = \frac{n}{2S}, \text{ where } n \text{ is the resonance index. In our calculations we assumed that the} \]

longitudinal and transverse fields are static, whereas in our experiment both fields

were swept simultaneously. The tunneling in our model is due to the presence of the

transverse field and/or transverse anisotropy.

Transverse Zeeman terms give contributions which can be expressed via raising and lowering spin operators:

\[ -\frac{2h_0}{S} (S_z \cos \varphi + S_y \sin \varphi) = -\frac{h_0}{S} ((\cos \varphi - i \sin \varphi)S_+ + (\cos \varphi + i \sin \varphi)S_-). \]

(5.3)

Operators \( S_\pm \) acting on the eigenstates \(| m \rangle\) of \( S_z \) operator give the well-known result:

\[ S_z | m \rangle = \nu_{m \pm} | m \pm 1 \rangle, \]

\[ \nu_{m \pm} = \sqrt{S(S+1) - m(m \pm 1)} \] (5.4)

Terms proportional to \( S_z^4 \) are equivalent to the action of the raising and lowering

operators repeated four times, so that

\[ S_z^4 | m \rangle = \lambda_{m \pm} | m \pm 4 \rangle, \] (5.5)

where the coefficients \( \lambda_{m \pm} \) are

\[ \lambda_{m \pm} = \sqrt{(Z-m(m \pm 1))(Z-(m \pm 1)(m \pm 2))(Z-(m \pm 2)(m \pm 3))(Z-(m \pm 3)(m \pm 4))} \] (5.6)

with \( Z = S(S+1) \). The matrix elements at positions \((i, j)\), where \( i \) is the row number

and \( j \) is the column number, are determined as follows:
\[ \langle j | \mathcal{H} | i \rangle = \]

\[
\begin{cases}
\alpha_m = -\frac{m^2}{S^2} - \frac{2\hbar m}{S}, m \equiv i = j \\
\beta_m = -\frac{\hbar}{S} (\cos \varphi - i \sin \varphi) \nu_{m^+}, m = i \text{ and } j = i + 1 \\
\beta_m^* = -\frac{\hbar}{S} (\cos \varphi + i \sin \varphi) \nu_{m^+}, m = j \text{ and } j = i - 1 \\
\gamma_m = \gamma_m^* = c \lambda_{m^+}, m = j \text{ and } j = i - 4; m = i \text{ and } j = i + 4 \\
0, \text{ in all other cases.}
\end{cases}
\]

(5.7)

This Hamiltonian constructed according to Eq. (5.2) and taking into account Eqs. (5.3)-(5.6), is therefore a 21 × 21 Hermitian matrix with the following structure:

\[
\mathcal{H}_r = \begin{pmatrix}
\alpha_{-10} & \beta_{-10} & 0 & 0 & \gamma_{-10} & 0 \\
\beta_{-10}^* & \alpha_{-9} & \beta_{-9} & 0 & 0 & \gamma_{-9} \\
0 & \beta_{-8}^* & \alpha_{-8} & \beta_{-8} & 0 & 0 & \gamma_{-8} \\
0 & 0 & \ldots & \ldots & \ldots & \ldots & \ldots \\
\gamma_{-10} & \ldots & \ldots & \ldots & \gamma_{10} & \ldots & \ldots \\
\ldots & \ldots & \ldots & \ldots & 0 & 0 & \gamma_8 \\
\gamma_8 & 0 & 0 & \beta_8^* & \alpha_8 & \beta_8 & 0 \\
\gamma_9 & 0 & 0 & \beta_9^* & \alpha_9 & \beta_9 & 0 \\
0 & \gamma_{10} & 0 & 0 & \beta_{10}^* & \alpha_{10} & \end{pmatrix}
\]

(5.8)
Numerical diagonalization of the Hamiltonian was performed using Mathematica program, and its eigenvalues were determined with high precision (160 digits after the decimal point). This was necessary to resolve the tunnel splittings of low lying magnetic sublevels. The tunnel splittings were calculated as the energy difference between the magnetic sublevels due to the presence of the off-diagonal elements in the Hamiltonian. We have calculated the tunnel splittings as a function of transverse field for different values of the transverse anisotropy, and the angle between the transverse field and the x-axis. We have also determined the dominant escape magnetic sublevels as a function of temperature for experimentally relevant situation. Finally, we have determined how a transverse anisotropy in combination with the transverse field affects the crossover from thermally assisted to quantum escape.

