Field effect controlled magnetism and magnetotransport in low dimensions
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Magnetic anisotropy is an intrinsic property of magnetic materials. The magnetization of a ferromagnet tends to align with certain preferential direction. Magnetic ion intercalated transition metal dichalcogenide is a family of layered materials that exhibits extremely large magnetic anisotropy. Depending on the element of intercalants, the resulting magnetic anisotropy can favor either the direction perpendicular to the lattice plane or within the lattice plane. In this chapter, we will focus on the magnetic measurement of the Mn intercalated tantalum disulfide with a stoichiometric ratio of $\text{Mn}_{1/4}\text{TaS}_2$. This material shows a giant magnetic anisotropy with an easy plane.
5.1 Introduction

5.1.1 Layered materials

Since the discovery of new physics on graphene and topological insulators, systems with hexagonal layers bound by van der Waals bonding have been refocused in the condensed matter physics society. Among them, the most well-known members are Xenes, carbides, nitrides, oxides, halides and transitional metal dichalcogenide.

Xenes refers to the monolayer of IVA group elements. The most famous one is the monolayer carbon, namely graphene. Ultrahigh mobility was achieved in graphene field-effect transistors (FET), which is of promise to be a good candidate of the next generation electronics [1]. Ever since that, monolayers of other elements in the IVA group have been discovered. A Silicene FET was prepared by depositing on Ag (111) film on mica substrate. Later the film was detached and flipped back to the top of SiO₂/Si wafer [2]. Germanene film was grown via molecular beam epitaxy on gold surface and then mechanically exfoliated [3]. Single layer of tin (stanene) was grown by molecular beam epitaxial (MBE) on Bi₂Te₃ (111) substrate [4]. Monolayer lead film was also been reported and the superconducting gap was measured [5].

One large group of the layered carbide (nitride) is called MAXene. It refers to a ternary system with a combination of transitional metal element (M), carbon or nitrogen (X) and a third element (A) in some specific compositions (M₂AX, M₃AX₂, M₄AX₃). It is useful in terms of energy storage [6]. The most widely used nitride is the hexagonal boron nitride (h-BN). Because of its highly insulating nature and easily cleavable characteristic, it has been used as insulating layer for fabricating nano-heterostructure [7, 8],

Layered oxides have been studied for decades in terms of their importance in energy storage. Lithium cobalt oxide is probably the material that is relevant to everyone because it is the cathode material for the battery inside our mobile phone and other portable devices [9]. In addition, hydrated sodium intercalated cobalt oxide is found to be superconducting [10].

Halogen elements can bond with oxygen or nitrogen atom and form covalent compound with transition metal elements, namely oxychloride and chlorine nitride. Intercalating alkali metal or applying ionic liquid gating can tune these materials into superconducting [11, 12]. Halogen elements can also form ionic compound directly with transition metal elements. For example, CrI₃ is a layered ferromagnetic insulator and when it is down to the monolayer limit, itinerant ferromagnetism emerges for monolayer while the magnetization is suppressed for bilayer film [13, 14].
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Recently, transitional metal dichalcogenide (TMD) attracts growing interests for their fascinating properties. TMD refers to a large family of compounds with formula MX$_2$, where M is transition metal atom (Mo, W, Ta, Nb, etc.) and X is chalcogen atom (S, Se or Te). Because of the large variation of the element selection, the electronic properties can vary from semiconducting (e.g. MoS$_2$ [15]), to semi-metal (e.g. WTe$_2$ [16]) till metallic (e.g. NbSe$_2$ [17]). They are also interesting in terms of optical properties. Because of the peculiar band structure that two minima at equal energies but different in momentum positions, different polarization will excite different valleys [18, 19].

Besides TMD, chalcogen elements also participate in forming topological insulators (M$_2$X$_3$) and thiophosphate (MPS$_3$). The former one has been widely studied since the emergence of the Dirac materials [20, 21] and the later one starts to be restudied for its interesting magnetic properties [22].

The quest of novel physics and promising application in “ultimate flatland” [23] has just started. Many more layered materials are ready to be discovered and new physical properties are also expected.

**Figure 5.1** Summary of layered materials. Different colors illustrate different material groups and are labelled with corresponding color in the legend.
5.1.2 Transition metal dichalcogenide

The study of TMDs has been carried on for decades. A wide range of interesting electronic, optical and mechanical properties has been discovered by researchers [24-26]. The isolation of monolayer graphene from bulk graphite [27] has opened up new opportunities for applications of atomically thin two dimensional (2D) materials. Although graphene has ultrahigh mobility up to $10^6 \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1}$, the linear dispersion relation near the Dirac point limits it as a semimetal with zero band gap. Therefore, the field effect transistor made by graphene has a very low on/off ratio. New materials with high mobility and energy gap are eager to be discovered. The large variety of TMD makes it a very interesting candidate.

Bulk TMDs, like graphite, can be regarded as stacking of monolayers with van der Waals attraction. It has been proved that they can be easily exfoliated into individual atomically thin layers due to weak interlayer coupling. As analogue of graphene, many monolayer TMDs have moderate band gaps of 1 to 2 eV, where the carrier density can be effectively tuned by the field effect [28, 29]. Monolayer TMDs can be directly grown by chemical vapor deposition method.

