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Magnetization and magnetoresistance in iron intercalated transition metal dichalcogenides

by

Jesse Choe

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APPROVED, THESIS COMMITTEE:

Emilia Morosan, Director Professor of Physics and Astronomy, Chemistry, Materials Science and NanoEngineering & Electrical and Computer Engineering

Kevin F. Kelly, Chair Associate Professor of Electrical and Computer Engincering

Doug Natelson Professor of Physics and Astronomy, Electrical and Computer Engineering & Materials Science and NanoEngineering

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ABSTRACT

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The understanding of magnetism in strongly correlated electronic systems is a vital area of research. Not only is it linked to other phenomena like high temperature superconductivity in the cuprates and iron pnictides, but magnetic materials have been used in electronics since before the computer. As it becomes harder to prop up Moore's law by increasing the density of transistors, mankind must look towards new methods to improve technology or risk stagnation. Research into alternative materials for technology, such as transition metal dichalcogenides, is a promising direction of research to maintain the rate of technological improvement. Our work focuses on the effect of iron intercalation in TiS₂. Single crystals of Fe_xTiS₂ ($0 \le x \le 1$) were grown using vapor transport. Anisotropic susceptibility and magnetization measurements of the samples were measured, showing ferromagnetism and sharp switching behavior in the magnetization. Finally electrical transport measurements were taken, both with and without field. Measurements of magnetoresistance for x = 0.2 and 0.3 show large magnetoresistance (up to ~ 60%) and an atypical 'bowtie' shape.

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Chapter 1

Introduction

1.1 Overview

The Stone Age. The Copper Age. The Iron Age. The materials mankind use not only define our technology, but name our history as well. Now we are in the silicon age, the plastic age, but are still limited by the materials we use. Recently, two dimensional materials been placed in the scientific spotlight. The material properties and small form factors of materials like graphene and transition metal dichalcogenides (TMDs) make them technologically and scientifically interesting materials. Much of the interest in these materials has been concentrated on monolayers of graphene due to its low electrical resistance and high mechanical strength [6]. However, as the race towards thin films progresses, an often overlooked aspect is doping in quasi-2D systems. While in graphene, dopants and defects tend to destroy the desirable properties of the system [7], in bulk TMDs, doping opens up the parameter space of a class of materials which has already found a variety of applications from chemical catalysis [8], lubricants [9], electrodes for batteries [10], and in nanotechnology [11, 12].

This paper will look at the specific case of iron intercalation in TS_2 (T = Ti, Ta) TMDs. Their magnetization, which can show sharp switching behavior seen first by Morosan *et al* [3], as well as the magnetoresistance in the system, which is strongly dependent on the iron concentration and can change by orders of magnitude with a small change in iron [5], will be investigated.

1.2 Transition Metal Dichalcogenides

1.2.1 Properties of Transition Metal Dichalcogenides

Layered TMDs, TX_2 (T = transition metal, X = S, Se, or Te), form a quasi-2D system of X-T-X layers bound together weakly by van der Waals forces. They bear a crystallographic similarity to graphite: strong intra-layer bonding; weak inter-layer bonds; easy intercalation; and high anisotropy. In contrast to graphite and graphene, the TMDs form a whole family of materials with their transport properties filling the entire spectrum from insulators to metals. In addition, superconductivity (SC) is observed in many TMDs and antiferromagentism can be seen in the undoped metals [13].

The crystal structure of the TMDs strongly affects the physical properties of the material. The polytype nomenclature is used to denote the different structures a TMD may exist in. It consists of a number, which denotes the layers required for a unit cell along the c axis, and a letter which denotes the symmetry of the system: trigonal (T), hexagonal (H), or rhombohedral (R) [14]. For some polytypes, this is insufficient information (eg. 2H and 4H), in which case a second lower case letter is used to uniquely identify the stacking sequence [14]. Examples of two of the most common polytypes are shown schematically in figure 1.1b-c. A clear example of the importance of polytype is in the TaS₂ system. For this system, the 2H-TaS₂ polytype shows a CDW transition at 78 K and a superconducting temperature at 1 K , while the 1T-TaS₂ polytype only has a CDW transition at 140 K [15, 16].



Figure 1.1 : TX_2 polytypes (unit cell outlined in black) result from different coordination T-X₆ polyhedra (octahedral or trigonal prismatic) and the stacking of the TX_2 layers. (a) One layer in a trigonal unit cell forms the 1T polytype, while (b) in the 2H polytype, the layers are staggered along the c axis, resulting in a hexagonal unit cell with 2 layers per unit cell. Other TX_2 polytypes include 3R (rhombohedral), 4H, and 6R.

1.2.2 Intercalation and Doping of the Transition Metal Dichalcogenides

While graphene is comprised entirely of carbon atoms, TMDs are made of two atoms, a transition metal (T = Ti, V, Zr, Nb, Mo, Hf, Ta, W) and a chalcogen (X = S, Se, Te), and the combinations of these two atoms, coupled with the different polytypes, yields a family of over 40 known TMDs [14]. With TMDs, finding the desired property can be as simple as changing a constituent atom. From insulators like HfS₂, to the semiconductor MoS₂, to semi-metals like WTe₂ or TcS₂, to metals like NbS₂ or VSe₂ [14] the variety in the TMDs is vast. But this array of possibilities is further increased through doping.

In addition to simply doping on an atomic site [17], The layered nature of TMDs opens up the possibility of intercalation of dopants between layers as a way to change material properties. Depending on the TMD and the intercalant, the end result can vary from inducing superconductivity (Cu, Pd, Fe, and K)[18, 19, 20, 21]; to creating magnetic properties through magnetic intercalants (Fe, Cr, V, Mn, Co, and Ni) [3, 22, 23]; to large organic molecules pushing the system towards the 2D limit (amine, or pyridine) [24]; to non-magnetic metals creating a more 3D system (Li, Na, K, Ca, Cu, Ag, and Au) [25]; to the creation of a misfit structure with no long range periodicity (Ln, Pr, Sm, Nd, Gd, Dy, and Er)[26, 27, 28, 29].

1.3 Charge Density Waves

A common phenomenological feature in the transition metal dichalcogenides is the charge density wave (CDW). Charge density waves are a periodic redistribution of the conduction electrons in a material coupled with an periodic lattice shift in the atomic sites. This is arises in materials with lower dimensionality (like the TMDs) where it becomes energetically favorable to open a gap in the Fermi surface by modulating the lattice potential [30]. The modulation in lattice potential in turn results in a modulation of the conduction electron density as represented in figure 1.2a. Due to their quasi-2D nature, the TMDs are often host to CDW behavior.