5.2 Calculations of tunnel splittings

Figure 5.2 shows the tunnel splittings between the magnetic sublevels ±m as a function of the normalized transverse field \( h_t \) applied along the x-direction. The splittings were calculated for zero longitudinal field (\( n = 0 \)) and the following Hamiltonian parameters: \( D = 0.556 \text{ K}, \ B = 1.1 \cdot 10^{-3} \text{ K} \) (here the fourth order term was included), \( C = 3 \cdot 10^{-5} \text{ K} \) [14]. The splittings are labeled \( \Delta_t - \Delta_g \), starting from the splitting between the two lowest lying levels, \( \Delta_t = |E_{-t0} - E_{t0}| \). The splittings increase towards the top of the barrier. Below \( h_t < 0.5 \) the tunnel splittings show almost periodic oscillations, which disappear at large transverse field.
Fig. 5.2 – Tunnel splittings versus transverse field for zero longitudinal field

($H_z = 0$, i.e. $n = 0$) and transverse field along the $x$-direction ($\varphi = 0$).

The splittings have alternating parity: the first one is even and ($\Delta_1(h_t = 0) \neq 0$), the second is odd and vanishes at zero transverse field, the third one is even, etc. This parity can be understood as resulting from a selection rule: The fourth order transverse anisotropy term has non-zero matrix elements $\langle m|CS^4|m'\rangle$ between states with $|m - m'| = 4k$, where $k$ is an integer, and therefore the splittings $\Delta_i$ with odd $i$ are non-vanishing at zero transverse field. This behavior was observed experimentally in Fe$_8$ and explained in terms of the Feynmann path integrals (see Chapter 2) [50, 94]. In
Mn$_{12}$ it was predicted theoretically [95], and our results are in agreement with these published data. Initial results showing oscillations of tunnel splittings have been obtained using manganese compounds with lower symmetry [96]. The oscillations of the tunnel splitting appear due to the constructive and destructive interference of the symmetric tunneling paths in the medium planes. Two semiclassical spin reversal paths of opposite winding lie in the medium planes due to the tetragonal symmetry of Mn$_{12}$, avoiding pointing along the hard magnetic axis. In Fe$_8$ oscillations occur only when the transverse field is along the hard axis ($\alpha$). The oscillations are present when the transverse field is aligned with either $x$- or $y$-axis. At non-zero angles between the transverse field and the hard axis, the oscillations disappear because the field breaks the symmetry between the spin reversal paths and makes one of them preferential. It will be shown later that the tunnel splittings are symmetric with respect to the medium planes. In Mn$_{12}$ the oscillations are not perfectly regular: their period decreases towards higher $h_t$. For the first tunnel splitting the distance between the first and second minima is $\Delta H_1 = 0.981$ T, between the second and third $\Delta H_2 = 0.956$ T, third and fourth $\Delta H_3 = 0.939$ T, and between the fourth and fifth $\Delta H_4 = 0.913$ T, with an average of $\Delta H = 0.947$ T. This period also decreases towards the top of the barrier. For example, for the third tunnel splitting the average period is only 0.812 T. The decrease of the period is due to the presence of the term $BS_z^4$. In the absence of this term, the period increases slightly towards higher transverse field. After a certain
critical field, which decreases towards the top of the barrier, the oscillations disappear and increase monotonically.

