Anisotropy in the Helimagnet $Cr_{1/3}NbS_2$

by

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A thesis submitted to the faculty of the University of Colorado in partial fulfillment of the requirements for the award of departmental honors in the Department of Physics 2014 $\begin{array}{c} {\rm This\ thesis\ entitled:}\\ {\rm Anisotropy\ in\ the\ Helimagnet\ Cr_{1/3}NbS_2}\\ {\rm written\ by\ A.\ C.\ Bornstein}\\ {\rm has\ been\ approved\ for\ the\ Department\ of\ Physics} \end{array}$

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Thesis directed by Prof. Minhyea Lee

The helimagnet $Cr_{1/3}NbS_2$ is investigated as a possible host of a nontrivial spin texture. Evidence for skyrmions was not observed. It is likely that high crystal anisotropy represses nontrivial spin textures from forming in this material. However, as a result of this structural anisotropy, another spin texture of interest, the Soliton Lattice, is permitted to form. An unexpected low temperature magnetocrystalline anisotropy is reported as well as an unusual field dependence of the Hall effect in the same temperature regime. As a general focus, the relationship between spin and lattice degrees of freedom and bulk properties is examined.

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Chapter 1

Introduction & Motivation

1.1Long Range Order and Spin Texture

The magnetic moment of an electron is generated by its intrinsic spin. When a material contains atoms with unpaired valence electrons, there exists a non-zero magnetic moment at the atomic site.¹ A material's magnetic texture is a description of the orientation of these localized spins. Recently, an increased interest in understanding and manipulating these spin textures has emerged [1, 2, 3]. Because conduction electrons are capable of coupling with spin texture, the underlying magnetic texture of a material is detectable in transport measurements. In light of this interaction, there are many technological applications in understanding magneto-transport properties.

There are a wide variety of spin textures. In paramagnetic materials the spin orientation is random. Thermal fluctuations dominate and there is no long range order. Upon cooling, when the exchange energy between spins overcomes thermal energy $k_B T$, long range order may develop.² Ferromagnetism, in which every spin is aligned, is the most topologically trivial of states that exhibit long range order. In materials in which the symmetric (ferromagnetic) exchange is not the only energy scale of importance, more interesting magnetic textures may form. In these materials (although neighboring spins are not parallel) long range order is present, incommensurate with the underlying crystal structure.

 $^{^{1}}$ neglecting nuclear spin 2 k_B: Boltzmann constant

Two of the more complex textures that possess long range order are helimagnetism and the skyrmion lattice. Helimagnetism is a magnetic state in which moments arrange themselves into a helix, pointing outward from a central q-vector as shown in Fig 1.1.a. The period of this helicoid is typically much larger than the size of the crystal's unit cell. A skyrmion lattice is a topologically nontrivial spin texture that is most simply described as a lattice of magnetic vortices. The cross section of a single skyrmion is shown in Fig 1.1.b. Among others, these spin textures are of interest in spintronics applications both because of their long range order, and the fact that they are tunable. Nontrivial spin textures are particularly desirable because of their ability to generate very large emergent magnetic fields [4].



Figure 1.1: Two different spin textures. Arrows represent orientation of magnetic moments.

Over the past five years, skyrmion lattices have been observed in several materials ranging from the insulator Cu_2OSe_3 to the metal MnSi [6, 7]. For these materials, the skyrmion phase exists in a small range of field and temperature. Prior to the formation of skyrmions, (at H=0) these materials all exist in a helimagnetic state. Therefore, in order to find potential hosts for skyrmion lattices, additional materials with helimagnetic ground states need to be identified. By discovering and studying new materials that exhibit helimagnetism, insight can be gained not only into the formation of nontrivial spin textures, but also the broader relationship between bulk transport properties and underlying spin and lattice degrees of freedom.

Cu₂OSe₃ and MnSi, as well as all other known skyrmion hosts, belong to the B20 crystal group. B20 crystals are noncentrosymmetric, meaning their unit cells lack an inversion center. Because crystal structure is the ultimate host of spin structure, it is usually the case that more 'complex' spin textures are induced by symmetry breaking in the crystal structure. Here 'complex' refers to any non-coplanar or non-collinear magnetic texture. For reference, helical ordering lacks both mirror and inversion symmetry: an example of coplanar, but non-collinear texture. While $Cr_{1/3}NbS_2$ is not a B20 crystal, it does belong to the noncentrosymmetric space group $P6_322$. Along with the B20 crystals, this is one of the space groups theoretically predicted to host a skyrmion lattice [8].