The structures of TMDs are shown in Figure 5.2. Each plane of transition metal atoms is sandwiched between two chalcogen atom planes (Fig. 5.2a), forming a hexagonal structure (Fig. 5.2b). Two type of polyhedrons are formed, which are hexagonal and trigonal prismatic coordination, respectively (Fig. 5.2c,d).

Depending on the stacking orders and metal atom coordination, TMD has three different polytypes: 1T, 2H and 3R as shown in Figure 5.3a. The repeating unit of each polytypes is one, two and three layers, respectively. The stacking geometry is better illustrated from the top view (Fig. 5.3b). The lattice constants are in the range of 3.1 to 3.7 Å for different materials and the interlayer spacing is around 6.5 Å. Because of its weak interlayer coupling, other intercalants can be inserted in between the layers. In this chapter, we will study the magnetism of manganese intercalated TaS$_2$ thin flake.

![Figure 5.2](image)

**Figure 5.2** (a) Side view of TMD layered structure (2-H), each transition metal layer (blue sphere) is sandwiched between two chalcogen layers (green sphere).
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Figure 5.3 (a) Schematic diagrams of three structural polytypes: 1T (tetragonal symmetry), same layer (in grey) repeats each other, M-X forms octahedral coordination; 2H (hexagonal symmetry) two unit layers (in grey and yellow) repeat one another, M-X forms trigonal prismatic coordination; 3R (rhombohedral symmetry), three different layers (in grey, yellow and cyan) repeat one another, M-X forms trigonal prismatic coordination. (b) Top views of layered TMD structure in one unit cell. For each repeating layer, one M plane (in big blue sphere) is sandwiched between two X planes (in small green sphere).

5.1.3 Types of magnetic anisotropy

There are several origins causing magnetic anisotropy. The first one is due to the crystal structure, hence is named magnetocrystalline anisotropy. If a ferromagnet takes more energy to be magnetized in certain directions, which is of the principal axes of its crystal lattice, then these axes are called hard axes, which means they are hard the be magnetized. At the same time, once they are magnetized, it is also difficult to be demagnetized that results in high coercivity. As a matter of fact, this type of ferromagnets is often be used as permanent magnets in applications, such as magnetic cores for transformers and inductors. To further strengthen the large anisotropy, rare earth elements are used for synthesizing the permanent magnets for the reasons that they possess large magnetic moments and strong spin-orbit interactions (SOC).

The microscopic origin of the magnetocrystalline anisotropy arises from the SOC. Although compared to the exchange interaction that causes the spontaneous
magnetization, SOC is a relatively weak effect; it does have significant impacts on the determination of magnetization direction. The spin of electrons interacts with the atoms of crystal via SOC, so that different atomic orbitals related to the particular crystal structure lead to different orientation of the spins. As a result, the magnetic moments from the spins are energetically favorable towards some directions: the easy axes.

Magnetic anisotropy is a prerequisite for hysteresis in ferromagnets. For magnetic isotropic materials, there are no preferential directions for the magnetic moment to lie on unless there is external magnetic field to do so, such as paramagnetic materials. If the crystal size is smaller than the magnetic domain, magnetic anisotropy energy \( (KV) \) can be relatively smaller than the influence of temperature \( (k_B T) \). Once the time interval \( (\tau_N) \) between two spin flips is shorter than the time of measurement \( (\tau_m) \), the magnetization behaves like a paramagnet, and the state is termed superparamagnetism although the magnetic susceptibility is much larger than the paramagnets. On the other hand, if \( \tau_m \ll \tau_N \), during the measurement, the magnetization will not flip and appear to be blocked in its initial state. The temperature at which \( \tau_m = \tau_N \) is called blocking temperature:

\[
T_B = \frac{KV}{k_B \ln \left( \frac{\tau_m}{\tau_0} \right)}
\]  

where \( K \) is the magnetic anisotropy density, \( V \) the volume, \( k_B \) the Boltzmann constant, \( \tau_0 \) the characteristic attempt time period of a material that spin flip takes.

When a ferromagnet is not perfectly spherical, the demagnetizing field that is created by the edge magnetic poles will be not equivalent, resulting in another type of magnetic anisotropy called shape anisotropy. In general, for thin film ferromagnet, the shape anisotropy will lead to an in-plane magnetization.

There is a presence of a symmetry breaking at material surface or interface. Hence, the orbital motion of electrons is affected and creates a surface anisotropy. The surface anisotropy is given by the sum of two terms, namely the surface contribution \( K_s/t \) and the volume contribution \( K_v \). If the film is very thin, the surface term dominates. Due to the perpendicular surface anisotropy, all magnetic moments point out of plane, leading to the perpendicular spontaneous magnetization.

Besides magnetic field, other external factor may cause change of magnetic susceptibility, such as mechanical stress. This effect is opposite of the magnetostrictive effect, so that the resulted magnetic anisotropy is called magnetoelastic anisotropy. In ferromagnets, applying a mechanical stress to the body will cause reorientation of the magnetization through magnetostrictive effect. The associated energy is proportional to the magnitude of magnetic moment polarization \( \sigma \) and a material dependent magnetostriction constant \( \lambda \) that represents the maximum response of the strain to the magnetic field, which is described as
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\[ E = \frac{3}{2} \lambda \sigma \cos^2 \theta, \]  
\[ (5.2) \]

where \( \theta \) is the angle between magnetization and the stress direction.