The oscillations are washed out and disappear when the transverse field is applied at an angle with respect to the x-axis. Figure 5.3 shows the splitting between the two lowest levels $\Delta_i$ as a function of the transverse field for different angles $\varphi$ between the transverse field and the x-direction, $\varphi = 0, \pi/100, \pi/20, \pi/8, \pi/6, \text{and } \pi/4$. At the smallest non-zero angle, $\varphi = \pi/100$, the oscillations are still distinguishable, but the minima are less pronounced than for $\varphi = 0$. At higher angles, the oscillations are suppressed and the tunnel splitting increases monotonically with the transverse field, as the applied field renders one of the tunneling paths preferential. The tunnel splitting is the largest at $\varphi = \pi/4$, for angles $\pi/4 < \varphi < \pi/2$ the data are identical to those obtained below $\pi/2$ due to the four-fold symmetry of the system. The symmetry of the tunnel splittings can be conveniently visualized on a polar plot shown on Figure 5.4. The first tunnel splitting was calculated as a function of angle $\varphi$ for 5 values of the transverse field, 0.1 to 0.5. The splitting has a distinctive four-lobe shape, reaching maxima at $\pi/4$ for every transverse field.
Fig. 5.3 – First tunnel splitting as a function of transverse field for zero longitudinal field ($n = 0$) at different angles.
Fig. 5.4 – Polar plot of the first tunnel splitting for zero longitudinal field 

\((n = 0)\) at five different values of the transverse field.
Fig. 5.5 – First tunnel splitting versus the transverse field applied along the \( x \)-direction at different values of the transverse anisotropy parameter \( C \) (at zero longitudinal field).
Figure 5.5 shows a graph of the first tunnel splitting at different values of the transverse anisotropy parameter $C$, from $10^{-7}$ to $5 \cdot 10^{-4}$ K. The behavior of the splittings at $C = 10^{-7}$ K and $10^{-6}$ K is very similar to that at $C = 0$. The splittings increase monotonically and show no oscillations (with the precision used). It means that when $C \leq 10^{-6}$ K, the transverse anisotropy does not play a significant role, and the splitting is the result of action of the transverse field. For higher transverse anisotropy parameters, the splittings are larger for higher values of $C$ and show the oscillations described above. The period of the oscillations also increases with increasing $C$ (compare the average period of $0.694$ T at $C = 10^{-6}$ K and $2.278$ T at $C = 5 \cdot 10^{-4}$ K), however the number of observed periods is unaffected by the $C$ value, but depends on the values of $D$ and $S$. 
Fig. 5.6 – First tunnel splitting versus the transverse field at different parameters of the transverse anisotropy $C$ at $n = 0, \varphi = \pi/8$.

Even when the oscillations are suppressed (Figure 5.6), the influence of the transverse anisotropy can be still seen in the behavior of the tunnel splitting. The first three curves are identical to that with $C = 0$ K, as in the previous case. For higher values of $C$, the splitting shows initially a plateau, where the splitting is changing insignificantly, followed by a monotonic increase. Again, splittings at higher $C$ parameters are found to be higher.
Fig. 5.7 – The field $h_c$, which marks the change in the behavior of the tunnel splittings versus $C^{1/4}$ ($n = 0, \varphi = \pi / 8$).

The field at which the behavior of the tunnel splitting changes from a plateau to a monotonic increase is plotted on Fig. 5.7 versus $C^{1/4}$. This scaling can be expected from the form of the matrix elements due to the transverse field and transverse anisotropy.
The transverse field terms in the Hamiltonian give rise to the tunnel splittings

\[ \Delta_h \sim \langle m|H_z S_x|m'\rangle \sim h_t^{m-m'}, \]  

(5.9)

and the fourth order transverse anisotropy produces the splittings of the form

\[ \Delta_C \sim \langle m|C S_x^4|m'\rangle \sim C^{m-m'}. \]  

(5.10)

These two contributions become comparable when

\[ h_t \sim C^{1/4}, \]  

(5.11)

therefore causing the scaling law for \( h_c \).
5.3 Calculations of the escape levels

