Micro-Hall Effect Magnetometry of Mn\textsubscript{12}

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Chapter 1

Introduction

In this report the study of the magnetic properties of several Mn$_{12}$ compounds is presented. These so called single molecule magnets (SMMs) [1] have a large magnetic ground state combined with high uniaxial magnetic anisotropy which leads to very slow relaxation of magnetization at low temperature. Below a certain blocking temperature this relaxation occurs predominantly via resonant quantum tunneling. The magnetic properties of SMMs are intrinsic to each individual molecule, i.e. their magnetic properties are not attributed to interactions between molecules as is the case in classical ferromagnets. SMMs allow the observation and study of quantum phenomena such as quantum tunneling of magnetization [2, 3], Berry phase oscillations [4] or spin mixing. In addition, control and manipulation of their properties is achieved via chemical synthesis. Due to all these properties SMMs constitute an interesting mesoscopic model system to understand the quantum origin of magnetization, the coupling of the spin to other degrees of freedom such as phonons or nuclear spins as well as relaxation processes and quantum decoherence. Furthermore, SMMs are promising candidates for application in high density data storage and quantum computing [5].

This work emerged from a collaboration between Kent Lab (New York University) and the group of Prof. Dr. Rüdiger (University of Konstanz). Device fabrication and characterization as well as the magnetometry measurements were performed in New York while samples were synthesized in Konstanz. In addition, high frequency electron paramagnetic resonance measurements were performed at Hill Lab, University of Florida. The intention of this study was the analysis of magnetic properties of a mono-layer of Mn$_{12}$ molecules attached to an Au surface, as well as characterization of single crystal samples of several Mn$_{12}$ compounds.

The characterization of the single crystal samples was performed on a pre-existing Hall effect
magnetometry setup. In order to measure mono-layers a new sensor design was developed and employed.

The relevant theoretical background is presented in Chapter 2. It covers the basics of SMMs, Hall effect magnetometry, two dimensional electron gases (2DEG) and electron paramagnetic resonance (EPR). Chapter 3 explains the experimental details including device fabrication and the measurement setup. Finally in chapters 4 and 5 the results of the measurements as well as their implications are discussed.
Chapter 2

Theoretical Background

2.1 Single molecule magnets

2.1.1 Structure and basic properties of Mn\textsubscript{12}-acetate and similar compounds

SMMs consist of a core of transition metal ions and a shell of organic ligands. The transition metal ions form an exchanged coupled cluster with a distinct magnetic ground state (except for the case of a frustrated system). The exchange is mediated by simple bridges such as O\textsuperscript{2−} or OH. To overcome this coupling fields of the order of several hundred Tesla are necessary. The surrounding ligand shell stabilizes the core and shields it from the crystal environment. SMMs therefore form weakly-bound Van der Waals crystals where the individual molecules behave like identical superparamagnets.

When SMMs are dissolved the molecules retain their identity and intrinsic properties. However, while in solution, there is a continuous diffusion of the ligands [7]. By adding appropriate ligand molecules to the solution, i.e. molecules with higher affinity to the core than the original ligands, different SMMs can be synthesized. Substituting the ligands should in principle influence the magnetic (as well as electronic) properties of the molecule [8]. This provides a clean way of “tuning” the properties of a SMM via chemical methods.

The first SMM was identified by Sessoli \textit{et al.} in 1993. It was shown that Mn\textsubscript{12}-acetate has a strong uniaxial magnetic anisotropy and displays very slow relaxation of magnetization, and magnetic hysteresis below 4 K [9]. This dodecanuclear complex is synthesized by reaction of Mn\textsuperscript{2+} with MnO\textsubscript{4} in acetic and propionic acids. It has the formula [Mn\textsubscript{12}(CH\textsubscript{3}COO)\textsubscript{16}(H\textsubscript{2}O)\textsubscript{4}O\textsubscript{12}] \textsuperscript{[10]} and is shown in Figure 2.1.
The core consists of a tetrahedron of four Mn$^{4+}$ ions surrounded by a ring of eight Mn$^{3+}$ ions. The four Mn$^{4+}$ ions (spin = 3/2) couple via superexchange ferrimagnetically to the eight surrounding Mn$^{3+}$ ions (spin = 2) to form a magnetic ground state $S = 10$ with a magnetic moment $m \approx 20 \mu_B$ [9]. The molecule is almost planar and has a crystal-imposed $S_4$ symmetry [10, 12, 13].

For this work several Mn$_{12}$ compounds were studied where the acetate ligands were substituted for other ligands. The basic structure and properties described in this section are common to all these molecules.

### 2.1.2 Magnetic properties of a spin $S = 10$ system with uniaxial anisotropy

One of the main interests in SMMs is the slow relaxation of magnetization at low temperature and quantum tunneling of magnetization. In the following the basic concepts of these phenomena will be explained.

Since the exchange interaction between the transition metal ions is much stronger than all other terms in the spin Hamiltonian, each molecule can be treated as a single effective spin $S = 10$. In the absence of transverse anisotropy the corresponding multiplet of $2S + 1$ states represent the $M_S$ eigenstates (with respect to a preferred crystalline direction, i.e. easy axis) of the molecule. Due to the strong uniaxial anisotropy, in the case of $S > 1/2$, these can be split up in zero field by spin-orbit coupling or dipolar interactions. Such a system can be described by a double well potential [7] as shown in Figure 2.2.
In first order expansion the spin Hamiltonian can be written as:

\[ H = -DS_z^2 - g\mu_B H S, \tag{2.1} \]

where the first term represents the energy of a state with projection \( S_z \) on the easy axis in the presence of an anisotropy barrier characterized by the zero field splitting constant \( D > 0 \), and the second term is the Zeeman energy of the spin \( S \) in an external field \( H \). Without external field all eigenstates except \( M_S = 0 \) are two-fold degenerate where the two states \( M_S = \pm S \) are separated by the anisotropy barrier. The zero field splitting can be determined experimentally by spectroscopic techniques such as high frequency electron paramagnetic resonance (HF EPR), inelastic neutron scattering (INS) or frequency domain magnetic resonance (FDMR) and is \( D = 0.548 \text{ K in Mn}_{12}\text{-acetate} \) \([14]\) which, for \( M_S = \pm 10 \), corresponds to an anisotropy barrier of approximately \( U = 55 \text{ K} \) (omitting all higher order terms!). At finite temperature the distribution of the spins in the \( M_S \) states is \( \propto \exp \left( -E_{M_S}/T \right) \).

### 2.1.3 Quantum tunneling of magnetization

If the magnetization has been saturated by applying a large external field along the easy axis, i.e. all spins are on the same side of the barrier in Figure 2.1.3, there are three different ways for it to relax into the other well: thermal activation (TA) over the barrier, thermally assisted...
tunneling (TAT) or pure quantum tunneling (QT) through the barrier. The three ‘paths’ are illustrated in Figure 2.3.

Relaxation over the barrier is described by the Arrhenius law:

\[
\Gamma_{TA} = \Gamma_0 \exp \left(-\frac{U}{T}\right),
\]

(2.2)

where \( \Gamma_0 \) is the amplitude, \( U \) is the barrier height and \( T \) the temperature. This process dominates the relaxation at high temperature whereas below the blocking temperature relaxation occurs predominantly via tunneling processes. When the temperature is low enough that only the lowest level is significantly populated (at roughly \( T = 1 \) K), the tunneling becomes independent of temperature and is solely determined by the barrier. This is called pure quantum tunneling and the probability is written as follows:

\[
\Gamma_{QT} = \Gamma_0 \exp \left(-P(0)\right),
\]

(2.3)

where \( P(0) \) is the tunneling probability from the lowest state at \( T = 0 \) K. When the temperature is high enough that higher states are populated the magnetization relaxation mechanism is a competition between the population of the states, which decreases towards higher states and the tunneling probability, which increases due to the lower and narrower barrier. The following approaches to the tunneling process focus on pure quantum tunneling.
To understand the tunneling processes in SMMs one has to consider a more detailed spin Hamiltonian:

\[
H = -DS_z^2 - BS_z^4 + C \left( S_z^4 + S_z^4 \right) - g \mu_B HS ,
\]

where the second term is a higher order uniaxial anisotropy term and third term is the lowest order transverse anisotropy term in a tetragonal symmetry such as in Mn_{12} [16].