The theory for charge density waves was first developed in a 1D system. These principles are then be applied to higher dimensions, with the exception of some exotic explanations of CDW formation, such as the Jahn-Teller effect, which will be covered at the end of this section.

In one dimension, CDWs are explained by the Peierls transition. Consider a 1D metal at T = 0 K without electron-electron or electron-phonon correlations, as shown in figure 1.2a. The atoms form a periodic lattice, with a constant electron density, $\rho(r) = \rho_0$. Its band structure follows that of the free electron theory $E = \frac{\hbar^2 k^2}{2m}$. By adding a periodic lattice distortion of period λ where $\lambda = \frac{\pi}{k_F}$, with k_F being the Fermi wave vector, there are two main effects. It introduces a modulation in the conduction electron density, $\rho(r) = \rho_0 + \rho_1 \cos(2k_F r + \varphi)$, and it induces a gap at the Fermi level (figure 1.2b). This gap removes bands from the Fermi level,



Figure 1.2 : (a) Real space depiction of the conduction electron density and atomic positions for a 1D metal (top, blue) and a 1D charge density wave(bottom, black). (b) Band structure of a 1D metal (top, blue) and a 1D charge density wave (bottom, black).

creating an insulating state. If no states above k_F are occupied, the overall energy is lowered by the opening of the gap. When non-zero temperature is considered, electrons may be excited to states above the gap, reducing the benefit of, and therefore the size of, the lattice distortion. At a finite temperature, denoted as the Peierls temperature T_p the distortion is no longer energetically favorable and a second order phase transition occurs [31]. This modulation in electronic density can be achieved through an electron-phonon interaction shifting the atomic lattice sites (and therefore the associated charge) inducing the modulation in the conduction electron density.

In CDW systems the existence of Fermi surface nesting could also drive the CDW state. This is explained by the Lindhard response function (equation 1.1).

$$\chi(\mathbf{q}) = \int \frac{d\mathbf{k}}{(2\pi)^d} \frac{f_{\mathbf{k}} - f_{\mathbf{k}+\mathbf{q}}}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}}$$
(1.1)

When large areas of the Fermi surface can be connected by the wavevector \mathbf{q} , this

is known as Fermi surface nesting. When the nesting vector $\mathbf{q} = 2k_f$, the Lindhard function will diverge. This results in an unstable system, and a reconstruction of the Fermi surface (via a CDW changing the electronic properties of the system) occurs.

The 1D description can generally be applied in the 2D case; however, in some materials (e.g. TiSe₂), different mechanisms are required to explain the emergence of the CDW. The two common explanations are the excitonic insulator and the Jahn Teller effect.

In an excitonic insulator, a material with a small number of charge carriers will form excitons, bound states of holes and electrons, if the band gap is smaller than the exciton binding energy. This removes charge carriers from the Fermi surface and creates an insulating state. For an indirect gap, this results in a non-zero exciton momentum, and in turn a CDW transition [32, 33].

The band Jahn-Teller effect is a structural distortion which breaks the degeneracy of the ground state energy [34]. Typically this involves a higher energy coordination, shifting atomic positions towards a lower energy coordination which create attractive potentials. This differs from Fermi surface nesting as the distortion is driven by the real space coordination [34].

Finally, the Peierls theory assumes the wavefunction of the conduction electrons, match that of the lattice distortion, but this is not necessarily true. Figure 1.2a shows the phase and wavelength of the conduction electron modulation perfectly aligned with the lattice modulation. This is known as a commensurate charge density wave (CCDW); however, CDWs do not have to be commensurate. Often at higher temperatures, a CDW will go through an incommensurate phase (*e.g.* the periodicity or phase of the electron periodicity does not match that of the atomic periodicity), known as an incommensurate charge density wave (ICDW). In certain materials (*e.g.* $1T-TaS_2$), a material may also go through a nearly commensurate CDW (NCDW) state, where the conduction electron periodicity is *nearly* aligned with the atomic periodicity. Both of these states (ICDW and NCDW) are attributed to pinning of the CDW to impurities and as temperature is lowered, a material (if exhibiting the states) will move from ICDW to NCDW to CCDW.

1.4 Magnetism in Non-Interacting Spins

Long range magnetic order in undoped TMD systems is typically absent, and paramagnetic or diamagnetic behavior dominates. However, when doping a TMD with a magnetic atom, variety of magnetic properties can arise. Additionally, just as CDW and SC behavior appear to be closely related [19, 35], magnetism and SC appear to have a deep connection as well. Therefore, it is prudent to cover the origins and types of magnetism and long range magnetic order before discussing the specific case of magnetism in the TMDs.

Consider the case of non-interacting spins. Magnetization is defined as the change of free energy, F, with applied magnetic field, H.

$$M(H) = -\frac{\partial F}{\partial H} \tag{1.2}$$

The susceptibility is defined as the derivative of magnetization with respect to field.

$$\chi = \frac{\partial M}{\partial H} \tag{1.3}$$

If this problem is treated classically, the Bohr-von Leeuwen theory can be applied to show that the magnetization falls out of this equation [36]. Since magnetism cannot be accounted for classically, it is by necessity a quantum phenomenon. Therefore, electrons need to be treated as quantum mechanical particles. For magnetism, the important attributes are an electron's orbital momentum (L) and spin (S), which when combined produces the total angular momentum (J = L + S).

The orbital angular momentum (L) can be derived from the classical picture of an electron moving in an orbit of radius r.

$$\mu_L = iA = -\frac{e}{T}\pi r^2 \tag{1.4}$$

$$L = mvr = m\frac{2\pi}{T}r^2 \tag{1.5}$$

Combining equations 1.4 and 1.5 and quantizing L in the form $n\hbar$ gives

$$\mu_L = -\mathbf{n}(\frac{\hbar e}{2m}) = -\mathbf{n}\mu_B \tag{1.6}$$

here the quantity, $\mu_B = \frac{\hbar e}{2m}$, the Bohr magneton which describes an electron's intrinsic spin momentum, has been introduced. Next the orbital angular momentum (L) and the spin angular momentum (S) are defined in terms of momentum operators and the Bohr magneton.

$$\underline{\mu_L} = -g_L \mu_B \underline{L} \tag{1.7}$$

with $g_L = 1$ and $\underline{L} = \sqrt{l(l+1)\hbar}$

$$\underline{\mu_S} = -g_S \mu_B \underline{S} \tag{1.8}$$

with $g_S \approx 2$ and $\underline{S} = \sqrt{s(s_1)\hbar}$.

Finally, since \underline{L} and \underline{S} are coupled and give rise to the total angular momentum $(\underline{J} = \underline{L} + \underline{S})$, the total magnetic moment μ_J is written as

$$\underline{\mu_J} = -g_J \mu_B \underline{J} \tag{1.9}$$

with $\underline{J} = \sqrt{J(J+1)\hbar}$.