The last but not least type of anisotropy occurs in the bilayer interface between a ferromagnetic and an antiferromagnetic thin film. The antiferromagnetic film is hard to be magnetized, while for the ferromagnetic film is comparably easy. The magnetization curve of the ferromagnetic film will be shifted due to the exchange anisotropy. Microscopically, this is because the spin of the ferromagnet is strongly exchange-coupled to the proximate antiferromagnet. Since the antiferromagnet has little magnetization response to the external magnetic field, the spin in the ferromagnet is pinned to the direction of the spin in the antiferromagnet. Therefore, an extra energy cost is necessary for reversing the magnetization of the ferromagnetic film. The difference (in magnetic field) between the centers of the hysteresis loop for the ferromagnetic film before and after attached to the antiferromagnetic film is called the exchange bias.

5.2 Concepts

5.2.1 Magnetocrystalline anisotropy

Ferromagnets contain magnetic domains that within each small region, the magnetization direction is the same, while may not be identical to other regions. This is why it is only necessary to apply a weak magnetic field to fully magnetize a ferromagnet. In contrast to paramagnets, where magnetic field is for aligning all magnetic moments, the effect of magnetic field on ferromagnets is to rotate the magnetization direction of individual domains.

Between two domains with different magnetization direction, there is a symmetry breaking in the domain wall. Considering two spins at the interface lie at an angle \( \alpha \) with respect to each other. This will produce an energy cost (for small \( \alpha \))

\[ E = JS^2 \alpha^2. \]
\[ (5.3) \]

Figure 5.4 The relative directions of the material easy axis with respect to magnetization and external magnetic field. The angles are denoted as \( \theta \) and \( \phi \), respectively.
It seems unlikely that domains can exist. However, there is some other interaction that prohibits the spins from aligning to each other, which is called the magnetocrystalline anisotropy. Originated from the crystal structure, it is in general easy to magnetize the crystal along certain axis that is termed as magnetic easy axis. In case of hexagonal system (Mn$_{1/4}$TaS$_2$) that is uniaxial with a six-fold rotation symmetry c-axis, the associated anisotropy energy can be written as

$$E_a = \sum_{n=1}^{\infty} K_n \sin^n \theta = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \cdots + K_n \sin^n \theta,$$

which the lowest order terms are given by

$$E_a = K_1 \sin^2 \theta + K_2 \sin^4 \theta,$$

where $K_1$, $K_2$, are anisotropy constants and $\theta$ is the angle between magnetization $M$ and easy axis (Fig. 5.4).

The minima in the energy with respect to $\theta$ satisfy

$$\frac{\partial E_a}{\partial \theta} = 0,$$  

and

$$\frac{\partial^2 E_a}{\partial \theta^2} > 0.$$

Therefore, we could map the phase diagram of the easy magnetized directions as a function of $K_1$ and $K_2$, shown in Figure 5.5.

In addition, the magnetostatic potential energy (Zeeman energy) of a ferromagnet under magnetic field $H$ is given by

$$E_p = -\mu_0 HM \cos(\phi - \theta)$$

where $\phi$ is the angle between external magnetic field $H$ and easy axis.

![Figure 5.5 Basic phase diagram based on the calculation from $K_1$ and $K_2$ values of an uniaxial ferromagnet.](image-url)
For a simple single-domain ferromagnet, the energy of the system with respect to an external magnetic field is a sum of these two terms

\[ E = E_a + E_p. \]  

Substituting Eq. 5.9 by Eq. 5.5 and Eq. 5.8, we have the expression of the energy in the system

\[ E = K \sin^2 \theta - \mu_0 H M \cos(\phi - \theta). \]  

(5.10)

Eq. 5.10 can be normalized to

\[ \eta = \frac{E}{2K} = 1 - \frac{1}{4} \cos 2\theta - \frac{\mu_0 H M}{2K} \cos(\phi - \theta). \]  

(5.11)

By defining

\[ h = \frac{\mu_0 M H}{2K}. \]  

(5.12)

Eq. 5.11 can be rewritten to

\[ \eta = 1 - \frac{1}{4} \cos 2\theta - h \cos(\phi - \theta). \]  

(5.13)

For each \( \theta \), we can plot the \( h \)-dependent of the \( E \) as a function of \( \phi \). The results are summarized in Figure 5.6a. Applying Eq. 5.6 and Eq. 5.7, we can find out the energy minima point. Consequently, we have the corresponding values of \((\phi - \theta)\). Then \( M/M_s \) can be derived from

\[ \frac{M}{M_s} = \cos(\phi - \theta). \]  

(5.14)

Since \( h \) is proportional to external magnetic field \( H \), by plotting \( M/M_s \) vs. \( h \), the angle dependence of magnetization is illustrated in Figure. 5.6b.

It is clear to see how hysteresis loop and the coercivity evolve. This model is called the *Stoner-Wohlfarth model*. It implies that even without domain wall motion, single domain magnet can have hysteresis in the magnetization curve due to domain rotation.

**Figure 5.6** Stoner-Wohlfarth model of the numerically simulated ferromagnetic magnetization curves. (a) The 3-D wire surface plot of the relations between \( \eta \), \( \phi \) and \( h \) for several characteristic angles between \( M \) and \( H \) direction. (b) The derived \( M/M_s \) vs. \( h \) shows hysteresis loops because there are two energy minima at each \( h (H) \) value.
The anisotropy constant $K$ is related to three terms: the surface, volume and shape anisotropy:

$$K = \frac{2K_S}{t} + K_V - \mu_0 M^2.$$  \hspace{1cm} (5.15)

The surface term is proportional to $1/t$, indicating that it can dominate in ultrathin film. The volume term is only obvious in strained or uniaxial single crystals. The shape anisotropy term is from the contribution of the dipolar energy, normally dominating for thick films and leads to the in-plane magnetization. Therefore, the magnetic properties of a monolayer film are expected to be different from the bulk.