We have also performed calculations of the escape levels that dominate the tunneling at a given set of parameters: fields $h_i$ and $h_z$, and temperature $T$. The relaxation rate can be written as a product of the tunneling rate between the pair of levels $i$ and $j$ split by the energy $\Delta_{ij}$, and the Boltzmann factor $\Gamma_{ij} \sim \Delta_{ij}^2 \exp(-E_{ij}/T)$, where $E_{ij} = (|E_i + E_j|/2) - E_0$ is the average energy of levels $i$ and $j$ above the lowest lying state in the metastable well $E_0$. The energy level $m_{\text{esc}}$, which dominates tunneling, is determined as the level for which the relaxation rate $\Gamma$ has a maximum at a given temperature, longitudinal and transverse field. The tunnel splittings were obtained as described above. A slightly higher value of $D = 0.66$ K was used so that the low-lying energy level spacing and overall barrier height was better approximated. Figure 5.7 shows the experimental positions of the $n = 4$ peak at two different angles, $\theta = 20^\circ$ and $\theta = 35^\circ$ compared with the calculated $m_{\text{esc}}$. First consider the $\theta = 20^\circ$ data (Fig. 5.7(a)). A few major discrepancies between the calculated and experimental results can be noticed. The experimental crossover temperature is higher than the calculated one ($T_{\exp} = 1.25$ K versus $T_{th} = 0.7$ K). Also, the experimental temperature interval in which the crossover occurs is larger than predicted by the model. Experimental escape levels involved in the crossover ($m_{\text{esc}} = 7 - 10$) are lying lower in the potential well than the calculated ones.
The observed escape levels change more gradually than predicted by the model: our observations show that none of the levels \( m_{esc} = 7 - 9 \) are skipped in the crossover, whereas the calculations show that as many as three levels \( (m_{esc} = 7, 8, 9) \) do not contribute significantly to the relaxation. Based on this comparison, we conclude that there are additional mechanisms, such as the transverse anisotropy, that enhance the tunneling rate of the low-lying levels.

For \( \theta = 35^\circ \) (Fig. 5.7(b)) the crossover is more gradual than for \( \theta = 20^\circ \), in qualitative agreement with the theoretical model. As in the \( \theta = 20^\circ \) case, experimental data show that lower-lying levels (8 and 9) are active over larger intervals of temperature than predicted by the model. The overall better agreement with the calculated data in this case suggests that a large enough applied transverse field can become a dominant factor in determining the tunnel splittings.

The presence of the transverse anisotropy has a significant effect on the escape levels and the crossover temperature. The crossover is computed for a small transverse anisotropy \( C = 10^{-5} \) K and the transverse field at an angle of \( \varphi = \pi / 8 \) to the \( x \)-axis. At this angle the oscillations of the tunnel splitting are suppressed and the splittings should increase monotonically with transverse field. In Fig. 5.9 this transverse anisotropy is seen to increase the crossover temperature. For larger transverse field the crossover temperature is again increased, although the increase is not as significant. The fourth-order anisotropy term should also lead to the selection rules \( \Delta m = \pm 4 \), which have not been observed in \( Mn_{12} \). It suggests the presence of other tunneling
mechanisms. Small transverse anisotropy terms may, however, play an important role in the tunneling processes. The influence of this term is most significant for the levels lying close to the top of the anisotropy barrier, and the tunneling from these escape levels is enhanced. Other mechanisms leading to the same effects, cannot be excluded, for example, the influence of the defects in the crystal, recently suggested as a major cause of tunneling in SMMs. In the next section some initial data testing the predictions of this theory will be discussed.
Fig. 5.8 – Experimental escape levels $m_{esc}$ as a function of temperature for $n = 4$ at two orientations (a) $\theta = 20^\circ$ (triangles) and (b) $\theta = 35^\circ$. Solid lines show $m_{esc}$ using Hamiltonian in Eq. (5.1) with $D = 0.66 \text{ K}$, $B = 0 \text{ K}$, $C = 0 \text{ K}$. 
Fig. 5.9 – Calculated escape levels for non-zero transverse anisotropy parameter \((C = 10^{-5} \text{ K, } \phi = \pi / 8)\).
5.4 Scaling analysis probing the distribution of tunnel splittings

A new model of tunneling in SMMs has been recently proposed by Chudnovsky and Garanin [97, 98], who consider the effect of the dislocations on tunneling. Dislocations cause a local tilting of the easy magnetic axis near the dislocation core, which produces additional symmetry-breaking terms in the Hamiltonian. These terms have the form of a second-order transverse anisotropy and a transverse field:

$$\mathcal{H}' = E(S_x^2 - S_y^2) - g\mu_B H_x S_x,$$

where $E$ and $H_x$ are functions of coordinate within a crystal. The dislocations have a dramatic effect on the tunnel splittings. In particular, due to the long range deformations, they lead to a distribution of $E$ values, and consequently, to a distribution of the tunnel splittings over many orders of magnitude. It has been suggested that this distribution, and therefore, a fraction of molecules that remain in the metastable well after a resonance crossing, obeys a scaling law. A scaling analysis of experimental data, obtained for Mn$_{12}$, supporting the predictions of this theory, has been reported [99].