For equation 1.9, g_J is dependent on the configurations of the electrons in the orbital.

$$g_J = \frac{3}{2} + \frac{1}{2} \frac{S(S+1) - L(L-1)}{J(J+1)}$$
(1.10)

In order to determine this configuration, Hund's rules are applied (section 1.4.1). Which describe the filling of orbitals for all but the heaviest ions [36].

1.4.1 Hund's rules

Hund's rules outline simple sequential steps to follow for placing n electrons into orbitals of an ion. These assumptions generally hold, though atoms with large spinorbit coupling will break them [36]. For a free ion with n valence electrons, there will exist 2(2l+1) states (where 0 < n < 2(2l+1) (since for a given l, 2l+1 states exist and two electrons of opposite spin can occupy a single state).

Hund's 1st Rule

Hund's first rule states that to minimize energy, one must maximize S. Due to the Pauli exclusion principle, maximizing S involves placing a single electron into each state, and simple addition suggests that they should be aligned parallel to each other. As shown in figure 1.3a where the dashed arrow (blue) shows the correct placement of the 5^{th} electron and the crossed out arrow (red) is incorrect.

Hund's 2^{nd} Rule

If there exist $n \ge (2l+1)$ states, then a second electron must be added occupied states, where Hund's second rule applies. Adding to half filled states should be done in a way which maximizes L, as shown in figure 1.3b.

Hund's 3rd Rule

Finally, the third rule deals with spin-orbit coupling in the system. Consider the total angular momentum, J. Its two extrema are when L and S are orientated in the same direction (L+S) and when they are anti-parallel (|L-S|). The coupling is represented by a term in the Hamiltonian, $\Lambda(L \cdot S)$. The sign of Λ is related to the filling of the shell, being positive for shells less than half full (when J = |L-S|) and negative for those over half full (J = L+S). Hund's third rule then is that for shells less than half full, J = |L-S|; while for shells more than half full, J = L+S [36].



Figure 1.3 : Examples of (a) Hund's first rule, (b) Hund's second rule. The dashed arrow (blue) shows correct electron placement, while the crossed out arrow (red) shows an incorrect placement

Now that Hund's rules have been spelled out, the magnetic susceptibility for the different scenarios can be considered. Rewriting the magnetic susceptibility (equation 1.3) as the molar magnetic susceptibility

$$\chi_{mol} \sim -\frac{\partial^2 E_n}{\partial H^2} \tag{1.11}$$

and taking the equation for the energy of the system.

$$\Delta E_n = \frac{e^2}{8mc^2} H^2 \langle n | \sum_i (x_i^2 + y_i^2) | n \rangle + \mu_B \mathbf{H} \cdot \langle n | \mathbf{L} + g \mathbf{S} | n \rangle + \sum_{n' \neq n} \frac{|\langle n | \mu_B \mathbf{H} \cdot (\mathbf{L} + g \mathbf{S}) | n' \rangle|^2}{E_n - E_{n'}}$$
(1.12)

equation 1.12 can be split into its three main constituents:

$$\Delta E_{n1} = \frac{e^2}{8mc^2} H^2 \langle n | \sum_i (x_i^2 + y_i^2) | n \rangle$$
 (1.13)

$$\Delta E_{n2} = \mu_B \mathbf{H} \cdot \langle n | \mathbf{L} + g \mathbf{S} | n \rangle \tag{1.14}$$

$$\Delta E_{n3} = \sum_{n' \neq n} \frac{|\langle n | \mu_B \mathbf{H} \cdot (\mathbf{L} + g \mathbf{S}) | n' \rangle|^2}{E_n - E_{n'}}$$
(1.15)

and considered individually as three scenarios are considered.

1.4.2 L=0, S=0

The simplest scenario to consider is that of a fully filled band which has no spin or orbital angular momentum (L = 0, S = 0). The first term, equation 1.13, is only remaining contribution to the ground state energy.

$$\Delta E_0 = \frac{e^2}{8mc^2} H^2 \langle 0|\sum_i (x_i^2 + y_i^2)|0\rangle = \frac{e^2}{12mc^2} H^2 \langle 0|\sum_i r_i^2|0\rangle$$
(1.16)

Note that $\sum_i (x_i^2 + y_i^2) \sim \frac{2}{3} \sum_i r_i^2$ for a spherical shell. Assuming this system remains in its ground state, plugging equation 1.16 into equation 1.11 leads to the Larmor diamagnetic susceptibility.

$$\chi_{mol} = -\frac{e^2}{6mc^2} \langle 0|\sum_i r_i^2|0\rangle \tag{1.17}$$

Where $\chi_{mol} \approx -0.79 Z_i \times 10^{-6} \text{cm}^3/\text{mol}$. Thus Larmor diamagnetism is negative and of the order of $10^{-5} \text{cm}^3/\text{mol}$.

1.4.3 J=0, L=S \neq 0: Shell one short of half filled

For the case of J = 0 (which occurs when the shell is one electron short from being half filled), the second (*i.e.* the linear) term, equation 1.14, still vanishes, but the first and third remain.

$$\chi_{mol} = \left[2\mu_B^2 \sum_{n \neq 0} \frac{|\langle 0|\mathbf{H} \cdot (\mathbf{L}_{\mathbf{z}} + g\mathbf{S}_{\mathbf{z}})|n\rangle|^2}{E_n - E_0} - \frac{e^2}{4mc^2} H^2 \langle 0|\sum_i (x_i^2 + y_i^2)|0\rangle\right]$$
(1.18)

The second term is the Larmor diamagnetism from equation 1.17. The first term is known as Van Vleck paramagnetism, and is of opposite sign to the diamagnetic susceptibility (that is, it favors aligning parallel to the applied field). In this case, the magnetic behavior will depend on the interplay between the two different terms in equation 1.18 or if an excited state is close to the ground state, more complicated behavior is expected [36].

1.4.4 $J \neq 0$: Curie Paramagnetism

In the case of $J \neq 0$, the linear term of equation 1.12 does not vanish, and is typically so large that it dominates the behavior of the system to the point that the second and third terms can be safely ignored.