From the itinerant ferromagnetism point of view, the atoms at the surface have smaller numbers of nearest neighbors compared with those in bulk. The reduction of the coordination number leads to the narrowing of the bandwidth and increases the density of states at the Fermi level, hence the opportunity that Stoner criterion being satisfied, which enhances the propensity of long range magnetic ordering.

### 5.2.2 SQUID Magnetometry

Superconducting quantum interference device (SQUID) magnetometry is one of the most effective and sensitive ways of measuring magnetic properties. In particular, it is the only method that allows direct determination of the overall magnetic moment of a sample in absolute units.

**Figure 5.7** Systematic diagram of the mechanism that how does the SQUID work. The left panel shows the schematic illustration of the SQUID pick-up coil as well as the sample. The right panel displays the signal corresponding to the movement of the sample straw.
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The working mechanism is based on the Josephson effect that was established by Brian David Josephson in 1962, which the electrical current density through a weak electric contact between two superconductors depends on the phase difference $\Delta \varphi$ between two superconducting wave functions. The time derivative of $\Delta \varphi$ is correlated with the voltage across the weak contact.

The magnetic results in this chapter were measured from a commercial SQUID magnetometer system produced by Quantum Design, San Diego. The equipment type is Magnetic Properties Measurement System (MPMS) XL-7. The image and basic sample preparation procedures will be discussed in Appendix. Here, we will focus on the principle of the SQUID.

Figure 5.7 shows the schematic diagram of the working principle of SQUID. The magnetic signal of the sample is obtained via a superconducting pick-up coil with 4 circles (in red). Sample straw was moving up and down along the magnetic field direction alternatively by a step-motor. The changing of the position in turn causes a change of the magnetic flux. A screening current hence generates in the pick-up coil to cancel the external flux. This will transfer the magnetic flux of the sample into a radio frequency voltage signal (in green). With the movement of the sample, the voltage response to the full measurement range can be extracted. Therefore the center of the sample and the amplitude of the magnetic flux can be calculated by fitting the curve (in blue). The core of the SQUID system is the pick-up coil, which is made of some superconducting metals, such as niobium (Nb). In order to maintain the superconductivity, the pick-up coil is located outside of the sample chamber and is placed in the liquid helium bath at constant 4.2 K.

The sample is located in the center of a superconducting solenoid (in different from the pick-up coil) producing magnetic fields up to 7 Tesla. The sample space is filled with helium at low pressure at temperatures ranging from 2 to 400 K. The sensitivity is up to $10^{-8}$ emu in reciprocating sample oscillation (RSO) mode, which is equivalent to the saturation magnetization of six billionth mm$^3$ of iron. The whole system is program and can be continuously operated.

5.3 Experiments

5.3.1 Crystal growth

A systematic crystal growth procedure was carried out to obtain large single crystal. First, the stoichiometric $\text{Mn}_{1/4}\text{TaS}_2$ powder was obtained by heat treatment of Mn, Ta and S powders in an evacuated quartz tube at 900 °C. The tube was open in glove box and the obtained powder was ground in agate mortar. The powder was sealed in quartz tube under vacuum again and heated at 900 °C for another 5 days. As a result, the pure $\text{Mn}_{1/4}\text{TaS}_2$ powder was synthesized and characterized by powder X-ray diffraction.
The single crystal Mn$_{1/4}$TaS$_2$ was grown using chemical vapor transport (CVT) with iodine as transport agent. The ratio between the iodine and the polycrystalline Mn$_{1/4}$TaS$_2$ powder is 10:1. Same to the synthesis of powder sample, 1 gram of as-prepared powder and 0.1 gram iodine were mixed and sealed in an evacuated quartz tube with a length of $\sim$20 cm. The tube was placed in a two-zone tube furnace with the hot zone at $\sim$1000 °C and the growth zone at $\sim$900 °C. Depending on the growth time, the single crystal shape can vary from large-flat thin flake to small-thick crystals with clear edge and corner. Because Mn$_x$TaS$_2$ exists in many phases, in reality, small amounts of impurity phases may exist. So small adjustment of the stoichiometry is necessary, namely $0.25 \times N$ (0.96$<N<1.15$).

### 5.3.2 X-ray diffraction

In order to confirm the crystallinity of the measured sample, x-ray diffraction experiment was performed. The data were collected using a Bruker D8 advance powder diffractometer. It employs Cu target as anti-cathode.

![Diffraction Setup](image)

**Figure 5.9** Principle of x-ray diffraction. (a) The diffraction measurement setup. (Bruker©) (b) Multiple reflections of a wave of an angle of incidence that equals the Bragg condition of constructive interference for a set of lattice planes.
The x-ray is generated with the following process. First the K-shell electrons are knocked out with the incident high-energy electron. The maximum accelerating voltage is 40 kV and the electron probe current range is up to 40 mA. The vacancies can be filled by electrons from the L-shell (or M-shell), radiating x-ray with a wavelength of 1.54 Å for the characteristic Kα spectrum. According to the Bragg’s law:

\[ n\lambda = 2d\sin\theta. \]  

where \( \lambda \) is the wavelength of the incident light and \( \theta \) is the angle between the incident light and the direction normal to sample plane. The lattice distance \( d \) can be calculated accordingly (Fig. 5.9).