**Zero field tunneling**

In the absence of transverse anisotropy in zero field the two states \( M_S = \pm 10 \) are degenerate and orthogonal, i.e. the eigenstates are pure \( M_S \) states. Their wave functions are localized and there is no overlap between them and therefore no tunneling. To facilitate tunneling a perturbation (transverse anisotropy) needs to be introduced. In this case the eigenstates are no longer pure \( M_S \) states but a mixing of the to states \( \pm M_S \). The wave function becomes delocalized and tunneling possible.

**Tunneling in an axial field**

Figure 2.4: Tunneling in an axial field. The degeneracy of the energy levels in the two wells is lifted by the external field and tunneling is no longer possible (middle). At certain fields two energy levels are again in resonance and tunneling takes place (right).

Application of an axial field changes the energy of the states according to the Zeeman interaction. This lifts the degeneracy of the states \( \pm M_S \) and tunneling is no longer possible. At certain fields the energy levels of the states are again in resonance and tunneling takes place. According
to Equation 2.1 this is the case when the following condition is met:

\[ H_k = \frac{kD}{g\mu_B}, \]  

where \( k = 0, 1, 2, \ldots \)

The tunnel splitting \( \Delta_{M_S,M'_S} \) for the anti-crossing of the states \( M_S \) and \( M'_S \) can be obtained from the Landau-Zener model by measuring the tunneling probability \( P_{M_S,M'_S} \) while the axial field \( H_z \) is swept at a constant rate [17, 18, 19]:

\[ P_{M_S,M'_S} = 1 - \exp\left( -\frac{\pi \Delta^2_{M_S,M'_S}}{2\hbar g\mu_B |M_S - M'_S| \mu_0 dH_z/dt} \right), \]  

with \( \hbar \) the Planck constant over \( 2\pi \) and \( \mu_0 \) the vacuum permeability. The anti-crossing of \( M_S = 10 \) and \( M_S = -9 \) is shown schematically in Figure 2.5.

![Figure 2.5: Landau-Zener tunnel splitting for the \( M_S = 10 \) and \( M_S = -9 \) level anti-crossing (From Lawrence [20])](image)

**Tunneling in an axial field with transverse anisotropy/field**

For tunneling in an axial field with an additional transverse field the following Hamiltonian is considered:

\[ H = -DS_z^2 + E \left( S_x^2 + S_y^2 \right) - g\mu_B HS, \]  

(2.7)
where $E$ is the transverse Hamiltonian parameter for a molecule with lower than tetragonal symmetry, which is the case for a molecule with rhombic distortions e.g.. $x$ and $y$ are the directions of the hard and medium axes in this case. Solving this Hamiltonian to second order shows that the tunnel splitting $\Delta_{M^S,M'^S}$ between to resonant states oscillates with the transverse field $H_T$ with a period given by [21]:

$$\mu_o \Delta H_T = \frac{2k_B}{g\mu_B} \sqrt{2E(E+D)}.$$  \hfill (2.8)

These oscillations are due to constructive or destructive interference of quantum spin phases of two tunnel paths (Berry phase oscillation). This is illustrated in Figure 2.6.

![Figure 2.6: Unit sphere showing degenerate minima A and B joined by two tunnel paths (From Wernsdorfer et al. [22])](image)

### 2.1.4 Single molecule magnets on surfaces

Attaching individual SMMs to surfaces, in particular (semi)conducting surfaces, is of great interest because in principle it allows the study and perhaps manipulation of individual molecules via techniques such as scanning tunneling microscopy (STM) and spectroscopy (STS).

Various techniques have been employed to attach Mn$_{12}$ molecules to Au surfaces, including direct deposition of molecules functionalized with sulfurous ligands [23], functionalizing the surface with long channed acids [24, 25] or short carboxylic acids [26] and deposition via substitution reaction, functionalizing the surface with anionic molecules and the SMMs with katicon ligands to attach them via Coulomb interaction [27] and deposition via Langmuir-Blodgett-Method [28].
The aforementioned methods have been predominantly investigated by atomic force microscopy (AFM) and/or STM. While the topography of such films shows clusters of different width and of a height consistent with the expected value (1-1.5 nm), these methods do not yield evidence for the chemical integrity of the molecules.

Using spectroscopic techniques such as X-ray photoemission spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and resonant photoelectron spectroscopy (RPES) and comparing them to LDA+U calculations Voss et al. [29] recently suggested that the deposition via substitution reaction on an Au(111) surface functionalized with a short benzoic acid produces chemically intact molecules, whereas the molecules deposited via direct deposition disintegrate. Figures 2.7 and 2.8 show XAS spectra and a STM image of Mn$_{12}$ molecules on Au surfaces.
2.1.5 Magnetic dipolar field of a monolayer of Mn\textsubscript{12}

In Hall effect devices the magnetic dipolar field emanating from the sample is detected. This comprises a great challenge in the attempt to measure a monolayer of Mn\textsubscript{12} since the out of plane component of the magnetic dipolar field of such a layer vanishes in the two dimensional limit (for out of plane magnetization of the sample, i.e. magnetization along the suggested easy axis). At a height of 1-1.5 nm this limit is already reached at lateral dimensions of a few µm. In the following the out of plane magnetic dipolar field of a two dimensional sheet of periodic spins is calculated.

The magnetic dipolar field of one spin is given by:

\[
B(m, r - r') = \frac{\mu_0}{4\pi} \left\{ \frac{3m \cdot (r - r') (r - r')}{|r - r'|^5} - \frac{m}{|r - r'|^3} \right\}
\]

where \(m\) is the magnetic moment associated with the spin, \(r\) is the point where the field is calculated, and \(r'\) is the location of the spin. Using cartesian coordinates and assuming that (1) the sheet is in the plane where \(z = \text{const.}\), (2) the equilibrium orientation of the spins is perpendicular to the sheet (out of plane easy axis) and (3) the field is probed in a two dimensional plane parallel to the sheet, Equation 2.8 simplifies for the perpendicular component of \(B\) to:

\[
B_z(m, x - x', y - y', d) = \frac{\mu_0}{4\pi} \left\{ \frac{3m \cdot (r - r') d}{(x - x')^2 + (y - y')^2 + d^2}^{5/2} - \frac{m_z}{(x - x')^2 + (y - y')^2 + d^2}^{3/2} \right\}
\]

with \(d\) the distance between the two planes.

To calculate the Hall voltage according to Equation 2.9 one has to sum over all spins and average across the active area of the Hall sensor. To facilitate the calculation this average is approximated by a sum with respect to the same lattice used for the spins. The lattice constant is chosen to be \(a = 3.5\ \text{nm}\) which corresponds to a coverage of roughly 0.5 monolayers. With a magnetic moment of 20 \(\mu_B\) the average field perpendicular to the Hall sensor is then for the two scenarios where the total magnetization is either out of plane \((m = m_z \hat{z} = 20 \mu_B)\) or in plane \((m = m_x \hat{x} = 20 \mu_B)\):
\[ B_{z,op} \left( \bar{x} - \bar{x}', \bar{y} - \bar{y}', \bar{d} \right) = B_0 \sum_{\bar{x}, \bar{y}, \bar{x}', \bar{y}'} \left\{ \frac{3\bar{d}^2}{\left[ (\bar{x} - \bar{x}')^2 + (\bar{y} - \bar{y}')^2 + \bar{d}^2 \right]^{5/2}} - \frac{1}{\left[ (\bar{x} - \bar{x}')^2 + (\bar{y} - \bar{y}')^2 + \bar{d}^2 \right]^{3/2}} \right\}, \quad (2.11) \]

\[ B_{z,ip} \left( \bar{x} - \bar{x}', \bar{y} - \bar{y}', \bar{d} \right) = B_0 \sum_{\bar{x}, \bar{y}, \bar{x}', \bar{y}'} \frac{3 (\bar{x} - \bar{x}') \bar{d}}{\left[ (\bar{x} - \bar{x}')^2 + (\bar{y} - \bar{y}')^2 + \bar{d}^2 \right]^{5/2}}, \quad (2.12) \]

where \( B_0 = \frac{20 \mu_0 \mu_B}{4\pi(3.5 \times 10^{-9} \text{ m})^3} \) and \( \{\bar{x}, \bar{y}, \bar{x}', \bar{y}', \bar{d}\} \) are dimensionless integers.