While $Cr_{1/3}NbS_2$ does host a helical magnetic ground state, there have been no observations of skyrmions as of yet. While predicted to do so, $Cr_{1/3}NbS_2$ may not be able to host nontrivial spin textures because of its' high crystalline anisotropy. Compared to $Cr_{1/3}NbS_2$, the B20 crystals are much more structurally isotropic. One of the main goals of this thesis is to better understand to what degree this crystalline anisotropy influences magnetic texture.

1.2 Introduction to $Cr_{1/3}NbS_2$

1.2.1 Crystal Structure

The high degree of anisotropy present in $Cr_{1/3}NbS_2$'s crystal structure is shown on the right in Fig 1.2. There are very well-defined planes of chromium atoms inter-spaced by layers of niobium disulfide. These crystallographic ab-planes are even evident macroscopically and bulk samples tend to flake along them. The unit cell contains two Cr atoms and is shown on the left in Fig 1.2. The chromium planes and the planes parallel to the Cr layers are referred to as the abplane. In the ab-planes the Cr atoms arrange in a hexagonal lattice, preserving a 6-fold rotational symmetry about the c-axis. The in-plane Cr-Cr distance is 5.74 Å while the distance between Cr planes (along the c-axis) is $a_0=6.05$ Å [9, 10].



Figure 1.2: Crystal Structure of $Cr_{1/3}NbS_2$ [10]. Noncentrosymmetric unit cell (left) and overall structure (right). There is a high level of anisotropy along the c-axis.

1.2.2 Magnetic Texture

Above ~ 120-135K $Cr_{1/3}NbS_2$ is paramagnetic. The spins point in random orientations and there is no net magnetization. Upon cooling below the critical temperature T_c , $Cr_{1/3}NbS_2$ undergoes a magnetic transition to the helical state. While there is still no net magnetization, (the average spin orientation is $\vec{0}$) long range magnetic order exists. The helicoid forms out of magnetic moments of the electrons localized to the Cr atoms. In the ab-planes spins align ferromagnetically. The ferromagnetic planes make small angles with the planes above and below it, forming a helix. The helix propagates along the c-axis, normal to the Cr planes. See Fig 1.3.a for helix formation in relation to crystalline structure.

Evolution with Field In B20 crystals, the skyrmion state is achieved through application of an external magnetic field. In these materials, the spins in the helix begin to cant up along the helix axis to align with a small external field, thanks to low crystalline anisotropy. A slight increase in the field (~0.2 T in MnSi) brings the spins non-coplanar and forms a skyrmion lattice, for temperatures very close to T_c . Unlike those materials, the q-vector of the helix in $Cr_{1/3}NbS_2$ appears to be strongly pinned to the crystallographic c-axis. This may cause skyrmion formation to be suppressed. However, this strong helical pinning opens the door for new spin textures.

Naturally, two field directions of interest arise: parallel to the helix axis (the c-axis) and perpendicular to it. When a field is applied along the helix axis the spins are pulled out of the plane through a conical phase. With large enough field ($H_{critical}^{c-axis}=H_c^c$), the spins polarize along the c-axis. This is observed to be the hard axis of magnetization. If a skyrmion lattice is to exists in $Cr_{1/3}NbS_2$, it is more likely that it would do so with fields along the c-axis (due to the strong c-axis pinning which forbids canting).

For fields applied perpendicular to the helix axis, the intermediate phase before polarization is a soliton lattice. This spin texture is able to form because of the strong c-axis pinning which forbids canting. A soliton lattice is modulated helix, containing long chains of ferromagnetic spins partitioned by single helical kinks. While the helical ground state of $Cr_{1/3}NbS_2$ has been know for some time, the direct observation of a soliton lattice was made last year via Lorentz Force Microscopy [5]. Soliton lattice formation under a field applied in the ab-plane is shown in Fig 1.3.b. As field is increased, spins leave neighboring helices and create ferromagnetic chains. As helical kinks are pushed out of the geometric boundaries of the sample, the ground state pitch L(0) increases to L(H). At some critical field ($H_{critical}^{ab-plane}=H_{c}^{ab}$), the spins are completely polarized: $L(H_{c}^{ab}) \rightarrow$ sample size.



(a) Helix formation from moments localized to Cr atoms.

(b) Helix pitch L(H) grows with field, forming a soliton.

Figure 1.3: Ground state helimagnetism of $Cr_{1/3}NbS_2$ (left), the soliton lattice formed when H is applied in the ab-plane (right) [5].