From the x-ray diffraction spectrum, we can read out the information about the crystal, such as the crystal plane direction. With further refinement, we can even derive the precise lattice parameters and atomic positions. Figure 5.10a shows the full-range XRD spectrum from a single flake of Mn$_{1/4}$TaS$_2$ sample. The sample was placed on top of a suspended kapton tape in order to minimize the signal background from the substrate. The data was collected with an angle step size of 0.02° from 10° to 90° and interval during time of 0.1 s.

The inset of Figure 5.10a shows the zoom-in of the spectrum at the main peak position \( \theta \approx 13° \). The data was re-collected with an angle step size of 0.001° (highest resolution) from 13.4° to 14.0°. We noticed that there are a number of fringes close to the main peak position. This is due to the highly crystalline and ordered structure that lead to interference of x-ray. The interlayer spacing can be calculated from the interference fringe period by

\[ d = \frac{\lambda}{2\omega \cos(\theta_{\text{Bragg}})}. \]  

where \( \omega \) is the full width half maximum (FWHM) (in radian), \( \lambda \) wavelength of the incident light, \( d \) the interlayer distance, \( \theta_{\text{Bragg}} \) the angle of the Bragg peak that the analysis is taken place. The above equation is similar to the Scherrer formula.

**Figure 5.10** (a) Full spectra of the x-ray diffraction of Mn$_{1/4}$TaS$_2$ single crystal, where (002) and (004) crystal planes are resolved clearly as peaks at 13.7° and 28.0°. The inset shows the zoom-in of the 2θ range for the (002) plane, where fringe
In Figure 5.10b, we analyze the fringe peak at the main peak position corresponding to the (002) plane. The FWHM at $\theta_{\text{Bragg}} = 13.722^\circ$ and $\omega = 0.00408^\circ$ (in degree). So by taking into account the wavelength $\lambda = 1.542$ Å of the Cu Kα ray, we can calculate the interlayer spacing between two TaS$_2$ layer is $\sim 3.29$ Å.

5.3.3 Electron diffraction

In order to study the atomic position of the intercalated Mn atoms and the crystallinity of the Mn$_{1/4}$TaS$_2$ samples, we performed the selected area electron diffraction (SAED) measurement in a transmission electron microscope (TEM). Figure 5.11 shows the SAED image recorded at incident electron energy of 200 keV.

For TEM measurement, a thin edge region was required for witnessing the transmitted or diffracted electrons. Large Mn$_{1/4}$TaS$_2$ single crystal was peered off till thin flake and placed on top of a copper grid. The diffraction pattern exhibits the expected superlattice reflections midway between the structural reflections of the host lattice, indicative of the $2 \times 2$ ordering of the intercalated atoms.

![Figure 5.11](image)

The selected area electron diffraction (SAED) pattern of the thin Mn$_{1/4}$TaS$_2$. The color circles guide the position of the diffraction dots for particular planes. White and yellow line illustrate the $2 \times 2$ superlattices. (The data from [30] was reanalyzed.)

5.4 Results and discussion

5.4.1 Magnetic susceptibility measurement

For ferromagnets and antiferromagnets, Curie-Weiss law describes the temperature dependence of susceptibility as

$$\chi = \frac{C}{T - T_C}.$$  

$C$ is the Curie constant and is described in a form of (in CGS unit)

$$C = \frac{N\mu_0\mu_{\text{eff}}^2}{3k_B}.$$
where $N$ is the number of atoms per unit volume, $k_B$ the Boltzmann’s constant, $\mu_0$ the vacuum magnetic permeability, $\mu_{\text{eff}}$ the effective magnetic that is related to the Bohr magnetron $\mu_B$ by $\mu_{\text{eff}} = g\sqrt{J(J+1)}$ ($g$ the Landé g-factor, $J$ the angular momentum quantum number).

The Curie-Weiss law is valid for describing susceptibility for $T \gg T_C$. However, because this theory is based on mean-field approximation, just like the Kondo theory (in chapter 3), the linear dependence is diverted in the vicinity of $T_C$. By plotting $1/\chi$ vs. $T$, we are able to fitting the high temperature with a linear dependence, and derive the phase transition temperature according to:

$$\frac{1}{\chi} = \frac{T - \theta}{C}$$

(5.20)

where $\theta$ is called the Weiss constant.

We measured $\chi$ of the ferromagnetic state for $B \perp c$ at 0.01 T (Fig. 5.12a) and the Weiss temperature was fitted to be $\theta \approx 105$ K (Fig. 5.12b). Interestingly, for $B \parallel c$, the exchange interaction of $\text{Mn}_{1/4}\text{TaS}_2$ changes to antiferromagnetic, shown as the turning point of $\chi$ at 85 K measured at 3 T (Fig. 5.12c) and anomaly of $1/\chi$ diverted from linear dependence at similar temperature. The Weiss constant $\theta \approx 105$ K was the same as $B \perp c$, implying the same paramagnetic state above its critical temperature.