From Equations 2.11 and 2.12 it is clear that there are negative contributions to the sum when:

- \( d < \frac{\rho}{2} \), where \( \rho = \sqrt{(x - x')^2 + (y - y')^2} \) (out of plane)
- \( x - x' < 0 \) (in plane)

On the other hand both equations are zero in the limit of \( d, \rho \gg 1 \). This means that in both cases the measurement is limited by the finite size of the Hall sensor! The implications on the measurement design will be discussed in Chapter 3. Figure 2.9 shows the magnetic dipolar field for different sample configurations.

Figure 2.9: Perpendicular component of the magnetic dipolar field in the 2DEG plane 49 nm below the sample; First row: out of plane magnetization, sample size: (a) 10.5x10.5 nm\(^2\); (b) 105x105 nm\(^2\); (c) 1050x1050 nm\(^2\); Second row: in plane magnetization, sample size: (d) 10.5x10.5 nm\(^2\); (e) 105x105 nm\(^2\); (f) 1050x1050 nm\(^2\).
CHAPTER 2. THEORETICAL BACKGROUND

2.2 Hall effect devices

Hall effect devices are magnetic field sensors whose operation is based on the classical Hall effect. The Hall effect was discovered by Edwin Hall in 1879 [30] and is a manifestation of the Lorentz force acting on moving charges in a magnetic field perpendicular to the motion. When a current is flowing through a sample the charge carriers are deflected in the magnetic field and accumulate at the sides resulting in a potential difference across the sample.

In a uniform magnetic field this voltage is:

\[ V_H = R_H \frac{IB}{t}, \]  \hspace{1cm} (2.13)

where \( R_H = \frac{1}{n_3Dq} \) is the Hall coefficient (\( n_{3D} \) is the carrier concentration in the device, \( q \) the charge of the carriers), \( t \) the thickness of the device, \( I \) the current through the device and \( B \) the magnetic field perpendicular to the current. For a 2DEG device it is favorable to express Equation 2.13 in terms of the two-dimensional sheet carrier concentration \( n_{2D} = n_{3D}t \):

\[ V_H = -\frac{1}{n_{2De}} IB \]  \hspace{1cm} (2.14)

for a device with electron transport (\( -e \) is the electron charge). The electron mobility \( \mu_e \) in such a device is given by:
\[ \mu_e = \frac{R_H I}{V_{xx} w}, \] (2.15)

where \( V_{xx} \) is the longitudinal potential change, \( l \) the distance across which the potential change occurs and \( w \) the width of the device.

### 2.2.1 Two dimensional electron gas

Although Hall effect devices have been used for a century, the interest was revived a few decades ago through the progress in micro- and nanofabrication along with the advances in growing high mobility 2DEG heterostructures. In the following the basic properties of an InAs/AlSb quantum well (QW) Hall sensor will be discussed.

![Figure 2.11: (a) Schematic of the InAs/AlSb QW heterostructure; (b) Energy band diagram of the InAs/AlSb QW; The two-dimensional carrier concentration \( n_{2D} \) is the sum of a contribution from the surface \( n_S \) and a combined bulk and interface contribution \( n_{BI} \). (From Nguyen et al. [33])](image)

InAs/AlSb heterostructures are extensively studied and used in many devices such as high electron mobility transistors [34], gate-controlled spin field effect transistors [35] or mid-infrared quantum-cascade lasers [36]. There are several reasons why this combination of materials has received so much attention. InAs has the second highest intrinsic electron mobility at room temperature, only surpassed by InSb for which no approximately lattice-matched barrier material exists. Another advantage is that the offset between the conduction bands of InAs and AlSb is exceptionally large (1.35 eV). In addition the InAs surface Fermi level is pinned slightly above the minimum of the conduction band [37]. This has two important consequences for
the fabrication of devices. First, there is no Schottky barrier in metal-InAs contacts, so that no alloying or annealing is necessary to form ohmic contacts. Second, the confining potential is approximately square and very high, so that the geometrical dimensions of the conducting channel are identical to the spread of the electron wave function [38]. This is important for the fabrication of submicron devices. Figure 2.11 (a) shows the different layers in the InAs/AlSb QW heterostructure used in the study of monolayers of Mn\textsubscript{12}. The QW is located in the InAs layer. In Figure 2.11 (b) a schematic of the energy band in the heterostructure is displayed. The conduction band forms a square well potential where only the ground state \( E_1 \) is populated. The charge carriers come from three different sources: shallow donors in the barrier layer, surface states in the GaSb cap layer and deep donors in the InAs/AlSb interface or AlSb barrier [39]. The carrier concentration in the QW can be controlled by modulation doping in the AlSb barriers. The advantage of this is that the donor ions are separated from the electrons thus reducing scattering and yielding high electron mobilities. Another way to increase the carrier concentration is by adding a GaSb cap layer which has a very high density of surface states that drain into the QW. Carrier concentrations of \( 1.5 \cdot 10^{16} \text{ m}^{-2} \) [38] and mobilities \( 2.8 \text{ m}^2/\text{Vs} \) [40] have been achieved at room temperature. In addition the carrier concentration and mobility in InAs/AlSb vary moderately with temperature to allow application in a broad temperature range.

### 2.2.2 Electronic noise in two dimensional electron gases

Electronic noise is a random fluctuation of the voltage or the current in the device. The RMS voltage output of such a device can be written as:

\[
V(t) = V_S(t) + V_N(t),
\]

(2.16)

where \( V_S \) and \( V_N \) are the RMS voltages of signal and noise respectively. Since the noise voltage in most cases is a function of frequency it is useful to define the noise voltage power spectral density (PSD) \( S_V(f) \) and the noise voltage spectral density \( N_V(f) \) as

\[
V_N = \sqrt{\int_{f_1}^{f_2} S_V(f) \, df},
\]

(2.17)

and
\[ N_V(f) = \sqrt{S_V(f)}, \]  

(2.18)

where \( f_1 \) and \( f_2 \) are the boundaries of the frequency range of interest, and \( S_V(f) \) and \( N_V(f) \) are given in units of \( \text{V}^2/\text{Hz} \) and \( \text{V}/\sqrt{\text{Hz}} \) respectively.

In a semiconductor Hall device there are three types of noise: thermal noise, generation-recombination (GR) noise and 1/f noise [41]. The PSD can be split up into its different contributions:

\[ S_V(f) = S_T + S_{GR}(f) + S_{1/f}(f), \]  

(2.19)

where \( S_T, S_{GR}(f) \) and \( S_{1/f}(f) \) are the PSDs due to thermal, GR and 1/f noise. \( S_V(f) \) is illustrated schematically in Figure 2.12.

Figure 2.12: Schematic illustration of the noise voltage power spectrum of a semiconductor Hall device. (From Popovic [41])

**Thermal noise**

Thermal noise is due to random thermal fluctuations in the charge distribution within the device [42, 43] and is independent of frequency and current. The PSD can be written as:

\[ S_T = 4k_BTR, \]  

(2.20)
where $k_B$ is the Boltzman constant, $T$ the temperature and $R$ the resistance of the device between the voltage leads. $S_T$ is completely determined by $R$ and $T$! In a 2DEG Hall device at 4 K with $R = 1 \, \Omega$, $N_T \approx 0.5 \, nV/\sqrt{Hz}$ ($k_B = 1.38 \cdot 10^{-23} J/K$), which for a driving current of $10 \, \mu A$ results in a field sensitivity of $\approx 2 \cdot 10^{-7} T/\sqrt{Hz}$ ($R_H \approx 375 \, \Omega/T$) if the thermal noise is the limiting source of noise.