We performed a similar analysis of our hysteresis data at different field ramp rates. Figure 5.10 shows the fraction of the molecules $R_n$, that remain in the metastable well after the $n$-th resonance as a function of logarithm of $(dH_x/dt)^{-1}$ for $n = 6-9$, extracted from the hysteresis data taken at different ramp rates on Fig. 4.2.
Fig. 5.10 – Fraction of molecules which remain in the metastable well after
the \( n \)-th resonance crossing versus the logarithm of \( (dH_z / dt)^{-1} \) for the data
on Fig. 4.2 at different ramp rates, 0.02, 0.05, 0.1, 0.2, 0.4 T/min.

The probability for a molecule after \( n \)-th resonance to remain in the metastable
well is given by the Landau-Zener formula

\[
P_n = \exp(-\pi \Delta_n^2 / 2\nu_n),
\]  

(5.13)

where

\[
\nu_n = \frac{g_z \mu_B \hbar}{k^2} (2S - n) \frac{dH_z}{dt}
\]  

(5.14)
is the energy sweep rate (see also Ref. [100]). For a distribution of tunnel splittings for different molecules, the overall probability is an average of (5.13) over all molecules:

\[ \langle P_{n,i} \rangle = \frac{1}{N} \sum_i \exp(-\pi \Delta^2_{n,i} / 2\nu_n) \]  

(5.15)

If the distribution is very broad, as suggested in [97, 98], on a logarithmic scale, the exponential in this probability can be approximated by a step function:

\[ \exp(-\pi \Delta^2_{n,i} / 2\nu_n) \approx \Theta(1 - \pi \Delta^2_{n,i} / 2\nu_n) \]  

(5.16)

It means that only those molecules would be able to tunnel at a given field ramp rate, for which

\[ \pi \Delta^2_{n,i} < 2\nu_n \]  

(5.17)

and the probability to remain in the metastable well can be written as

\[ R_n = \langle P_{n,i} \rangle = \frac{1}{N} \sum_i \Theta(1 - \pi \Delta^2_{n,i} / 2\nu_n) \]  

(5.18)

The tunnel splittings of a molecule due to the second-order transverse anisotropy is given by

\[ \Delta_{n,i} = \eta_n g_n \left( \frac{|E_i|}{2D} \right)^{\xi_n} \]  

(5.19)

where

\[ g_n = \frac{2D}{[(2S-n-2)!!]^{2}} \sqrt{\frac{(2S-n)!(2S)!}{n!}} \]  

(5.20)

For resonances with even \( n \), \( \xi_n = \frac{S-n}{2}, \eta_n = 1 \), the main contribution is due to the transitions with \( \Delta m = \pm 2 \). Odd numbered resonances can be caused by the presence of
the internal transverse fields, caused by the local tilting of the easy axis relative to the applied field, and the main contribution will be due to the virtual transitions with \( \Delta m = \pm 2 \) due to the transverse anisotropy and one transition with \( \Delta m = \pm 1 \) due to the transverse field. For the odd-numbered resonances, \( \xi_s = S - (n - 1)/2 \), \( \eta_s = An/2 \), where \( A \) is an adjustable parameter of the order of unity. Using Eq. (5.19), the threshold condition \( \pi \Delta^2 \xi_s = 2 \nu_n \) can be written as

\[
X = -\ln\left( \frac{|E_0|}{2D} \right) = -\frac{1}{\xi_s} \ln \left[ \frac{1}{\eta_s g_n} \sqrt{\frac{2 \nu_n}{\pi}} \right] \tag{5.21}
\]

and is independent of \( n \). Therefore, if we plot \( R_n \) as a function of this variable \( X \), they should collapse onto a single curve. According to Ref. [99] the \( R_n \) data collapsed onto a curve, which can fit by an error function. A good quality fit was obtained for the adjustable parameter \( A = 1 \). Our data for \( R_n \) on Fig. 5.10 were processed according to the same method and the results are shown on Fig. 5.11 (a) and (b). A significant difference between the data for even- and odd-numbered resonances is noticeable on Fig. 5.11(a), where the parameter \( A \) is taken to be equal to unity. We obtained a satisfactory fit \( (R = 0.997) \) with an error function only with \( A = 1.04 \) (Fig. 5.11(b)).