**Figure 5.12** Temperature-dependent magnetic susceptibility for in-plane (a) and out-of-plane magnetic field (c). The plot of inverse magnetic susceptibility vs. temperature for in-plane (b) and out-of-plane magnetic field (d). The linear fits of the high temperature part from the Curie-Weiss law showing the critical temperature $\theta$ (Weiss temperature).
5.4.2 Determination of the phase transition temperature from Arrott plot

The critical phase transition temperature can also be determined from another approach. According to the Ginzburg-Landau mean field theory of magnetism, the free energy of a ferromagnetic material close to a phase transition can be written as

\[ F(M) = -HM + aT - T_C M^2 + b M^4, \]  

(5.21)

where magnetization \( M \) is the order parameter, \( H \) the applied magnetic field, \( T_C \) the critical temperature and \( a, b \) material constants. When \( T \) is close to the phase transition temperature \( T_C \), Eq. 5.21 can be rewritten as

\[ M^2 = \frac{1}{4bM} \frac{H}{T} - \frac{a}{2bT - T_C}. \]  

(5.22)

Therefore, by plotting \( M^2 \) vs. \( H/M \), we get a series lines for different \( T \). The one without an intercept corresponds to the dependence that \( T = T_C \). This method of deriving the phase transition temperature is called Arrott plot.

Figure 5.13a shows the temperature-dependent magnetization curve of the Mn\(_{1/4}\)TaS\(_2\) with in-plane magnetic field (\( B \perp c \)). The saturation magnetization decreases with decreasing temperature and the saturation magnetic field \( H \) decreases as well. The corresponding Arrott plot was shown in Figure 5.13b. It is clear to see that intercept of the \( H/M \) vs. \( M^2 \) becomes zero at temperature between 100 K to 105 K, which is referred as the Curie temperature.

Similar analysis of magnetization curve can be performed in the case of under out-of-plane magnetic field (\( B \parallel c \)), when Mn\(_{1/4}\)TaS\(_2\) sample orders antiferromagnetically (Fig. 5.14). We extracted the phase transition temperature to be between 100 K and 120 K, which is the same as ferromagnetically order situation.

![Figure 5.13](image)

**Figure 5.13** (a) The field dependence of magnetization with in-plane magnetic field at various temperatures for Mn\(_{1/4}\)TaS\(_2\). (b) The Arrott plot (\( M^2 \) vs. \( H/M \)) of the measured data. It is clear to see that Curie temperature is between 100 K to 105 K.
5.4 Results and discussion

Figure 5.14 (a) The field dependence of magnetization with out-of-plane magnetic field at various temperatures for Mn_{1/4}TaS_{2}. (b) The Arrott plot \((M^2 \text{ vs. } H/M)\) of the measured data. It is clear to see that Curie temperature is between 100 K to 120 K.

We further studied the magnetization curve carefully (Fig. 5.15a). In the ferromagnetically ordered state \((B \perp c)\), we observe a very small coercivity at low temperature, which is roughly only 100 Oe at 5 K (Fig. 5.15b). This indicates that the ferromagnetic state is magnetically very soft.

Soft magnet means that it is easy to be magnetized and also demagnetized. In general, soft materials have broad domain walls with small anisotropy energy \(K\), which are easy to move.

Figure 5.15 (a) The temperature-dependent magnetization curve for in-plane magnetic field \((B \perp c)\). (b) The zoom-in of the low magnetic field region. (c) The field dependence of magnetization under large magnetic field. The measured magnetization at each field \(M\) is normalized to the saturation magnetization \(M_s\).
There are two types of domain walls: the Bloch wall and the Neél wall. The former one refers to the situation that magnetization rotates in the plane parallel to each other, like a stack of clocks with hands indicating different orientations. Considering Mn$_{1/4}$TaS$_2$ has layered structure with easy plane, we presumably ascribe it to the Neél type of domain wall, where the domain boundaries lie between each layer. Based on this assumption, the observed magnetic anisotropy may be thickness dependent.

5.4.3 Field dependence of magnetization

In order to understand the change of $M$ with respect to the different angles between the external $B$ field and sample easy plane, we performed field dependent magnetization measurements at different $θ$.

Figure 5.16 shows the magnetization curve of Mn$_{1/4}$TaS$_2$ sample under a series of $θ$. At $θ = 0^\circ$ ($B \perp c$), we have the ferromagnetic state, where $M$ saturates rapidly due to the alignment of the Mn dopant ions. Afterward, $M$ decreases slightly with further increasing $B$ field due to the diamagnetic contribution from the non-magnetic TaS$_2$ layers and little contribution from the attached kapton tape and plastic straw. At $θ = 90^\circ$ ($B \parallel c$), Mn$_{1/4}$TaS$_2$ enters the antiferromagnetic state, where $M$ grows linearly with the increase of $B$.

This might looks similar to the temperature-dependent of magnetization curve for $B \perp c$ (Fig. 5.15a). However, there are several differences. First, the slope of $M$ vs. $B$ curve changes significantly for each angle, because the response of the magnetic moments of Mn to the effect of $B$ varies a lot for each $θ$. In contrast, Figure 5.15a shows the decrease of the $M$ due to the influence of temperature, while the sample remains ferromagnetic ordered. As a result, the slope of $M$ vs. $B$ curve is more or less the same for each $θ$ after $M$ saturates.