**Generation-recombination noise**

GR noise has its origin in the fluctuation of charge carrier density due to generation-recombination processes between the conduction band and charge traps. The PSD for one type of GR noise is written as [44]:

$$S_{GR}(f) = \langle \Delta N^2 \rangle \frac{4\tau}{1 + (2\pi f \tau)^2}, \quad (2.21)$$

where $\langle \Delta N^2 \rangle = \int_0^\infty S_{GR}(f) df$ is the equilibrium number of fluctuating charge carriers and $\tau$ is the relaxation time of the GR process.

**1/f noise**

1/f noise is a random fluctuation where the PSD follows a $S_{1/f} \propto 1/f^\alpha$ law where $\alpha$ is equal or close to 1. It is observed in many solid states materials and devices but also in non-electrical systems such as earthquakes. The electrical 1/f noise usually comes from the random motion of impurities [45] or two level fluctuations such as the trapping and untrapping of charge at defects. The PSD can be expressed by an empirical equation given by Hooge in 1969 [46]:

$$S_{1/f}(f) = \frac{\gamma_H}{N f^\alpha} V^2, \quad (2.22)$$

where $\gamma_H$ is the Hooge parameter and characteristic to the material, $N$ the total number of charge carriers in the device and $V$ the voltage applied across the current leads. 1/f noise only occurs when a current is flowing through the device!
2.3 Electron paramagnetic resonance

EPR is a spectroscopy technique based on the interaction of unpaired electron spins with microwaves in a magnetic field. In the field the afore degenerate magnetic energy levels of Mn\textsubscript{12} split into \( 2S + 1 \) separate energy levels according to the Zeeman interaction:

\[
E = g\mu_B BM_S
\]  

(2.23)

where \( g \) is the Landé factor, \( \mu_B \) the Bohr magneton, \( B \) the external magnetic field and \( M_S \) the quantized component of the spin along \( B \). Transitions between these energy levels can occur via absorption/emission of microwaves of energy \( E = \hbar \omega \). By fixing the microwave frequency and sweeping the magnetic field (or vice versa) a spectrum of the possible transitions can be obtained. Figure 2.13 shows the energy levels for a \( S = 10 \) system such as Mn\textsubscript{12} for a magnetic field along the easy axis (to lowest order): \( E = -DS_z^2 + g\mu_B B_0 M_S \) with \( D = 0.5 \text{ K} \).

![Figure 2.13: Energy levels of a \( S = 10 \) system with lowest order uniaxial anisotropy, field along easy axis, \( D = 0.5 \text{ K} \)](image)

By applying longitudinal or perpendicular fields the axial parameters \( D \) and \( B \) or the transverse parameters \( E \) and \( C \) of the Hamiltonian can be determined.
Chapter 3

Experimental Details

3.1 Device fabrication

This section describes the fabrication process of micro-Hall magnetometers from an InAs/AlSb QW heterostructure. The substrate was grown at Ohno Laboratory, Tohoku University. Details about the fabrication of the pre-existing GaAs/AlGaAs magnetometers can be found in Bokacheva [15].

3.1.1 Substrate cutting and cleaning

The substrate was cut by first slightly cleaving the surface along a preferred crystalline direction at the edges. The substrate was then put on a glass slide with the cleavage exactly above the edge of the slide and broken by applying slight pressure on the suspended side with a q-tip.

Before lithography the substrate was cleaned in ultrasounds for 10 minutes in Acetone, Isopropanol and Ethanol each. Between each cleaning process the substrate was washed thoroughly with the respective solvent and dried with extra dry and filtered N$_2$.

3.1.2 Photolithography and etching

For the photolithography the following procedure was used:

- The substrate was glued to a glass slide with a tiny amount of S1813 photoresist and then baked on a hot plate at 110°C for 15 minutes to harden the photoresist and to evaporate any remaining solvents from the substrate surface. The substrate was covered with a glass dish to protect it from contamination whenever applicable.
• S1813 photoresist was spun for 30 seconds at 5000 rpm yielding a thickness of approximately 1.1 µm. After that the substrate was baked at 110°C for 12 minutes to harden the photoresist.

• The photoresist was patterned by exposing the respective areas with a mask aligner system for 10 to 15 seconds at a power of 250 W.

• The photoresist was developed in a solution of de-ionized water and 351 developer (ratio 3.5 : 1) for 15 to 25 seconds.

• For small sensor patterns the photoresist was removed from the edges of the substrate by exposure/developing for 1 minute/15 seconds or manually with a sharpened q-tip and EBR PG photoresist remover to achieve better contact between mask and sample.

• After developing the substrate was baked at 100°C for 10 minutes to harden the photoresist again and to remove solvents.

• The sample was then ready for etching or thin film deposition. Etching was performed in a solution of H₃PO₄ : H₂O₂ : H₂O = 1 : 1 : 4 for 45 seconds to 4 minutes yielding etching depths from 150 to 1000 nm. The rate was ≈ 4 nm/s, but was non-uniform through the different layers.

Figure 3.1: (a) Exposure of the photoresist layer with UV light; (b) Developing the photoresist; (c) Etching the structure into the substrate; (d) Removing the photoresist
3.1.3 Thin film deposition

The base pressure for all depositions was below $1 \cdot 10^{-7}$ Torr.

Contacts

For the ohmic contacts a 2–5 nm adhesion layer of Pt was evaporated at 0.1 Å/s using an electron beam evaporation system, followed by 100 nm of Au at 1–2 Å/sec. Just before the substrate was introduced into the deposition chamber it was dipped into a solution of NH$_3$ : H$_2$O = 4 : 1 for 5 seconds, rinsed with de-ionized water and blown dry with N$_2$ to remove any oxides on the contact area.

Dielectric

A 25 nm SiO$_2$ film was deposited by radio frequency sputtering at 100 W and 1 mTorr partial pressure of Ar$^+$ to insulate the Au film from the substrate.

Au film for monolayer deposition

On top of the dielectric film a 25 nm Au film was deposited at 1 Å/sec via electron beam evaporation.

3.2 Device characterization

After inspection of the device under a light microscope, it was wire bonded and the resistance of all conduction channels was checked at room temperature and 77 K to detect bad contacts at the Au–InAs interfaces or damages to the device as soon as possible. Magnetic field sweeps at 10 K with several driving currents and at 0.5 K with a current of 1 µA as well as noise measurements were performed to obtain the Hall coefficient $R_H$ and the electron mobility $\mu_e$.

3.3 Monolayer preparation

A monolayer of Mn$_{12}$-thiophencarboxylate [Mn$_{12}$O$_{12}$(O$_2$CC$_4$H$_3$S)$_{16}$(H$_2$O)$_{4}$] was prepared on the Au film according to the method described by Burgert et al. [47].
3.4 Measurement setup

The low temperature Hall effect magnetometry setup is shown in Figure 3.2. A micro-Hall sensor is mounted on the tip of the probe of a Heliox $^3$He/$^4$He system (Oxford Instruments) with base temperature of 0.3 K. A superconducting Heliox vector magnet system allows application of magnetic fields in all directions. The maximum field is 7 Tesla in axial direction and 1/0.7 Tesla in the two perpendicular directions. The field is swept continuously at rates between 0.1 and 1.5 Tesla/minute.

A 800 Hz ac current of 1 to 10 µA is supplied by a floating battery powered low-noise current source. The Hall voltage is detected with a lock-in amplifier at a time constant of 300 ms with a band pass filter with slope of 12 dB/octave and the amplified dc signal is passed on to a digital voltmeter. The sample temperature is obtained via four-point measurement of the resistance of a Cernox sensor. The sensor is placed directly on the device and is well thermalized to it with thermal grease.
3.5 Operation of the $^3$He/$^4$He system

The $^3$He/$^4$He system consists of three main parts: A reservoir of $^3$He with a heatable carbon sorption pump, a 1 K pot with a heat exchanger coupled to the liquid $^4$He bath that surrounds the probe and an evacuated cap at the tip of the probe in which the sensor and sample are mounted. The two cryogens are separated and never come into contact with the sensor or sample. Basic operation of the system is as follows: The 1 K pot is cooled to a temperature below 1.6 K by pumping on the $^4$He in the heat exchanger of the pot. Heating the carbon sorption pump to 45 K releases the absorbed $^3$He and causes it to condense in the 1 K pot which is already below the liquification temperature of $^3$He. After condensing all $^3$He the heater of the sorption pump is turned off and the element starts pumping on the condensed $^3$He, lowering the temperature to base temperature. The sensor stage is thermalized to the 1 K pot with high purity copper wires. The system stays at base temperature until all condensed $^3$He has been absorbed by the sorption pump. Depending on the load and the amount of condensed $^3$He, base temperatures down to 0.35 K (measured at the sample) and condensation times of up to 12 hours can be achieved. An average condensation lasts approximately 6 hours and has a base temperature of 0.4 to 0.5 K.