Returning to the original definition of magnetization in equation 1.2 and plugging in the statistical form of the free energy

$$F = -kT\ln Z \tag{1.19}$$

and writing the partition function as

$$Z = \sum_{m_J} e^{-x} \tag{1.20}$$

where $x = g_J J \frac{\mu_B H}{kT}$, the magnetization takes the form

$$M = \frac{\partial}{\partial H} \left[\sum_{m_J} e^{-x} \right] \tag{1.21}$$

the summation term can be rewritten using the geometric series

$$\sum_{i=-n}^{n} x^{i} = x^{-n} \frac{x^{2n+1} - 1}{x-1} = \frac{x^{n+1} - x^{-n}}{x-1}$$
(1.22)

resulting in

$$M(x) = M_0\left[\frac{2J+1}{2J}\coth(\frac{2J+1}{2J}x) - \frac{1}{2J}\coth(\frac{1}{2J}x)\right] = M_0B_J(x)$$
(1.23)

with $M_0 = Ng_J J \mu_B$. Equation 1.23 gives the magnetization M as a function of the Brillouin function B_J .

The two energy limits of this equation are now considered. When the temperature dominates the energy scale (x < 1) and when the magnetic field dominates (x > 1). In the case of x < 1, that is, the temperature much greater than the applied field, performing a Taylor expansion on $\operatorname{coth}(x)$ leads to

$$M(\frac{\mu_B H}{kT}) \approx N \frac{[g\sqrt{J(J+1)\mu_B}]^2}{3kT} H$$
(1.24)



Figure 1.4 : (a) Plot of Brillouin function. (b) Schematic of χ vs. T. (c) Schematic of $1/\chi$ vs. T.

dividing by susceptibility gives χ (as in equation 1.3).

$$\chi(T) = \frac{N\mu_B^2}{3k} \frac{p_{eff}^2}{T}$$
(1.25)

Where $p_{eff} = g\sqrt{J(J+1)}$ is the effective number or $\mu_{eff} = g\sqrt{J(J+1)}\mu_B$, the effective moment. Combining constants leads to

$$\chi_{mol} = \frac{1}{8} \frac{p_{eff}^2}{T} = \frac{C}{T} [\text{emu/mol}]$$
(1.26)

giving the Curie law, where $C = \frac{p_{eff}^2}{8}$ is the Curie constant.

On the opposite end of the energy scale is x > 1, the field much stronger than the temperature. In this case the Brillouin function goes to 1, and $M \approx M_0$.

$$M(H) \approx gJ = \mu_{sat}[\mu_B/\text{atom}]$$
 (1.27)

In this scenario, all ions are aligned with the field and have the maximum (*i.e.* saturated) value.

So far, discussion of contributions to the magnetism have been limited to moments on the ions. There is however, another source of magnetic moments which must be addressed before considering electron-electron interactions: the conduction electrons. Conduction electrons will contribute to magnetism in two ways. The spins will contribute to a phenomenon known as Pauli Paramagnetism, while the orbital momentum will result in Landau diamagnetism.

1.4.5 Pauli Paramagnetism

Consider the conduction band of a metal in the absence of an applied field (in standard quadratic form $(E = \frac{\hbar^2 k^2}{2m})$, an equal distribution of electrons with opposite spins is expected. By adding an applied field, this distribution will shift, with the energy band for parallel spins (+) lowering and the anti-parallel (-) band increasing. The resulting energy in each band will be shifted from the original by $E_{shift} = gS_z\mu_BH$. Since g = 2 and $S_z = \pm \frac{1}{2}$ for electron spins, a shift of $\mu_B H$ for each band occurs, resulting in an overall shift of $2\mu_B H$. In general a quadratic form cannot be assumed and the electron density must be taken into account.

$$M = \mu_B (n_+ - n_-) \tag{1.28}$$

Where n is the number of electrons per unit volume and is given by

$$n_{\pm} = \int d\varepsilon g_{\pm}(\varepsilon) f(\varepsilon) \tag{1.29}$$

with $g(\varepsilon)$ as the density of levels

$$g_{\pm} = \frac{1}{2}g(\varepsilon \mp \mu_B H) \tag{1.30}$$

and f is the Fermi function

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}$$
(1.31)

with μ as the chemical potential.

It can be shown [36] that the resulting magnetization is

$$M = \mu_B^2 H g(\varepsilon_F) \tag{1.32}$$

and therefore

$$\chi = \mu_B^2 g(\varepsilon_F) \tag{1.33}$$

this gives the Pauli paramagnetism. It's important to note that unlike Curie's law (equation 1.26), Pauli paramagnetism is (practically) independent of temperature. Additionally, in the case of free electron theory, it will be of the same order as the

diamagnetic susceptibilities (e.g. much smaller than Curie's Law). Finally, due to its relation to $g(\varepsilon_F)$, χ_{Pauli} will be proportional to the density of states at the Fermi level.

1.4.6 Landau Diamagnetism

Finally consider the orbital motion of the conduction electrons. In an applied field, the orbital motion of conduction electrons gives rise to Landau diamagnetism. In the case of free electrons in a material [36]

$$\chi_{\text{Landau}} = -\frac{1}{3}\chi_{\text{Pauli}} \tag{1.34}$$

however, since the Landau, Pauli, and Larmor susceptibilities are all temperature independent, these phenomenon are often measured as a single value χ_0 the temperature independent susceptibility.

1.5 Magnetism and Long Range Magnetic Order

So far, the magnetism in the absence of interactions between the moments has been considered. By introducing interactions, a variety of magnetic states including long range magnetic order can occur. There are two primary methods of moment interaction: dipole and exchange interactions. The magnetic dipole interactions are typically of the order of ≈ 1 K, which is comparatively small for most materials. Exchange interactions, on the other hand, can be vital and are split into several categories: direct, indirect, itinerant, and superexchange. Exchange interactions refer to moment coupling to the overlap of electron orbitals. Direct exchange occurs through direct overlap of the electrons' wavefunctions. Indirect exchange is mediated through a coupling of the f electrons and the conduction electrons, like in RKKY interactions [37]. Itinerant exchange is mediated through conduction electrons. Superexchange is mediated through non-magnetic ions, and is of importance in oxides.

1.5.1 Ferromagnetism

The first form of magnetism discovered and still the most important form is ferromagnetism (FM). This state is characterized by magnetic order occurring (below a critical temperature T_C) in the absence of an applied field, that is, the system orders spontaneously. While this also occurs in antiferromagnetism (AFM), in FM, the spins align parallel to each other, whilst in AFM, they align antiparallel. The FM ordering through the mean field approach will be investigated, the Curie-Weiss law derived and the concepts of domains and hysteresis for ferromagnetic systems discussed.

In mean field, the Hamiltonian is written as:

$$\mathcal{H} = -\sum_{ij} I_{exc} \mathbf{J}_{\mathbf{i}} \cdot \mathbf{J}_{\mathbf{j}} + g\mu_B \sum_{i} \mathbf{J}_{\mathbf{i}} \cdot H$$
(1.35)

where I_{exc} is the exchange coupling between the spins, while $\mathbf{J}_{\mathbf{i}}$ is the response to the applied field H.