Figure 5.16 Field dependence of magnetization at 5 K respect to each angle between $B$ and sample $ab$ plane (easy plane). The $M$-$H$ curves measured at each angle $θ$ are illustrated with different markers and colors, where $0^\circ$ and $90^\circ$ denote $B \parallel ab$ and $B \perp ab$ plane, respectively.
5.4.4 Temperature dependence of magnetization

The aforementioned angle-dependent magnetic anisotropy can also be illustrated in the following phase diagram. Figure 5.17 shows the field-dependent magnetization behavior of Mn$_{1/4}$TaS$_2$ as a function of temperature and angle in a polar configuration.

$M$ is in general larger at low temperature (red) than high temperature (blue) because thermal vibration will cancel out the effect from the $B$ field for the alignment of the magnetic moments. The $M$ shows symmetry of $\pi$ that the behavior is identical for $\theta = 0^\circ$ and $180^\circ$ ($90^\circ$ and $270^\circ$ as well).

![Figure 5.17 Phase diagram (in polar plot) of the temperature and angle dependence of magnetization at different magnetic fields: 7 T (a), 5 T (b), 3 T (c), 1 T (d), 0.5 T (e), 0.2 T (f), 0.02 T (g) and 0.01 T (h). The absolute magnetization scale is the same for all measurements, normalized to the maximum measured value and illustrated as a color bar from 0 to 1.](image)
When the external $B$ field is strong enough ($B = 7$ T), magnetic moments will be aligned to the field direction anyway, so there is no difference in $M$ among each angle $\theta$, i.e. $M(\theta=0°) \approx M(\theta=90°)$. We slowly decreased the magnitude of $B$, at low temperature, the difference in $M$ between $\theta = 0^\circ$ and $\theta = 90^\circ$ started to emerge, indicating as the color separation. This is due to the magnetic anisotropy energy that overcomes the Zeeman energy, giving $M$ a preferential direction.

The magnetic anisotropy is mainly from the magnetocrystalline anisotropy because of the high-ordered layer structure and the strong spin-orbit interaction in Mn$_{1/4}$TaS$_2$. The magnetic anisotropy reached maximum at $B = 0.02$ T, demonstrating the intrinsic magnetic property of Mn$_{1/4}$TaS$_2$ with easy plane.

### 5.4.5 Magnetic phase diagram

To virtualize the evolution of the magnetic phase in Mn$_{1/4}$TaS$_2$, we plotted the normalized magnetization in a contour figure as a function of temperature and magnetic field for four $\theta$ angles.

Figure 5.18 shows the resulted magnetic phase diagrams. At $\theta = 0^\circ$, the maximum of $M$ appears at the top-right corner, which implies the emerging AFM phase. With further decrease of temperature, the gain of Zeeman energy cannot compensate the cost of anisotropy energy. Magnetic moments are difficult to be aligned out-of-plane due to strong in-plane anisotropy exchange interaction, referring as the decrease of $M$ (Fig. 5.18a).

![Figure 5.18 Phase diagrams of the temperature and magnetic field dependence of magnetization at four $\theta$ angles: $0^\circ$ (a), $5^\circ$ (b), $30^\circ$ (c) and $90^\circ$ (d). The absolute magnetization scale is the same for all measurements, normalized to the maximum measured value and illustrated as a color bar from 0 to 1.](image)
The effect that $M$ decreases with decreasing temperature becomes weaker with the increase of $\theta$. From 0° to 90°, we can see that the $B$ field needed to fully align magnetic moments decrease, indicating the spins become less robust and easier to rotate. The emerging AFM phase quickly vanishes with a slightly increase of $\theta$, for the reason that a small in-plane component of $B$ is enough to fix the magnetization within the lattice plane.

5.4.6 The appearance of spin-flop phase at low temperature

One interesting phenomenon we encountered occasionally is the appearance of spin-flop behavior below 30 K. When the sample was placed slightly away from $\theta = 0°$, at temperature, the sample shows time reversal symmetry broken. The sample exhibits one metastable saturated magnetic state before a spin-flip transition occurs and reaches to the stabilized magnetic state.

![Figure 5.19](image1.png)

**Figure 5.19** The field dependence of magnetization of s with out-of-plane magnetic field at various temperatures. The measured magnetization at each field $M$ is normalized to the saturation magnetization $M_s$.

![Figure 5.20](image2.png)

**Figure 5.20** Illustration of the spin-flip transition of the process from B to C in Figure 5.19.
In Figure 5.19, from A to B, spins of layer X (in Fig. 5.20) are aligned to the $B$ field, while spins of the adjacent layer Y rotate accordingly and are coupled to antiferromagnetically to the neighboring interlayer spins. This weak AFM coupling will be destroyed by further applying strong $B$ field. From B to C, those spins in layer Y that are antiferromagnetically coupled to spins in layer X flip 180° to the $B$ field direction, resulting in a jump of the $M$. Consistently, the magnitude of $M$ increases doubly. From C to D, spin structure of ferromagnetically aligned spins in both X and Y layers are stable and $M$ does not change too much until $B$ becomes not large enough to fix spin direction of both layers the same. From D to E, spins start to randomize within each layer and $M$ decreases significantly.

When temperature further increases, this metastable state becomes unstable and spins are aligned to the field direction directly. As we see from Figure 5.19b, no intermediate state is seen and sample behaves like a normal ferromagnet with easy plane.