The scaling shows that a more accurate procedure is necessary to describe the odd-numbered resonances. The above analysis cannot be considered a definitive test of the model. A distribution of the tunnel splittings stretching over 30 orders of magnitude [97] is likely to suppress the quantum effects in Mn_{12} and make their experimental observation impossible, which is not the case. The probability of switching, approximated by a step function (Eq. (5.16)), indicates that there is a sharp boundary
between the molecules with a non-zero probability to tunnel in given conditions. After sweeping the field through the \( n \)-th resonance in a typical hysteresis experiment, these molecules would switch and tunneling at this resonance would cease. In our minor loop experiments we have shown that the tunneling from different relaxation channels is possible on field sweeps through a resonance in both directions. The relation between the actual energy sweep rate and the applied field sweep rate, which is essential for the model described above, may actually be much more complicated than that described by Eq. (5.14). The presence and role of the defects in the crystals of SMMs have not been studied, and the typical concentration of dislocations have been only estimated. In order to establish the role of the dislocations in the tunneling process, an experiment which enables a systematic comparison of samples with different concentrations of defects must be performed.
Fig. 5.11 – Fraction of molecules $R_n$ that remain in metastable well as a function of a scaled variable $X$: a) $A = 1$, b) $A = 1.04$. The data in b) are fit with the function $m_1 \text{erf}(m_2 x + m_3) + m_4$, where $m_1 = -0.528$, $m_2 = 2.215$, $m_3 = -8.998$, $m_4 = 0.502$. 
CONCLUSIONS

The main results of this thesis can be summarized as follows. We have conducted systematic studies of the magnetization reversal in single molecule magnet Mn$_{12}$ ($S = 10$) using micro-Hall effect magnetometry. At high temperatures (above 3 K) Mn$_{12}$ behaves as a superparamagnet. In the low temperature region its magnetization reversal becomes slow on the experimental time scale and its magnetic response shows evidence of resonant tunneling of magnetization. We associated the maxima in the field derivative of magnetization with the maxima in the relaxation rate and identified magnetic sublevels that dominate the tunneling at a given temperature, applied field and magnetization. We observed a crossover between thermally assisted and pure quantum tunneling predicted by the recent theory and showed that its form can be controlled by external conditions, such as the direction and magnitude of the applied magnetic field. Two forms of the crossover were distinguished: an abrupt (first-order) and a gradual (second-order) crossover. An abrupt crossover occurs in a narrow temperature interval of less than 0.1 K, when the field is applied parallel to the easy axis of the crystal. In this case, the energy, at which the system crosses the anisotropy barrier, shifts from the top of the anisotropy barrier to the bottom of the metastable well abruptly. There are competing maxima in the relaxation rate, and the global maximum, which occurs for only one or two magnetic sublevels, shifts upon lowering temperature in a narrow temperature interval. A gradual crossover was observed at higher longitudinal and transverse fields. It occurs in a much broader
temperature interval than the abrupt crossover (about 1 K), and is characterized by a
global maximum in the relaxation rate that shifts gradually towards the lowest level in
the metastable well as the temperature is reduced. In agreement with theoretical
predictions, perturbations to the system, such as a transverse field, make the crossover
more gradual.

We have shown that a temperature independent quantum relaxation regime
exists below 0.6 K, which was also confirmed by the relaxation experiments. The form
of the observed magnetic relaxation was best described by a stretched exponential
function, as previously reported by other groups. The same stretched exponential form
of the relaxation curves has been observed for all initial magnetization states of the
sample, including the demagnetized state. The mechanisms causing this form of
relaxation are not completely understood. Although there are suggestions that in Mn$_{12}$
faster-than-exponential initial relaxation is caused by the presence of the fast relaxing
minor species, we observed the same relaxation form in Fe$_8$, which is thought to have
a more uniform chemical composition.