1.3 Origins of Helimagnetism

In noncentrosymmetric materials, the mechanism for helix formation is a competition between the exchange interaction and the Dzyaloshinsky-Moriya (DM) interaction [11, 12]. The symmetric exchange energetically favors spin states with neighboring spins aligned, while the DM exchange favors perpendicular spins. The DM exchange is understood to be a relativistic spin orbit interaction [11, 12]. The ground state Hamiltonian of this system is given by

$$H = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - \vec{D} \cdot \sum_{[i,j]} \vec{S}_i \times \vec{S}_j$$
(1.1)

where J > 0 is the ferromagnetic coupling between spins, \vec{S}_i is the spin at site *i*, \vec{D} is the Dzyaloshinsky-Moriya vector, \langle , \rangle is a sum over nearest neighbors, while [,] is a sum over out of plane nearest neighbors. Notice that \vec{D} is a vector, its direction determines the propagation direction/handedness of the helix, while its magnitude (relative to J) determines the pitch length of the helix. In $Cr_{1/3}NbS_2$, \vec{D} points along the c-axis and the chirality is left handed [5].

Consider a Helix as a 1-D chain of spins with \vec{D} pointing along the axis of propagation. Setting |S| = 1, the Hamiltonian of a 1-D chain is $H = -J\cos(\theta) - D\sin(\theta)$ where θ is the angle between adjacent spins (spins lie in plane perpendicular to \vec{D}). Setting $\frac{dH}{d\theta} = 0$ to find the minimum, one sees that $J\sin(\theta) = D\cos(\theta)$. The angle between spins is therefore $\theta = \tan^{-1}(D/J) \cong \frac{D}{J}$ for $\frac{D}{J} << 1$. The number of spins in a single helix is $n = \frac{2\pi}{\theta} = \frac{2\pi}{D/J}$. The pitch length of the helix is na_0 where $a_0=6.05$ Å is the distance between Cr atoms along the c-axis.

$$\lambda = \frac{a_0 2\pi J}{D} \tag{1.2}$$

The measured pitch length of $\operatorname{Cr}_{1/3}\operatorname{NbS}_2$ is ~ 48 nm [5] which gives a relative strength for J/D of ~ 13. When an external field is applied the term $-\mu_0 \sum_i \vec{S}_i \cdot \vec{H}$ is added to the Hamiltonian to account for the Zeeman energy of each spin in an external field.

1.4 Measurements

The following chapter offers a description of the experimental approach and major measurements. Bulk magnetization measurements were taken with respect to different crystallographic axes. Both transverse and longitudinal DC resistivity were measured against field and temperature. The Seebeck coefficient and thermal conductivity were measured as a function of temperature. Last, the electrical response to strain was explored.

Chapter 2

Methodology and Experimental Setup

2.1 Samples

Single crystals of $Cr_{1/3}NbS_2$ were grown via chemical vapor transport. Samples from two different batches were investigated over the course of this research. The first set of samples have $T_c=120K$ (Sample A) and the second set $T_c=133.5K$ (Sample B). They are both confirmed to form helical magnetic order in small angle neutron scattering. Their behaviors are qualitatively the same under the control parameters of study. The residual resistivity ratios $[RRR = \rho(300K)/\rho(2K)]$ are 10 and 5, respectively, for the two samples. The higher RRR for the Sample A indicates that it likely has less impurities. Data from both samples will be presented and comparisons made when appropriate. Unless otherwise noted, all data presented is from the Sample B batch.

Samples with lateral dimensions of ~ 1/2 mm x 2 mm and thickness ranging from 10 - 200 μ m were used in measurement. Specific geometries were chosen to maximize signal to noise depending on the measurement i.e. magnetoresistance and thermopower measurements used long samples, while thin samples were prepared for hall and strain measurements. Samples were adhered to quartz substrates with VGE-7031 Lakeshore varnish which is electrically insulating with high thermal conductivity. Electrical contacts were made using 1 mil diameter Au wires and Ag conducting paint.

2.2 Experimental Setup

Electrical measurements on samples were made with a Keithley 6221 source meter in conjunction with a 2182A nanovolt meter. To eliminate thermally induced voltage offsets in the voltage lines, 'Delta Mode' was used. Delta mode is an averaging technique performed internal to the Keithleys that rapidly switches the current direction during a measurement. By subtracting the negative voltage reading from its positive counterpart and dividing by two, any offset voltages between the sample and the voltmeter are averaged out. This is important as the thermal gradient down the line can easily exceed 100K/meter. For acceptable signal to noise, averaging was performed for each measurement. Each data point presented will be the mean of anywhere from 10 to 200 individual voltage readings, taking between 1 and 20 seconds to complete. Additional electrical measurements (strain gauges, thermocouples) were made with Keithley voltmeter models 2000, 2002, 2400.