Writing an effective mean field \mathbf{H}_{eff} such that

$$\mathcal{H} = -g\mu_B \sum_{i} \mathbf{J}_{i} \cdot (H + \mathbf{H}_{eff})$$
(1.36)

where

$$\mathbf{H}_{eff} = \lambda \mathbf{M} \tag{1.37}$$

leads to

$$M = M_0 B_J(y) \tag{1.38}$$

notice this is the same form as for the paramagnetic case in equation 1.23; however, y is dependent on both H and M.

$$y = \frac{gJ\mu_B(H+\lambda M)}{kT} \tag{1.39}$$

such that

$$M = \frac{1}{\lambda} \left(\frac{kT}{gJ\mu_B}y - H\right) \tag{1.40}$$

this give equation 1.38 as a function of y. However, equation 1.39 shows that y is a function both H and M. However, setting the boundary condition that at y = 0, the slopes must be equal gives

$$\frac{M}{M_0} = B_J(y) \approx \frac{J+1}{J} \frac{y}{3} \tag{1.41}$$

$$M = \frac{1}{\lambda} \left(\frac{kT}{gJ\mu_B}y - H\right) \tag{1.42}$$

at T_C , this becomes

$$\frac{kT_C}{\lambda g_J \mu_B J} = \frac{J+1}{3J} M_0 = \frac{J_1}{3J} g_J \mu_B \tag{1.43}$$

leading to

$$T_C = \lambda \frac{(g_J \mu_B)^2 J(J+1)}{3k} = \lambda \frac{\mu_{eff}^2}{2k}$$
(1.44)

additionally, take equation 1.39 and 1.41 and apply it in the limit of small H and large T.

$$\frac{M}{M_0} \approx \frac{J+1}{3J} \frac{g\mu_B J}{kT(H+\lambda M)}$$
(1.45)

Plugging in equation 1.44.

$$\frac{M}{M_0} \approx \frac{T_C}{\lambda M_0} \frac{H + \lambda M}{T} = \frac{T_C}{T} \frac{H}{\lambda M_0} + \frac{T_C}{T} \frac{M}{M_0} \Rightarrow M(1 - \frac{T_c}{T}) \approx \frac{T_C H}{\lambda T}$$
(1.46)

Gives for small H and T >> T_C

$$\chi = \frac{M}{H} = \frac{C}{T - T_C} \tag{1.47}$$

where $C = T_c/\lambda$. Equation 1.47 is known as the Curie-Weiss law and is used to describe the magnetic ordering of many materials.

At high temperatures (*i.e.* $T \gg T_c$), $1/\chi$ vs. T is linear and both C and T_C can be extracted from the slope and intercept.

$$\frac{1}{\chi} = \frac{1}{C}T - \frac{T_C}{C} \tag{1.48}$$

However the mean field calculations which lead to equation 1.47 were made for $T \gg T_C$, and the Curie-Weiss law breaks down when $T \sim T_C$. In this regime, the mean

field theory used to derive the Curie-Weiss law fails due to short correlations and low temperature fluctuations which are neglected in mean field. This results in the correction.

$$\chi = \frac{C}{T - \theta_W} \tag{1.49}$$

Where θ_W is the Weiss temperature, which would be T_C without the aforementioned fluctuations, but is typically higher. From C the effective moment is found.

$$C = \frac{p_{eff}^2}{8} \tag{1.50}$$

$$\mu_{eff} = p_{eff} \cdot \mu_B = \sqrt{8C}\mu_B \tag{1.51}$$

Finally, since real data deviates from the Curie-Weiss law at low temperatures (figure 1.6c), the Arrott method is used to accurately determine T_C (Figure 1.6d). The Arrott method involves taking the derivative of free energy with respect to magnetization and plotting M^2 vs. H/M at different temperatures. The temperature that goes through the origin is the critical temperature.

When measuring magnetization, M(T), a difference between the zero field cooled (ZFC), and field cooled (FC) measurements is seen. When field cooling the domains orientate as it is cooled below T_C ; however, when the sample is zero field cooled that is, cooled without an applied field, then measured on warming with low field, the domains are locked in place until thermal vibrations are large enough to move the domains (figure 1.6a).

Hysteresis and Domains

While magnetic ordering occurs in ferromagnets without an applied field, on the macro scale, this magnetization is hard to detect. This is due to domains. When a ferromagnet goes below T_C , the spins order ferromagnetically in small regions known as domains. The domains; however, need not be aligned with each other and result in a weak magnetization. These domains are a result of the competition between dipole interactions and the exchange energy. While a fully polarized (*i.e.* single domain)

system favors the exchange energy, it is quite unfavorable for the dipole energy. To reduce dipole energy, we can create domains which point in different directions. This reduces the dipole energy, but increases the exchange energy. However, the exchange energy is only increased for spins near the walls of the domains, resulting in an overall decrease in energy. Additionally, much like the overall dipole energy can be reduced by breaking up the sample into domains, the large exchange energy due to an abrupt boundary between domains can be reduced by creating domain walls. These walls are areas between domains where the spins slowly cant from one orientation to another. Since the exchange energy will be reduced the more gradual the rotation is, barring all other effects, this wall would stretch over the whole sample. However, crystals have anisotropy that creates an 'easy' axis of magnetization which the spins prefer to orientated for. This limits the canting in the domain walls and thus their size.

Domains also result in the hysteresis seen in the magnetization vs. field plots (figure 1.5). In weak fields, the spins not aligned with the field begin to cant increasing magnetization. As field increases the walls begin to move as spins at the edges of aligned domains begin joining the domains. As this occurs, even if the field is removed, pinning to defects can prevent a return to the original state. With increasing field, whole domains align with the field, and eventually, all domains are merged into one single domain and reach a saturation magnetization M_{sat} . Removal of the field at this point reduces the field to a remanent value, larger than the initial value, but lower than M_{sat} . Application of field in the opposite direction results in the same process occurring. Together, this all results in the hysteresis curve seen in figure 1.5.



Figure 1.5 : Typical hysteresis curve shown for a ferromagnetic sample, sketches of domains inset.

1.5.2 Antiferromagnetism

Much like ferromagnetism, antiferromagnetism (AFM) in materials is characterized by magnetic ordering below a critical temperature (for AFM T_N the Néel temperature). However, in AFM materials the ordering is anti-parallel. Since the spins align antiparallel to each other, a bipartite lattice, two lattices with the spins on each aligned

$$H = \lambda H_A \cdot \sum_{i \in A} S_i + \lambda H_B \cdot \sum_{i \in B} S_i i$$
(1.52)

giving two coupled equations

$$M_A = M_0 B_J \left(-\frac{g_J \mu_B J \lambda M_B}{kT}\right) \tag{1.53}$$

and

$$M_B = M_0 B_J \left(-\frac{g_J \mu_B J \lambda M_A}{kT}\right) \tag{1.54}$$

with equal and opposite magnetizations. Resulting in

$$M = M_0 B_J \frac{g_J \mu_B J \lambda M}{kT} \tag{1.55}$$

above T_N , the Curie-Weiss law (equation 1.49) still applies. The difference is that for AFM $\theta_W < 0$, while for the FM case $\theta_W > 0$ (figure 1.6c).