The system is equipped with heaters at the 1 K pot and the carbon sorption pump. To control the temperature between base temperature and 300 K two methods are used depending on the operation temperature: For temperatures below roughly 1.5 K the temperature is controlled via the pump rate of the sorption pump. By heating the sorption pump less $^3$He is evaporated resulting in higher temperature. Above 1.5 K, when all $^3$He is evaporated, the temperature is controlled by directly heating the 1 K pot. In addition the sorption pump is heated to release the $^3$He. The gas is then free to move between the 1 K pot and the other parts of the probe which helps stabilize the temperature.

3.6 Sensor design

As discussed in section 2.1.5 the design of the Hall sensor had to be adapted to be suited for the monolayer experiment. In principle the problem could be solved by even more minutiarizing sample and sensor. Minutiarization to sub-micron dimensions requires improved fabrication techniques. Although the fabrication of devices of the order of hundreds of nm is easily accomplished with electron beam lithography, no such devices were considered for this work. The reasons is that the electronic noise increases drastically at a critical size and that the maximum
current that can be applied through the device before the onset of Joule heating scales with the conduction channel width, thus reducing the Hall signal. Instead two sensor designs were developed for the operation with out of plane (i.e. along presumed easy axis) and in plane (i.e. in presumed hard plane) magnetic fields. Both designs will be introduced in the following:

**Sensor for field sweeps along easy axis**

Figure 3.3 shows the basic idea of the out of plane sensor design. By patterning a large asymmetric Hall cross this way, the dimensions of each active area $A'$ can be chosen at the optimum size while at the same time the overall conduction channel width of the device remains considerably larger than for a single device of optimum size.

Figure 3.3: Pattern of the Hall device for easy axis field sweeps. On the left the current flows uniformly in a wide conduction channel and the signal is detected at narrow voltage leads. On the right the wide conduction channel is sectioned into narrow channels. The active regions of the device are indicated in red.

In principle the Hall signals should add up to:

$$V_H = R_H I'B,$$

(3.1)

where $I' = ni$ is the total current passed through the device, $n$ is the number of small Hall crosses and $i$ is the current in each small Hall cross. For such an array ($R_H = 375 \Omega/T$, $n = 1000$, $i = 1 \mu A$) and a RMS noise voltage $V_N = 1 \mu V$ in the frequency range of detection the field sensitivity would be $B_{min} \approx 3 \cdot 10^{-6} T$. 
To achieve better field sensitivity by using this sensor design it is important to learn about the correlations of the noise between the individual Hall crosses. It has to be determined whether the noise contributions of the individual crosses add up just like the signals add up as illustrated in Figure 3.4, or whether the total noise is reduced versus the sum due to correlations. Thermal noise is limited by the device resistance and therefore simply adds. The origin of the other noise contribution underlies a more complex process and it is not straightforward whether a better signal-to-noise ratio could be achieved.

![Figure 3.4: Hall signal and noise for two Hall crosses in parallel configuration.](image)

**Sensor for field sweeps in hard plane**

The sensor design for the hard plane field sweeps is shown in Figure 3.5 (Left). The basic idea of the design is that no negative contributions to the out of plane component of the magnetic dipolar field arise by increasing the lateral dimensions of the sample. In fact the sample can be treated as a chain of magnetic mono-poles at the edges of the sample as demonstrated in Figure 3.5 (Right).

Figure 3.6 shows photographs of the actual sensor in a light microscope.

**3.7 Electron paramagnetic resonance measurements**

The setup used for the HF EPR measurements is shown in Figure 3.7. A detailed description can be found in Lawrence [20].
Figure 3.5: Left: All spins are aligned in plane; Right: The magnetic dipolar field can be treated as a monopole field in the two-dimensional limit.

Figure 3.6: Photographs of the hard plane Hall sensor. The magnification is 10x for the left and 50x for the right picture. The area of the right picture is outlined in the left picture.
Figure 3.7: Schematic of the EPR setup (From Mola et al. [48])
Chapter 4

Results and Discussion

4.1 Characterization of InAs/AlSb quantum well Hall device

The InAs/AlSb quantum well Hall devices were characterized in a closed cycle cryostat at \( \approx 10 \text{ K} \) and during measurements in the \(^3\text{He} / ^4\text{He} \) system at 0.5 K. Figure 4.1 (a) shows the Hall voltage for several currents applied through a device with 1.2 \( \mu \text{m} \) conduction channel width at 10 K. The voltage scales linearly with the field. It also scales linearly with the current indicating that the device is still below the onset of Joule heating at \( I = 10 \mu\text{A} \). A Hall coefficient of \( R_H = 375 \Omega/\text{T} \) and electron concentration of \( n_{2D} = 1.66 \times 10^{16} \text{ m}^{-2} \) were deduced from the data. The electron mobility extracted from the data in Figure 4.1 (b) is \( \mu_e = 7.6 \text{ m}^2/\text{Vs} \).

Figure 4.1: (a) Hall voltage in a 1.2 \( \mu \text{m} \) InAs/AlSb Hall device at 10 K; (b) Longitudinal voltage in the same device between two crosses separated by 10 \( \mu \text{m} \) at a current of 10 \( \mu\text{A} \)
The Hall voltages at 10 and 0.5 K is shown in Figure 4.2. For a better comparison the voltage was normalized by the respective currents. The Hall coefficient at 0.5 K is reduced by more than 20% compared to \( T = 10 \) K and is \( R_H = 294 \Omega/T \) corresponding to an electron concentration of \( n_{2D} = 2.12 \times 10^{16} \text{ m}^{-2} \). This increase in the intrinsic carrier concentration of the quantum well at lower temperature seems rather unlikely. The change in \( R_H \) and \( n_{2D} \) could be due to an interaction of the Au electrode with the quantum well. Furthermore, the 25 nm SiO\(_2\) barrier could be insufficient to prevent leakage into the Au film. The electron mobility is \( \mu_e = 3.2 \text{ m}^2/\text{Vs} \) which also indicates that the quantum well is significantly affected by the electrode.

Figure 4.3 shows noise data of a 1.2 \( \mu \)m device at 10 K. The current through the Hall cross is 1 \( \mu \)A. The data in the frequency domain was fitted to \( N_V(f) = 1/(\alpha f) + N_T \). The fit yields \( N_T = (11.2 \pm 0.2) \text{nV} / \sqrt{\text{Hz}} \) for the noise voltage spectral density of the thermal noise. Considering only the device configuration \( (R = 10 \text{k}\Omega) \) \( N_{T,device} = 2.3 \text{nV} / \sqrt{\text{Hz}} \) is expected. This suggests that the limitation does not arise from the device, but the measurement circuit.

The RMS noise voltage (given by the standard deviation) for currents from 0 to 10 \( \mu \)A is plotted in Figure 4.4. It is \( \propto I \) as expected for 1/f noise (Equation 2.22. Note that \( V \propto I \) when \( I \) is small enough that no Joule heating occurs). The data point at 0 \( \mu \)A was excluded from the fit since 1/f noise only occurs when a current is applied through the device.
Figure 4.3: (a) Random noise $V(t)$ in an InAs/AlSb Hall cross in real time measurement, $I = 1\, \mu A$, $T = 10\, K$; (b) Histogram of $V(t)$ (grey) and fit to a Gaussian distribution function (red); (c) Corresponding noise voltage spectral density $N_V$ (grey) and $1/f$ fit (red)

Figure 4.4: RMS noise voltage $V_N$ for currents from 0 to 10 $\mu A$
4.2 Mn$_{12}$-thiophencarboxylate

This compound was synthesized by substituting the CH$_3$COO groups for O$_2$CC$_4$H$_3$S in order to attach the molecules to an Au surface via the S–Au interaction. It has the formula [Mn$_{12}$O$_{12}$(O$_2$CC$_4$H$_3$S)$_{16}$(H$_2$O)$_4$]. It has been shown that the molecule is likely to be destroyed during the deposition [30].