Comparison of our experimental data to the results of the numerical
diagonalization of the model Hamiltonian show that despite a general agreement with
the predictions of theory, there are few discrepancies. The experimental crossover
temperature is much higher than the theoretical one and seems to decrease with
growing transverse fields, contrary to the predictions of theory. We have also shown
that the hysteresis and relaxation experiments provide a lower bound of the crossover
temperature, and therefore underestimate the real temperature at which the crossover
occurs. The experimental crossover is more gradual than predicted, and the factors that cause the smearing are not fully understood. These discrepancies suggest the existence of additional tunneling mechanisms, such as a transverse anisotropy. The fourth order transverse anisotropy term included into the model Hamiltonian leads to a significant increase in the crossover temperature and emphasizes the tunneling from the levels close to the top of the anisotropy barrier. However, the presence of this term must impose selection rules on the tunneling transitions, which have not been observed in the magnetic response of Mn$_{12}$. The transverse anisotropy therefore may be acting in combination with other tunneling mechanisms. The role of the fourth order transverse anisotropy term in the Hamiltonian of Mn$_{12}$ can be studied using Landau-Zener method, which was successfully applied in experiments on Fe$_8$. The behavior of the tunnel splittings as a function of the magnetic field applied along the hard magnetization axis may provide important information about the symmetry of the Hamiltonian. The non-monotonic behavior of the tunnel splittings predicted by theory, if observed in an experiment, may shed light on the effect of higher order transverse anisotropy terms.

A few other questions need to be addressed by the future studies. In order to explain the initial results, it was sufficient to consider SMMs as ideal monodisperse systems with no distribution of parameters. Further understanding of physics of these materials requires taking into account more complex aspects, such as disorder and interactions within a crystal. A theoretical model proposed by Chudnovsky and Garanin showed that the presence of even a small number of dislocations has a
dramatic effect on the distribution of the tunnel splittings, and therefore the tunneling processes. Even high quality crystals contain defects, however it is not known whether their presence has the consequences predicted by this theory. Systematic studies of the role of defects and magnetostriction phenomena in SMM crystals are necessary to test this model.

Interactions among the molecules are another important issue. Dipolar interactions may have a significant effect on tunneling, yet they have not been studied systematically. SMMs provide a unique opportunity to alter the interactions in a controlled way, since the intermolecular distances in these materials can be varied using materials with different ligands and introducing non-magnetic buffer molecules. It would be interesting to investigate the possibility of dipolar ordering in SMMs at very low temperatures. Also, more efforts are needed to understand the role of the hyperfine interactions within Mn$_{12}$ molecules. Observation of quantum coherence also requires better knowledge of the tunneling mechanisms and decoherence factors. Theorists have considered SMMs as potential systems for quantum computing, but the experimental status of this work is far behind the advances of theory. A picture of a memory element consisting of a single high-spin molecule, enclosed in two miniature SQUIDs (for reading and writing) has already appeared in a few theoretical works, yet such a device will not become a reality without further investigations of switching mechanisms in SMMs.

Numerous possibilities of chemical modification of SMM materials are far from being exhausted, such as creating two-dimensional films of ordered molecules,
creating clusters with higher spin and magnetic anisotropy, and other interesting properties. Antiferromagnetic low-spin clusters and half-integer spin molecules are yet to be studied in detail. Creating a conducting SMM material could be another exciting achievement in this field.

The vast variety of SMM materials and their unique properties suggest that in the near future they will remain in the focus of attention of experimentalists and theorists alike, and will yield many more interesting discoveries in addition to those already made.
LIST OF PUBLICATIONS AND PRESENTATIONS


- Studies of the crossover between thermally assisted and pure quantum tunneling in single molecule magnet Mn$_{12}$-acetate. Bokacheva, L., Kent, A.D.,
Walters, M.A., APS March Meeting, Seattle, Washington, 2001 (contributed talk)


REFERENCES