2.2.1 Magnetic and Electrical Measurements: MPMS

DC magnetic susceptibility as well as Hall and Magnetoresistance (MR) measurements were made using a Quantum Design Magnetic Properties Measurement System (MPMS) cryostat. The MPMS system allows for temperature control between 2 and 300 Kelvin with a magnetic field range of -7 to 7 Tesla. Temperatures down to 4.2 K are achieved by thermally syncing with a liquid helium bath. Temperatures between 2 and 4.2 K are achieved by pumping on the helium, consequently reducing the vapor pressure and evaporatively cooling the system. A simple schematic of the system is shown in Fig. 2.1.

<u>Bulk Magnetization</u> Samples were placed inside plastic straws during magnetization measurements. Measurements were made using Squid detection coils. The Squid coils are four loops of wire interior to the super conducting magnet on the MPMS (see Fig. 2.1). Magnetized samples are moved up and down through the coils by the sample transport at the top of system. The changing magnetic flux from the sample induces an \mathcal{E}_{mf} in the squid coils, creating a current which is measured. The values reported for magnetization are in Bohr Magnetons per Formula Unit (μ_B/FU) , or effectively μ_B/Cr_{atom} .

Hall Effect & Magnetoresistance A set of current contacts as well as longitudinal and transverse voltage contacts were made on each sample and measurements were taken using the four probe technique.



Figure 2.1: Schematic of cryostat (left) with enlargement of the superconducting magnet shown (right) [13]. The sample is located at the end of the sample rod, inside the superconducting magnet. Temperature range is 2-300K with a field range of -7T to 7T. SQUID coils used to detect magnetization are inside central bore of the magnet.

2.2.2 Angle dependent MR, Thermopower, Strain: Helmholtz Coil

Angle dependent magnetoresistance, thermopower, and strain measurements were taken in a refurbished Janis cryostat. The system achieves the same field and temperature regime as the MPMS. However, unlike the MPMS which uses a solenoid to generate magnetic fields, the Janis contains a large Helmholtz coil. The Helmholtz coil lies flat, perpendicular to the central bore of the cryostat. The relatively large separation between the two coil loops provides room for the vacuum can used in thermopower measurements as well as a piezoelectric used in strain measurements. The orientation of the field with respect to the bore allows for control of magnetic field direction with respect to sample orientation, critical for angle dependent MR.

Before measurements could be taken, the cryostat was refurbished. A vacuum can probe was created, baffles were added, and thermometry and magnet control were implemented.

<u>Thermopower Measurement</u> A schematic of the setup used to measure thermopower is show in Fig 2.2. To minimize heat exchange with the environment, experiments were done in a vacuum can at 10^{-7} mbar of pressure. Samples were mounted vertically and held upright in Ag epoxy. A 1 k Ω resistor (shown in red) was mounted atop the sample to generate the temperature gradient (ΔT). The temperature gradient across the sample was kept under 10% the surrounding temperature T_{bath}. As with hall and MR, voltage leads were attached with Au wire and Ag paint.

The temperature gradient was measured with a pair of thermocouples (shown in purple). Thermocouples themselves work by the thermoelectric effect. Simply the junction of two different metals, they generate a voltage proportional to the difference in temperature between the two leads (held at the same temperature, T_{bath}) and the junction (held at $T_{bath} \pm \Delta T$). The thermocouples are connected in series, with opposite polarity. Therefore, the measured voltage is the difference between the two voltages $V_2 = V_U - V_L$ which is directly proportional to the temperature difference ΔT . The manufacturers of the Type-E thermocouples provide the Seebeck coefficient in $\mu V/K$ as a function of temperature. A cernox thermometer on the probe was used to determine the surrounding temperature T_{bath} .



Figure 2.2: Schematic of thermopower measurement. Voltage leads in orange. Thermocouples in purple. $1k\Omega$ heater shown in red. Heat flows down the sample, creating a temperature gradient ΔT . Lower end of sample is held at T_{bath} .



Figure 2.3: Thermopower measurement Routine. All x-axes are time [seconds]. Temperature of sample at base (a). Power delivered to heater (b). Temperature gradient across sample (b). Voltage gradient measured (d).