The crystal measured was a parallelepiped with one of the faces considerably larger than the other two. One of the corners was slightly chipped. Assuming that the easy axis of the molecules points perpendicular to the largest face, the crystal was placed on the second largest face so that the easy axis would be parallel to the x-axis. The actual alignment was partially deduced from the zero field shifts when applying constant transverse fields of different magnitudes and polarities in the paramagnetic regime. The misalignment in the x-y-plane was found to be $\approx 32^\circ$ whereas the misalignment in the z-x-plane could only be estimated to be $> 20^\circ$. This is due to nonlinear effects in the 2DEG when applying large fields perpendicular to the 2DEG-plane. The alignment could be sufficiently corrected in the x-y-plane at temperatures above 2 K by sweeping $H_x$ and $H_y$ concurrently. At lower temperatures however, the field necessary to saturate the sample was too large to compensate the misalignment with the maximum available transverse field. Application of $H_z$ produced artifacts due to the afore mentioned nonlinearity of the Hall coefficient and the alignment could not be corrected.

![Mn$_{12}$-thiophencarboxylate](image)

**Figure 4.5:** Temperature dependence of the hysteresis. The sweep rate was decreased during the low temperature sweeps to avoid avalanches.
Figure 4.5 shows the temperature dependence of the hysteresis loop. In these measurements the misalignment was not corrected. The blocking temperature is $T_B > 2.2$ K. At very low temperature the magnetization relaxes in avalanches and the characteristics of the hysteresis are not consistent (note that the red curve is not symmetric). At higher temperatures this effect is reduced due to better spin phonon coupling. Further data also shows that there are less avalanches when the sweeping rate is decreased.

In addition, HF EPR measurements were performed on this compound. The hard plane data (Figure 4.6) shows Mn$_{12}$-like features. Unfortunately, the ground state transition was out of the maximum field range which can be seen in the temperature dependence: The first dip from the right increases from 2.5 to 4 K. This indicates that it cannot be the ground state transition as the population of the ground state always decreases with increasing temperature. For lower frequencies the coupling of the the microwaves to the crystal in the cavity is too weak to observe clear features in the transmission spectrum (blue and magenta curves in figure 4.6 (b).

Figure 4.6: EPR spectra for fields applied in the hard plane; (a) Temperature dependence at $f = 80.9$ GHz; (b) Frequency dependence at $T = 6$ K

The data for fields applied along the presumed easy axis of the crystal is shown in Figure 4.7. The only distinct feature is a double dip around 0.5/1.0 T in the 308 GHz spectrum. The ratio of this double feature changes with temperature. This is an unusual feature for Mn$_{12}$ and could be due to a coupling between neighboring molecules.
4.3 Mn$_{12}$-biphenyl

For this derivative the acetate ligands were substituted for O$_2$CC$_{12}$H$_9$ groups to produce the derivative [Mn$_{12}$O$_{12}$(O$_2$CC$_{12}$H$_9$)$_{16}$H$_2$O]$_4$. This substitution was done to create a derivative with high sterical finesse to get higher ordering on surfaces. There is no proof about the intact deposition to date.

The crystal used for these measurements had a similar shape to the Mn$_{12}$-thiophencarboxylate.
crystal, but with a slightly higher symmetry. It was positioned on the Hall bar again assuming that the easy axis is perpendicular to the largest crystal face. The actual alignment was deduced using the same method described above in the paramagnetic regime and at 1.15 K. At both temperatures no shift of the zero field position or the steps could be seen when applying a constant transverse field $H_y$. The data for the z-x-plane does not provide a precise result, the misalignment was estimated to be 20°.

Figure 4.8 shows the temperature dependence of the hysteresis loop. The hysteresis vanishes at $\approx 3$ K. This can be interpreted as a lower bound for the blocking temperature since there is a small transverse field due to misalignment. The hysteresis is perfectly symmetric and has two interesting features: A sharp step at zero field followed by a very broad step.

![Figure 4.9: (a) Sweep rate dependence at 0.41 K; (b) Derivative of (a).](image)

To clarify this the dependence of the hysteresis on the sweep rate and on a transverse field $H_y$ was investigated. Figure 4.9 shows that the position of the steps does not depend on the sweep rate. The zero-field step increases with decreasing sweep rate. This is consistent with the idea that at lower sweep rates the energy levels are longer in resonance and more spins can relax. It shows that this step is not a measurement artifact. The second step is exceptionally broad, which is due to the phonon bottleneck effect and is essentially an out of equilibrium measurement artifact, where the spin phonon coupling is so weak that the energy from spin relaxation cannot be dissipated fast enough.
In Figure 4.10 the transverse-field dependence was investigated. The transverse field was applied along $y$ from 0 to 0.9 T in 0.05 T steps. A significant dependence on the magnitude of the transverse field can be observed for the first and second steps. There is a minimum in the derivative of the first step at a certain field. This might be due to quantum phase interference. The relaxation rate $\Gamma$ (taken as proportional to the maximum $dM/dt$) of the zero field step versus the magnitude of the transverse field is shown in Figure 4.11.

The second step flattens and eventually the curvature changes signs. At the same time it develops a fine structure. An explanation of this behavior is that the applied transverse field reduces
the phonon bottleneck effect. Steps three, four and five are less affected. We observe a decrease of steps four and five with the transverse field because there is less remaining magnetization.

The zero field splitting parameter $D$ was derived from the positions of steps three to five at $H_y = 0$ T. In this rough estimate $D \approx 0.65$ K. This has to be considered with care since the misalignment could only be estimated. Assuming symmetry around $H_T = 0$ T, $E$ was estimated from the data in Figure 4.3 using equation 2.7 to be $E = 0.04$ K.

### 4.4 Mn$_{12}$-parabromobenzoate

Mn$_{12}$ compounds with benzoic acids (O$_2$CC$_6$H$_5$) in their ligands have been deposited successfully on functionalized Au surfaces [29]. Several derivatives where one or more of the H atoms were replaced by halogens were studied. In this derivative a Br atom substitutes one H atom to form the derivative with the formula [Mn$_{12}$O$_{12}$(O$_2$CC$_6$H$_4$Br)$_{16}$(H$_2$O)$_4$]. This molecule is also interesting because it does not sit on top of another molecule in the crystal, but rather on top of the gap between neighboring molecules.

![Figure 4.12: Temperature dependence](image)

The crystals basically lacked any coherent shape and were very fragile. The sample had roughly the shape of a cuboid with aspect ratio 1 : 1 : 0.5. A misalignment of 12° in the x-y-plane was corrected. The misalignment in the z-x-plane remains undetermined. There are huge non-linearities which suggest that this misalignment is quite large. Overall, this sample does not produce good
data.

The signal was very small (about three to four times less than the other samples) and there were no clear steps. This sample was cooled to 77 K and then warmed to room temperature twice before going to low temperature. It may have degraded because of this. The temperature dependence does not give much information, but there is a hysteresis whereas at 6 K the crystal is completely paramagnetic, so there is blocking at low $T$.

### 4.5 Mn$_{12}$-difluorbenzoate

For this compound two of the H atoms were substituted for F atoms to produce the derivative [Mn$_{12}$O$_{12}$($\text{O}_2\text{CC}_6\text{H}_3\text{F}_2$)$_{16}$($\text{H}_2\text{O}$)$_{4}$].

The crystal used for the measurement was a parallelepiped and all axes were tilted. Perfect alignment was achieved in the x-y-plane, the alignment in the z-x-plane remains undetermined.

![Figure 4.13: (a) Temperature dependence; (b) Derivative of (a)](image)

Figure 4.13 shows the temperature dependence of the hysteresis loop and its derivative. There is a large paramagnetic background which could be due to contamination of the sensor with debris from prior crystals or due to a partial degradation of the sample. The blocking temperature is $T_B > 1.88$ K. There is fast relaxation at zero field 1.2 to 1.5 K (green and dark yellow curves) which is largely suppressed at lower temperature. At higher fields there is also faster relaxation above 1 K (dark cyan curve). Both features are due to the transition from pure quantum tun-
neling to thermally assisted tunneling.