The final thing to note about AFM vs. FM ordering is the differences in susceptibility below the critical temperature. For the FM material, χ has two different curves depending on the applied field H it was put under while cooling, due to the hysteresis from domains (see section 1.5.2). For the AFM material, the two different curves below the critical temperature are still an effect of H, but with respect to its direction in relation to the orientation of the spins. When the field is aligned perpendicular to the direction of the spins, the spins cant, but this does not change the magnetization as the canting strength is constant. When the field is aligned parallel to the spins, as the temperature increases, more spins aligned anti parallel to the field are likely to have enough thermal energy to flip and align with field. Thus when the field is parallel to the spins, the T < T_N magnetization increases with temperature (figure 1.6).

1.5.3 Magnetoresistance

At the intersection of transport and magnetization lies magnetoresistance (MR). Magnetoresistance is simply the change in resistance of a material in response to an applied



Figure 1.6 : (a) Zero field cooled (ZFC) and field cooled (FC) susceptibility for a ferromagnetic material (b) χ_{\parallel} and χ_{\perp} denoting applied field parallel and perpendicular to the spins' orientation in an antiferromagnetic sample. (c) diagram of typical $1/\chi$ vs. T behavior for the CW law. (d) Arrott plots for determining T_C.

magnetic field. In regular metals, this effect is quite small. For example in copper, the change in magnetoresistance at room temperature is around 0.25% [38]. And indeed, even bismuth, which shows one of the strongest magnetoresistive responses, there is only about an 18% increase in a field of 24 T [39].

Thankfully, this is not all there is to magnetoresistance in materials. In many materials, unexpectedly high magnetoresistive values have been discovered. While all these effects result in large magnetoresistances, the constituent material and underlying physics changes, necessitating names for the different phenomena (which mostly take the form of *adjective for large* magnetoresistance). Three examples will be covered: giant magnetoresistance (GMR), colossal magnetoresistance (CMR), and a newly discovered phenomenon in WTe₂. However, it is important to note that these are just a few examples and other examples such as anomalous magnetoresistance (AMR), tunneling magnetoresistance (TMR), and extraordinary magnetoresistance (EMR) also exist.

While not the first to be discovered, giant magnetoresistance has arguably had the most impact. Discovered independently in 1988 by Albert Fert and Peter Grünberg, it went on to win a Nobel Prize in 2007 [40]. GMR arises in alternating layers of magnetic and non magnetic materials, electrons with different spins experience different resistances due to the differences in the density of states for the spin directions [40]. The ability to create materials with larger magnetoresistances, led to the creation of more sensitive hard drive read heads, allowing smaller bits to be used, leading to higher density disks, and therefore, larger capacity hard drives.

Colossal magnetoresistance is found in the manganite perovskites, $T_{1-x}D_xMnO_3$, where T is a trivalent lanthanide cation (La), and D is a divalent alkaline earth (Ca, Sr, Ba) [41], the pyrocholores (*e.g.* Tl₂Mn₂O₇ [42]), and in the spinels (ACr₂Ch₄; A = Fe, Cu, Cd; Ch= S, Se, Te [43]) [41]. In these materials, at the right doping levels, the ground state is ferromagnetic and the ferro-to-paramagnetic transition is accompanied by a large increase in resistivity and potentially the MR as well [41, 44]. Recently, Ali *et al.* discovered what appears to be a new magnetoresistive effect in the semimetal WTe₂ [45]. It exhibits magnetoresistance of a form similar to other semimetals like graphite and bismuth, with the resistance showing quadratic field dependence. However, the magnetoresistance of WTe₂ does not saturate up to 60 T [45], unlike graphite and bismuth which saturate at relatively low fields [46, 47]. With the applied field perpendicular to the *ab* plane, the magnetoresistance reaches up to 13,000,000% in fields up to 60 T. The very large magnetoresistance is attributed to the effect of the semimetal's two band charge transport, with both p and n type carriers. This model predicts a resonance in the magnetoresistance when the p and ncarriers are perfectly balanced (when $p/n \approx 1$). In graphite and Bi, slight deviances from p/n = 1 result in saturation at high fields [46, 47]. The small overlap between the bands in WTe₂ is similar to an excitonic insulator, which could mean that the balance between electrons and holes in this compound is close to perfect, preventing the magnetoresistance from saturating even at high fields [45].

Chapter 2

Experimental Methods

2.1 Crystal Growth

Single crystal growth of the layered transition metal dichalcogenides (TMDs) was done by vapor transport. Samples of $\operatorname{Fe}_x \operatorname{TiS}_2$ ($0 \le x \le 1$) were prepared by adding pure powders of constituent elements together in the desired amounts ($m_{\text{total}} \sim 1$ g) with iodine ($0.3 \le m_I \le 0.5$ g) as the vapor transport agent. The elements were then vacuum sealed in a quartz tube ($d_{\text{inner}} = 0.5$ inches, $l \approx 6$ inches.) Synthesis took place in a gradient furnace. Temperature was first ramped up to 500°C and left dwell for 10 hours. The oven was then ramped up to 800°C for the cold end and 900°C for the hot end and left to dwell for 6-10 days. The furnace was then cooled to room temperature. Crystals produced were of a gold on the lightly doped end and became more black with increasing iron concentration. They formed thin hexagonal plates as seen in figure 2.1.

2.2 Powder X-Ray Diffraction

Powder X-ray diffraction was used to check the crystal structure of the grown crystals as well as to search for the presence of any impurities or secondary phases in the crystals. X-ray diffraction measurements were taken using a Bruker D8 Advance Xray powder diffraction instrument with a Cu K- α beam ($\lambda = 1.5406$ Å). Samples for powder X-ray diffraction were ground using a mortar and pestle. Special care is required with the layered dichalcogenides as their flat, plate-like structure makes it difficult to grind homogeneously and can result in a preferred orientation. Once



Figure 2.1 : Quartz tube containing single crystals of $Fe_x TiS_2$. Inset: crystal of $Fe_x TiS_2$ showing hexagonal structure, grid on paper is 1 mm corrugation.

the sample has become a uniform powder, it is mounted on a plastic sample holder (to minimize background signal). Samples are rotated continuously throughout the measurement, again to reduce any preferred orientation effects. Measurements were typically taken over a range from 5°to 90°at $\Delta = 0.02$ °with t ≈ 3 second for each step. The diffraction pattern is then compared with patterns from the ICDD-PDF database to confirm that the correct phase was obtained. Finally structural refinement is performed using EVA to obtain precise lattice parameters.