### 5.4.7 Spin structures of the Mn$_{1/4}$TaS$_2$

The aforementioned metamagnetism has also been reported in Cr$_{1/3}$NbS$_2$ [31] and Mn$_{1/4}$NbSe$_2$ [32]. From the single crystal X-ray diffraction data, the distance between the nearest Mn ions is almost the same between the two along $c$-axis and in the same plane, which are 6.27 Å and 6.66 Å, respectively. It is reasonable to assume that the TaS$_2$ layer reduces the direct exchange interaction between Mn ions in the $c$-axis direction. Therefore, Mn ions in the van der Waals gap sites form ferromagnetically ordered planes that develop into helical spin structure along the $c$-axis.

![Figure 5.21 Schematic illustration showing evolution of spin structure in Mn$_{1/4}$TaS$_2$ with in-plane magnetic field.](image)
Figure 5.22 Schematic illustration showing evolution of spin structure in Mn$_{1/4}$TaS$_2$ with out-of-plane magnetic field.

When in-plane external $B$ field is applied, the helical structure is gradually destroyed and finally evolves into a field-induced ferromagnetic state (Fig. 5.21). On the other hand, out-of-plane $B$ field first changes the spin structure from helical to conical. With further increasing $B$ field, eventually it reaches the field-induced ferromagnetic state (Fig. 5.22).

5.5 Supplementary information

5.5.1 Temperature dependence of magnetization

The temperature dependence of the magnetization can be reviewed in another perspective. Figure S5.1 shows the contour plot of field-induced magnetization under various $B$ fields with respect to different angles.

In general, the magnetization is quite low below 100 K, because the material is in the paramagnetic phase. Above 100 K, when $\theta$ is close to 90° the material is in the ferromagnetic phase as indicated by the growing large magnetization. When $\theta$ is close to 0°, the magnetization behavior is much complex. At large field, the magnetization first increases with decreasing temperature, and then slightly decreases due to antiferromagnetic interaction (Fig. S5.1a-d).
Figure S5.1 Phase diagram of the temperature and angle dependence of magnetization at different magnetic fields: 7 T (a), 5 T (b), 3 T (c), 1 T (d), 0.5 T (e), 0.2 T (f), 0.02 T (g) and 0.01 T (h). The absolute magnetization scale is the same for all measurements, normalized to the maximum measured value and illustrated as a color bar from 0 to 1.

5.5.2 Field dependence of magnetization with perpendicular magnetic field

Figure S5.2 shows the magnetization curve of Mn_{1/4}TaS_2 under out-of-plane magnetic field at different temperature. The linear $M$ vs. $B$ behaviors below 60 K indicate that the magnetic moments of Mn are antiferromagnetic ordered.

Considering the saturation field is very small with respect to the in-plane $B$ field (Fig. 5.15), magnetic moments are lay within the lattice planes. Due to the thermal fluctuation, initially the spins are oriented randomly within the $ab$ plane. Applying external $B$ field will rotate the spin towards the same direction. The layered crystal structure leads to the helical spin structure and it is in analogous to the Bloch type of domain wall. In this sense, the thicker the film is, the less robust the domain wall will be. Therefore, the coercivity force should be smaller. In chapter 6, we will study the electrical transport properties of Mn_{1/4}TaS_2 approaching the two-dimensionality limit.
Figure S5.2 The field dependence of magnetization with out-of-plane magnetic field at various temperatures. The measured magnetization at each field \( M \) is normalized to the saturation magnetization \( M_s \).

5.5.3 Field-dependent magnetization as a function of temperature

Figure S5.3 shows the temperature dependence of magnetization under various \( B \) field. The magnetic ordered state is highly anisotropic as evidenced by comparing the data of \( B \perp c \) and \( B \parallel c \). A sharp increase of \( M \) is observed at \( B \perp c \). Instead, cusp-like transitions occur for \( B \parallel c \) below certain temperature. Rounding of the transitions near the ordering temperature is observed upon increasing \( B \) field for both cases as expected for ferromagnets due to spin fluctuations close to \( T_C \).

\( M \) saturates much easier with \( B \perp c \) than \( B \parallel c \). A rather smaller \( M \) is seen for the lowest applied \( B = 0.01 \) T, because from Figure 5.15b, we know the finite coercivity field \( H_c = 200 \) Oe is necessary to fully saturate the \( M \). In addition, \( M \) decreases slightly for \( B > 0.2 \) T for the diamagnetic contribution of the TaS\(_2\) layers. This is in consistent with the field dependence measurement (Figure 5.15c)
Figure S5.3 The field dependence of magnetization with out-of-plane magnetic field at various temperatures. The measured magnetization at each field $M$ is normalized to the saturation magnetization $M_s$.

5.6 Summary

Magnetic elements intercalated transition metal dichalcogenides are of great interests in application of spintronics. Because their layered structure, it is possible to access atomically thin film that shows new physics and technological potential. In this chapter, we investigate Mn intercalated TaS$_2$ with 25% doping concentration. It shows $2 \times 2$ superlattice, with Mn ions intercalated between two TaS$_2$ lattices. The material exhibits magnetic ordering below 100 K with the resulted magnetization highly anisotropic. Under perpendicular magnetic field, the exchange interaction between two adjacent Mn ions favors antiferromagnetic ordering, while in-plane field can easily align the magnetic moment within the lattice plane. On the other hand, there is a narrow region on the phase diagram where $\theta$ is close to 90°, the material shows a spin-flop transition, inferring a helical spin structure along the $c$-axis.
5.7 References


5.7 References