### 4.6 Mn$_{12}$-trifluorbenzoate

For this compound three H atoms were substituted for F atoms to produce the derivative [Mn$_{12}$O$_{12}$(O$_2$CC$_6$H$_2$F$_3$)$_{16}$(H$_2$O)$_4$].

The crystals were very robust and had cuboid shape with “rounded” edges on one end. There was again perfect alignment in the x-y-plane and unidentified misalignment in the z-x-plane.

![Figure 4.14: (a) Temperature dependence; (b) Zoom-in of (a)](image)

The blocking temperature of the sample is $T_B > 1.51\text{ K}$. The hysteresis at 1.90 K (red curve) is a measurement artifact from the magnet. There are two distinct species of molecules in this sample. 50% of the molecules are always fast relaxing at zero field whereas the other 50% shows thermally assisted relaxation at high temperatures and develops small steps below 1 K (see Figure 4.14 (b)). This is in agreement with the transverse-field dependence (Figure 4.15). The zero field step splits into two steps when a transverse field is applied (indicated by the dotted arrows). No splitting is observed for the other steps suggesting that they are related to a different species of molecules. In addition, the splitting indicates that the fast relaxing species does not have a unique easy axis. There are two axes tilted symmetrically from the direction of the field sweep. At very high transverse fields the relaxation becomes quasi-continuous and almost all features are smeared out.
Figure 4.15: (a) Dependence on the transverse field at 0.5 K; (b) Derivative of (a)

Figure 4.16 shows the dependence on the sweep rate. The amount of magnetization that relaxes at zero field is independent of the sweep rate. This suggests that the step comes exclusively from the fast relaxing species and that all magnetization related to this species relaxes.

Figure 4.16: a) Dependence on the sweep rate at 0.51 K; (b) Derivative of (a)

4.7 Mn$_{12}$-diphenylphosphinate

This derivative was synthesized by replacing only the equatorial ligands by O$_2$PC$_{12}$H$_{10}$ groups whereas the four axial ligands remain acetates. It has been shown by X-ray crystallography that it crystallizes in the space group $I4_1/a$ with the two different molecular species [Mn$_{12}$O$_{12}$(O$_2$-PC$_{12}$H$_{10}$)$_{12}$(O$_2$C$_2$H$_3$)$_4$(H$_2$O)$_4$] and [Mn$_{12}$O$_{12}$(O$_2$PC$_{12}$-H$_{10}$)$_{12}$(O$_2$C$_2$H$_3$)$_4$]. In the
first species four of the sites of the Mn$^{3+}$ ions a occupied by four water molecules whereas in the second species they remain unoccupied. Because acetate ligands are easily exchanged this configuration is expected to produce a high orientation of the molecules on surfaces when deposited via ligand substitution reaction. Further studies showed that the diphenylphosphinate ligands are quite voluminous and there appears not to be enough space for a substitution for the acidic groups used to functionalize the surface [52].

The crystals had a nice and consistent shape, shiny faces and were quite robust. The sample measured had the shape of a cuboid with aspect ratio 1:1:0.5. There was a small misalignment between easy axis and $H_x$ due to a misalignment of the crystal on the Hall bar. The misalignment was corrected in the x-y-plane (Hall bar plane) to $<1^\circ$, in the z-x-plane it was not corrected in favor of less non-linearities in the Hall bar. The overall misalignment was $<2^\circ$.

Figure 4.17: Temperature dependence. The transition from pure quantum tunneling to thermally assisted tunneling (TAT) is visible.

The hysteresis versus temperature (Figure 4.17) shows the onset of the paramagnetic regime at $T_B > 2.4$ K. The small hysteresis at 2.88 and 3.21 K is an artifact from the magnet. The transition from pure quantum tunneling to thermally assisted tunneling is also clearly visible. This crossover is field dependent and occurs at $\approx 0.7$ K for transitions at higher field and at $\approx 1.5$ K for those at low field. The steps from the relaxation out of excited levels are slightly shifted towards lower field, which is due to the transverse term $BS_z^4$ in the Hamiltonian. In principle the axial parameters $D$ and $B$ can be determined by fitting the energy levels $\varepsilon = -DS_z^2 - BS_z^4$. 
to the obtained data. In this case this was not possible because the molecule seems to have a more complicated Hamiltonian (see next paragraph).

Figure 4.18 shows the hysteresis and its derivative versus the sweep rate. The slope has been corrected by subtracting a polynomial. There are four equally spaced, interrelated steps at high field and three interrelated steps at low/zero field. These two sets of steps appear to be independent from another. From the spacing $\Delta H = 0.365$ T of the four high-field steps $D = 0.49$ K was obtained (assuming $g = 2$). These steps occur at 5.6 $\Delta H$, 6.6 $\Delta H$, 7.6 $\Delta H$ and 8.6 $\Delta H$, which is unusual and could be due to an intermolecular exchange $H_{ex} = JS_1 \cdot S_2$ as in Mn$_4$ dimers [50] ($J$ is the coupling constant between the spins $S_1$ and $S_2$ of two neighboring molecules). There are no ground state transitions of this molecule species at low or even negative field to confirm this idea. The fact that the transitions occur at non-integer multiples of $\Delta H$ but at regular intervals cannot be explained by considering only the axial terms of Equation 2.4.

![Figure 4.18: (a) Dependence on the sweep rate at 0.4 K; A polynomial background was subtracted; (b) Derivative of (a); The amount of magnetization that relaxes at this transition increases with decreasing sweep rate as expected from Equation 2.6.](image)

The sample was further investigated by applying constant transverse fields in different directions in the hard plane during the sweeps. The step at 0.8 T splits into two, three or four steps (as denoted in Figure 4.19 (a)) with a 90° periodicity for the two- and three-step features and 45° periodicity for the four-step feature. This splitting of the low field steps in a transverse field is due to a misalignment of the longitudinal field with the easy axis. The fact that there are two to four steps depending on the direction of the transverse field can be explained by four different molecules with their easy axes slightly tilted from the longitudinal direction to four different directions. The arrangement depicted in Figure 4.19 (b) illustrates the four-fold symmetry for
the two- and three-step splitting and eight-fold symmetry for the four-step splitting.

Figure 4.19: (a) Dependence on the angle of the transverse field in the hard plane at 0.4 K; (b) Schematic of the orientation of the easy axes of the molecule species that produce the splitting of the transition at 0.8 T

Figure 4.20: (a) Dependence on the angle of the longitudinal field in the x-y-plane at 0.4 K; (b) Schematic of the orientation of the easy axes of the molecule species that produce the splitting of the transition at 0.8 T

To clarify the alignment of the different molecule species the longitudinal field was rotated in the x-y-plane (Hall sensor plane). All steps (low and high field) move to higher longitudinal field
when rotating away from the assumed easy axis (from black/brown to green in figure 4.20 (a)).

This supports the idea that the easy axes of the low-field molecules point mainly in the same
direction as the easy axis of the high-field molecules, but with a small symmetric tilt. From
the schematic drawing (Figure 4.20 (b)) it can be seen that the 0.8 T step will always split into
two steps when rotating in the x-y- plane. The splitting increases towards 0° due to a higher
transverse component of the field.