2.3 Magnetization Measurements

Magnetization measurements were performed on a Quantum Design Magnetic Properties Measurement System (MPMS) for temperature from 2 to 300 K and fields up to 7 T. Additional magnetic measurements at higher fields up to 9 T were performed



Figure 2.2 : Schematic of apparatus to use the Faraday effect to view magnetic domains on a sample.

using the Quantum Design Physical Properties Measurement System (PPMS) AC measurement system (ACMS).

2.4 Electrical Transport

Transport measurements were preformed using the Quantum Design PPMS system using standard four point probe techniques with silver paint to secure the contacts. Temperatures ranged from 2 to 300 K. Measurements in field were done up to 9 T with the field applied parallel to the c-axis of the samples. Samples were done with DC resistivity measurements unless specified.

2.5 Faraday Effect

The Faraday effect can be used to study magnetic materials. In the Faraday effect, the polarization of light is rotated proportionally to the magnetic field in the sample. The most common example of this phenomena being birefringence. Thus the relative magnetization in a sample can be detected by shining polarized light at a sample, then measuring the polarization of the transmitted light. Imaging domains in a magnetic sample can be achieved with a setup similar to that in figure 2.2. Light is polarized then shined on a sample. Depending on the magnetization of the area struck, (in figure 2.2, spin left or spin right) it picks up a different shift in polarization. By sending this subsequent light through another polarizer, the change in polarization and thus the magnetization can be detected.

Chapter 3

Magnetization and Transport of $Fe_x TaS_2$

The doping of magnetic atoms in the TMD system is of particular interest due to the ease of intercalating the large magnetic atoms between layers. In addition, the magnetic properties can be tuned using multiple methods as the resulting magnetic properties depend on the dopant type, the dopant location (typically either intercalated between layers or substituted with the transition metal), dopant concentration, and the parent compound. For example, in the Cr doped TiSe₂ system, magnetic behavior can be tweaked from spin glass [22], to cluster glass [48], to antiferromagnetism [48]. The TMDs create a richly varied system in which to study magnetism, which is vastly important in regards to its own technological uses [40], but also for its close relation to superconductivity in the cuprates and iron-pnictides.

The Fe_xTaS₂ system exhibits many of the interesting magnetic behaviors found in the TMDs. It has two common polytypes: 2H and 1T (as seen in figure 1.1). The undoped 1T polytype goes through several different CDW transitions. Starting with an incommensurate (IC) CDW state at high temperatures, then cooling to a nearly commensurate (NC) and finally a commensurate (C) state [49]. The 1T polytype does not show doping naturally, though it can be induced by doping iron atoms onto the tantalum site [20]. In contrast, the 2H polytype does show superconductivity naturally [16]; however, doping with iron results in intercalation rather than substitution and upon doping, the superconductivity is suppressed and magnetic order arises [23].

Iron doping in the 2H-TaS₂ system produces rather unintuitive results. At x=1/4and x=1/3, a superlattice appears as the iron atoms intercalate in a periodic manner with order a' = 2a and $a' = \sqrt{3}a$ respectively (with a as the lattice parameter in



Figure 3.1 : Weiss temperature θ_W as a function of Fe content x in Fe_xTaS₂. Open squares from [1]. Closed circles from [2].

for the *ab* axis) [3]. The Weiss temperature, θ_W , changes non monotonically with the iron concentration, seen in table 3.1. Note that at x = 0.45, θ_W goes negative, indicating a shift from ferromagnetism to antiferromagnetism. Also of interest is that near the x = 0.25 composition T_C is large, $T_C \sim 160$. Naively, one would assume an even larger T_C for the larger concentration x = 0.33. However, this is not the case as $T_C \sim 35$ K for x = 0.33 [3]. Finally, T_C seems strongly dependent on iron composition as even small variations in x can result in appreciable changes in T_C [50]. Its clear the system's interactions with the intercalants are crucial to the magnetic behavior of the system.



Figure 3.2 : M(H), hysteresis curves of $Fe_{0.25}TaS_2$ at 2K for H|| c (triangles) and H $\perp c$ (crosses). [3].

3.1 Sharp Switching in M(H) and $\rho(H)$

Initial interest in $Fe_x TaS_2$ arose due to the interesting behavior in its hysteresis curve. Anisotropic magnetization measurements, shown in figure 3.2, on the x = 0.25 system reveal two interesting features. First, there is a strong anisotropy in the system with the easy axis along H||c. Second, the hysteresis curve of the sample is atypical. While a typical hysteresis curve is 'S' shaped as seen in Fig 1.5, the hysteresis curve for $Fe_{0.25}TaS_2$ is square shaped with a sharp switching at a field (M_{sat}) as seen in figure 3.2.

3.2 Magnetic Domain Imaging

The magnetic behavior of the $Fe_{0.25}TaS_2$ was also investigated through magnetic domain imaging using the Faraday effect by Vannette *et al.* [4]. After field cooling, the



Figure 3.3 : Images of domain moments in $Fe_{1/4}TaS_2$ with MOKE. Left to right corresponds to increasing field [4].

crystal formed a monodomain, which persisted after switching the field off, suggesting high anisotropy (agreeing with the anisotropy in the H||c and H \perp c measurements in Morosan *et al.* [3]).

The results show a dendritic formation of the domains. Which proceed to spread, following the hexagonal structure of the crystal but do not seem correlated to any defects in the structure. However, this does imply that the domain move easier along the axes of the crystal.

3.3 Magnetoresistance

In 2015, Hardy *et al.* presented work on magnetoresistance in the Fe_xTaS₂ system [5]. In this work, they found the x = 0.28 composition shows up to a staggering 60% value for $\Delta \rho / \rho_0$ [5]. This is sharply contrasted by the magnetoresistance in the x= 0.25 sample where the change in magnetoresistance is less than a percent (figure 3.4) [3]. These results are surprising and still not fully understood. One proposed explanation is due to the spin disorder scattering [5]. The x = 0.28 can be viewed as



Figure 3.4 : $\rho(H)$, magnetoresistance curves of (a) Fe_{0.25}TaS₂ (120 · $\Delta\rho$) and (b) Fe_{0.28}TaS₂ at 2 K. Reproduced from [3] and [5].

either $x = 0.25 + \delta$ or $x = 0.33 - \delta$. Either way, we have two different classes of iron atoms, those within the ordered superstructure, and those in a disordered area (either outside the superstructure or in an iron deficient area). Either way, the disordered spins would be expected to have weaker exchange [51] and therefore would be more easy to flip. We should then expect the scenario of the disordered spins flipping in low fields, resulting in high spin disorder scattering and when all the spin flip, a drastic decrease in magnetoresistance, as is seen in the magnetoresistance curve in figure 3.4.