Figure 4.21: (a) Dependence on the angle of the transverse field in the hard plane at 0.4 K;
(b) Oscillatory dependence of the relaxation rate on the angle of the transverse field

Figure 4.21 (a) shows the dependence of the high-field steps on the direction of the transverse
field in the hard plane. The step at 2.03 T (k = 6), 2.41 T (k = 7) and 2.77 T (k = 8) change
in height when the direction of the transverse field is rotated in the hard plane. The relaxation
rate $\Gamma$ (taken as $\Gamma = \Delta M / (M - M_S)$, $M_S$ is the saturation magnetization) of $k = 6, 7$ has
four-fold symmetry, superimposed by a one-fold symmetry due to a small misalignment of the
longitudinal field and in the case of $k = 6$ by a two-fold symmetry. A four-fold symmetry of
molecular origin has never been observed in Mn$_{12}$. Instead it could be due to a superposition
of two-fold symmetries of different isomers of the molecule as proposed by Cornia et al. [50]

Furthermore the dependence on the magnitude of the transverse field was investigated (Figure
4.22). The amount of magnetization that relaxes at zero field shows oscillatory behavior as
expected from the predicted oscillations of the tunnel splitting (Berry phase oscillations) [23].
According to Equation 2.8 the transverse Hamiltonian parameter $E = 0.083 \text{K}$ was determined
($D = 0.49 \text{K}$, $g = 2$). This has to be considered with care since $E$ and $D$ were determined for
different molecular species!
4.8 Mn$_{12}$-thiophencarboxylate monolayer

A schematic picture of the sensor is shown in Figure 4.23. The leads marked with $I$ are the current leads, those marked with $R_{xy}$ and $R_{xx}$ the voltage leads for the Hall voltage and longitudinal voltage respectively. Originally the two wide leads were supposed to be the current leads. This was changed due to a wiring problem in the probe. The field was applied in the Hall sensor plane along the x-direction (direction of the wide channel) for the magnetometry measurements and out of plane to characterize the sensor.
The change with field of both $R_{xy}$ and $R_{xx}$ cannot be explained by a misalignment of field and sensor plane, as this would result in opposite sign changes for positive and negative fields. The same is expected if the signals are due to the magnetic dipolar field of the sample as indicated in Figure 3.5. The symmetry and shape of the curve suggests that the signal is due to a magneto resistance (MR) effect. The MR is negative and could be due to either the applied in plane field or the dipolar field from the sample. The latter is unlikely since the resulting change in the Hall resistance, which is expected to be higher than the MR, cannot be seen in Figure 4.24 (a). Negative MR in narrow 2DEG channels is partly due to diffusive scattering at the edges of the channel [51]. This negative MR increases with decreasing current and temperature which can be seen from the difference between the red ($I = 10 \mu A$, $T = 6 K$) and the black ($I = 1 \mu A$, $T = 0.51 K$) curve and was also observed by Li et al. [32]. It is unusual that the negative MR persists even at high fields.
Chapter 5

Summary

Magnetic properties of six different Mn$_{12}$ compounds have been investigated by micro-Hall effect magnetometry at 0.4 to 6 K with sensors fabricated from high mobility 2DEG quantum well heterostructures and by high frequency electron paramagnetic resonance measurements. All compounds display the characteristic hysteresis and step-like relaxation of the magnetization separated by plateaus of slow relaxation below blocking temperatures between 1.5 and 3 K, which is a clear indication of single molecule magnetism. The compound Mn$_{12}$-thiophencarboxylate was identified as SMM by Lim et al. [53], but no magnetometry measurements in the mK regime had been performed on this compound. Furthermore, the new compounds Mn$_{12}$-biphenyl, Mn$_{12}$-parabromobenzoate, Mn$_{12}$-difluorbenzoate, Mn$_{12}$-trifluorbenzoate and Mn$_{12}$-diphenylphosphinate were for the first time identified as SMMs. Magnetometry measurements at temperatures down to the pure quantum regime are essential towards the understanding of the complex character of SMMs.

The crossover from pure quantum tunneling to thermally assisted tunneling of magnetization was observed in Mn$_{12}$-trifluorbenzoate and Mn$_{12}$-diphenylphosphinate. Furthermore oscillations in the tunneling probability with the magnitude of applied transverse fields were observed in some compounds confirming the theory of resonant tunneling of magnetization. The Hamiltonian parameters $D$ and $E$ were extracted from the data whenever possible and are in good agreement with the expected values for Mn$_{12}$ compounds. A dependence of the tunneling probability on the direction of the transverse field in the hard plane was investigated in Mn$_{12}$-diphenylphosphinate. For at least two of the compounds the existence of several molecular species within a single crystal was observed and their respective alignments investigated in detail. Isomerization has been known to have symmetry breaking effects [50] and can change the orientation of a molecule and affects its properties such as barrier height, transverse anisotropy etc. This study in combination with more detailed experiments on the structure of the samples can enhance the understanding...
and thus control of the synthesis of new SMMs. For deposition on surfaces in particular, it is necessary to know the exact structure of the molecules. An overview of the extracted parameters is given in Table 5.1.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$</th>
<th>$T_B$ [K]</th>
<th>$D$ [K]</th>
<th>$E$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_{12}$-thiophencarboxylate</td>
<td>$&gt;20^\circ$</td>
<td>$&gt;2.2$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Mn$_{12}$-biphenyl</td>
<td>$\approx20^\circ$</td>
<td>$&gt;3$</td>
<td>$0.65$</td>
<td>$0.04$</td>
</tr>
<tr>
<td>Mn$_{12}$-parabromobenzoate</td>
<td>$-$</td>
<td>$&gt;2.9$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Mn$_{12}$-difluorbenzoate</td>
<td>$-$</td>
<td>$&gt;1.9$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Mn$_{12}$-trifluorbenzoate</td>
<td>$-$</td>
<td>$&gt;1.5$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Mn$_{12}$-diphenylphosphinate</td>
<td>$&lt;2^\circ$</td>
<td>$&gt;2.4$</td>
<td>$0.49$</td>
<td>$0.083$</td>
</tr>
</tbody>
</table>

Table 5.1: Overview of the extracted parameters ($\delta$ is the misalignment between easy axis and longitudinal field).

One of the main challenges that was overcome in the micro-Hall magnetometry measurements was the lack of detailed knowledge about the orientation of the molecules in the crystal with regard to the macroscopic crystal features. To get high quality data it is essential to control the alignment of the molecule with respect to the applied magnetic fields. In the measurements the easy axes of the samples could be identified in-situ using the vector magnet system and the transverse field method. In some cases non-linearities in the Hall response of the sensor prevented the exact localization of the easy axis in the plane perpendicular to the sensor. In these cases the quantitative results, such as Hamiltonian parameters, could only be estimated. Determination of the orientation of the easy axis relative to macroscopic features of the crystal via spectroscopic techniques can help to improve the measurements as this knowledge would allow for a more sophisticated ex-situ alignment of the crystal, which, in combination with the in-situ control, can improve and accelerate the measurements. Furthermore advances in the growth of 2DEG QW heterostructures tuned to have less non-linearities will be helpful in this matter.

The most challenging experiment undertaken during this study was the measurement of a mono-layer of Mn$_{12}$ molecules attached to an Au surface. Magnetic hysteresis has never been observed in an individual SMM. The direct observation of hysteresis or even resonant tunneling of magnetization of spatially isolated SMMs on a surface would be the first proof that SMMs retain their characteristic properties as individual molecules and thus a giant step in both the understanding
of SMMs as well as their potential as bits in data storage or qbits in quantum computing. Two new sensors were designed for the measurement of out of plane and in plane magnetization respectively. To find the best design for the experiment the configuration yielding the highest Hall signal was identified by calculation of the magnetic dipolar field of the sample prior to the design. In principle the expected signal of several hundred nV can be detected. Noise levels of less than 100 nV have been achieved routinely with the setup. The measurement was planned, prepared and performed in a very short time frame and in the results there is no evidence of molecular magnetism in the sample. These results are by no means representative for the magnetic properties of a monolayer of SMMs but give an understanding of the properties of the new Hall sensor. With regard to the importance of the topic and the fact that, on one hand, many details during the sensor fabrication were not systematically developed and analyzed due to lack of time (layer design, success of monolayer deposition) and, on the other hand, there were few minor problems with major consequences on the measurement (wiring in the probe) which can easily be improved, this experiment should definitely be repeated. The fact that to date there is no evidence for the ordered deposition of SMMs on surfaces justifies the measurement geometry (hard plane field sweeps) yielding higher Hall signals than the geometry for the easy axis field sweeps. In case of evidence of an out of plane orientation of the easy axis, the geometry for easy axis field sweeps should nevertheless be optimized and additionally be used for the measurements.
Bibliography


[52] Fonin et al., unpublished.