Chapter 4

Magnetization and Transport of $Fe_x TiS_2$

In the TaS₂ system, the underlying physics of these effects has not been definitively determined. By studying systems with similar behavior, a better understanding of what is happening in the TaS₂ system may arise. Negishi *et al.* produced results on the Fe_xTiS₂ system whose hysteresis curve looks strikingly similar to the sharp switching seen in Fe_{0.25}TaS₂ [23]. This motivated our work in performing single crystal measurements of the anisotropy and magnetoresistance on the Fe_xTiS₂ system. Crystal were grown using the chemical vapor transport method (section 2.1) with iodine as the transport agent. Anisotropic magnetization measurements (H||c and $H\perp c$) are being taken for Fe_xTiS₂ ($x_{nominal} = 0.1 - 0.9$) for both magnetization M(T) and hysteresis M(H). All *x* values denoted as either the nominal value, x_{nom} or as $x_{\mu_{sat}}$. $x_{\mu_{sat}}$ is calculated by scaling M(H) to a saturated moment of $4\mu_B$ (when possible). A sample M vs. T plot is shown in figure 4.1a and b. As seen, a high level of anisotropy exists between different crystallographic directions, with a much larger magnetization along the *c* axis.

A sample inverse χ plot is shown in figure 4.1c, showing the sample is clearly ferromagnetic. The Curie-Weiss law was calculated for both H||c, H \perp c, as well as for the average susceptibility (calculated as $\chi_{avg} = (2 \cdot \Delta \chi_{ab} + \Delta \chi_c)/3$. Where $\Delta \chi = \chi - \chi_0$) [3].

Hysteresis (M vs. H) curves for the $\text{Fe}_x \text{TiS}_2$ system bear a striking similarity to those of $\text{Fe}_x \text{TaS}_2$. While this has been previously reported [23], our results show some interesting additional features. Anisotropic hysteresis curves for the samples show a large variation in the strength of the H \perp c signal. For example, figure 4.2e shows



Figure 4.1 : χ vs T plot for Fe_{0.5}TiS₂ with (a) H||c and (b) H||ab. (c) $1/\chi$ plotted for χ_{\parallel} (open squares), χ_{\perp} (closed squares), and χ_{avg} (closed diamonds).

a H||ab curve with a max around $2\mu_B$ /Fe while in figure 4.2h, its nearly zero. This suggests that the anisotropy of the system has some dependence on iron concentration. Additionally, figure 4.2c and f show a step in the hysteresis, which appears in several measured samples.

Resistivity plots show a sharp drop near the critical temperature, showing the loss of spin disorder scattering below the critical temperature. This behavior is seen both for H = 0 T and H = 9 T.

Finally, as shown in figure 4.4a, the maximum difference in magnetoresistance was $\sim 60\%$. This, in addition to the similar bowtie shape seen in figure 4.4a and b shows that we do indeed appear to have an analog for the magnetoresistance in Fe_xTaS₂.



Figure 4.2 : M(H) curves for Fe_xTiS_2. Colored symbols are H||c, open symbols are H⊥c



Figure 4.3 : Resistivity (H = 0 T, and H = 9 T) for $Fe_{0.5}TiS_2$



Figure 4.4 : Magnetoresistance of $Fe_x TiS_2$ samples

Chapter 5

Discussions and Outlook

Future work on the Fe_xTaS₂ and Fe_xTiS₂ is focused on better understanding the mechanisms behind the sharp switching in hysteresis and the large magnetoresistance. The next step upon finishing magnetization and magnetoresistance measurements is to run inductively coupled plasma (ICP) on the samples. ICP can accurately determine the relative compositions of the materials, and thus determine a more accurate value for x. Then electron energy loss spectroscopy (EELS) and transmission electron microscopy (TEM) will be performed. TEM will search for a superstructure in the Fe_xTiS₂ systems. Determination of a superstructure similar to the Fe_xTaS₂ (x = 0.25, 0.33) system would further reinforce the idea of spin scattering off superstructure defects. EELS in these samples will give a nanoscale view on the distribution of the iron in the samples. While ICP accurately determines the relative compositions of the sample, it does not give information of the local distribution of atoms. Since the iron atoms do not necessarily form a consistent superstructure, the breaking of the symmetry of the crystal through areas where iron has aggregated or sparsely accumulated could also help explain the unusual properties of these materials.

Work on the iron doped TaS₂ and TiS₂ systems has shown in both, sharp switching of the magnetization, and unusually high magnetoresistance for a bulk system. In Fe $_x$ TaS₂, the sharp switching is attributed to the strong anisotropy in the system [3], while the large magnetoresistance is theorized to arise from spin disorder scattering off defects in the iron superstructure [5]. In Fe_xTiS₂, both these features have been observed, but more evidence is required on the origin of these behaviors. These materials do draw light to a question: 'what causes large magnetoresistance in materials?' This question is of value philosophically, as the physics behind magnetoresistance is varied, scientifically, as the materials can be related to other interesting phenomena such superconductivity, and practically, as magnetoresistance is used in magnetic data storage. Large magnetoresistive drove an exponential increase in hard drive density as read heads with more sensitive magnetoresistive materials could read smaller bits [40]. Sharp magnetization switching could also be used to improve magnetic bits as a more binary state and more definitive threshold field would reduce write errors. While neither TiS_2 nor TaS_2 are good candidates (T_C for both is too low for practical use), understanding the properties in these systems may allow for the engineering of other materials with the same switching and magnetoresistance, but a more practical Curie temperature.

Chapter 6

Appendix

All magnetoresistive data currently taken is shown in figure 4.4. While figure 4.4a and b have bowtie shapes similar to those of the Fe_xTaS_2 , the rest do not. And instead they have an asymmetric curve. While the root cause for this is yet to be determined, there are possibilities that have been ruled out. The samples are all single crystal so unless twinning or a similar effect occurred, this isn't due to grain boundaries. This could be due to the Hall effect, as a sizable Hall effect was seen in the Fe_xTaS_2 samples. Additionally, the leads are placed by hand and shocked afterwards to remove any oxide layers formed. Both of these could contribute to a small ρ_{xy} contribution to the resistance measurement.



Figure 6.1 : Magnetoresistance of $Fe_x TiS_2$ samples

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