A typical routine to measure thermopower is shown in Fig 2.3. The sample is given time to equilibrate with the surrounding temperature T_{bath} . Then current flows through the resistor and heats one end of the sample. The temperature gradient ΔT and the voltage difference ΔV are measured. The current is turned off and ΔT drops to 0. The probe itself is a large piece of Cu, acting as heat sync to quickly absorb heat. The process is repeated at a higher power to check that the response is linear. The first 10-25% of each heating cycle is thrown out. Only after equilibrium is reached and ΔV and ΔT are linear with slope 0 do measurements begin to be averaged.

In-situ Mechanical Strain It was shown recently that mechanical strain could be transferred in-situ to samples at liquid helium temperatures with use of a piezoelectric [14]. This offers a novel way to measure a materials response to mechanical stress at low temperatures without going the traditional route of hydrostatic stress applied with a pressure cell. Up to this point in our research data was only collected down to liquid nitrogen temperatures, around 50 K below T_c . Samples of $Cr_{1/3}NbS_2$ with thickness between 10 and 50 μ m were measured which is less than the 100 μ m thickness previously shown to effectively transfer strain in GaAs [14]. GE varnish as well as epoxy were used as adhesives. GE varnish was found to perform much better than epoxy. Setup is shown in Fig 2.4.

A typical strain measurement routine is shown in Fig 2.5. A voltage (typically 50-150V) is applied across the piezoelectric. The piezo increases in length, stretching both the sample and the strain gauge. The strain gauge has a known linear relationship between changes in resistance and strain. Specifically $\frac{\Delta R}{R_0} = G \frac{\Delta L}{L_0}$ where G is the gauge factor. Typical changes in length were on the order of a micron. Due to lack of temperature control during the experiment, measurements were made during warming cycles. A temperature drift of 1-2K during the course of a measurement was average. Temperature drifts were always linear and were subtracted from gauge resistance and sample voltage during processing.



(a) Sample adhered to piezo with GE varnish. (b) Longitudinal and transverse strain gauge Strain applied along long axis of the sample. adhered to back of piezo with GE varnish.





Figure 2.5: Strain measurement routine. All x-axes are time [seconds]. Voltage applied to piezo (a). Longitudinal gauge resistance (b). Sample voltage (c). Temperature (d).

2.3 Data Analysis

Data acquisition was done through the MPMS interface Multiview and with the programming languages Borland Delphi and MATLAB. Data processing was performed in MATLAB. Magnetoresistance and Hall plots have been symmetrized/antisymmetrized to reflect the symmetry of the longitudinal/transverse elements of the resistivity tensor.

Chapter 3

Results

3.1 Magnetic Transition

With a small magnetizing field of 0.01 T, the magnetic transition is evident in temperature sweeps at fixed field Fig 3.1. Measuring magnetization vs temperature is a good way to define T_c as this is a thermodynamic measure of the order parameter (magnetization) of the system, without disturbing it (small field). The transition occurs at 133 K which is a relatively high transition temperature for a helimagnet (see MnSi $T_c=30$ K [15]).



Figure 3.1: Magnetization as a function of temperature at 0.01 T. H||ab-plane. Onset of helimagnetism at 133K.



Figure 3.2: Resistivity as a function of temperature in blue. $d\rho/dT$ in green.

Resistivity as a function of temperature for both samples is shown in Fig 3.2. Another method used to determine T_c is the temperature at which $d\rho/dT$ is a maximum. Both samples exhibit a dramatic decrease in resistivity through the magnetic transition which indicates a large portion of the resistivity is due to spin scattering. Above 175 K the resistivity of sample A decreases with temperature. This type of behavior is typical of semiconductors. Sample B exhibits a more traditional metallic dependence on temperature with $d\rho/dT>0$ over the entire temperature range. It is worth noting that while the magnetic texture is generated by moments localized to the chromium atoms, the conduction electrons exist in unfilled bands of the NbS₃ layers [10]. Due to the interesting temperature dependence above 175 K, as well as the magnitude of the resistivity, $Cr_{1/3}NbS_2$ may either be described as a metal with low carrier concentration or as a highly doped semiconductor, as other groups have noted [10]. A phase diagram, deduced from magnetization data, is shown in Fig 3.3 for fields applied in the ab-plane. It is constructed out of temperature sweeps at various fixed fields. Above 133 K the order is paramagnetic (PM). Upon cooling at 0 field, the system enters the helimagnetic (HM) state. With the application of in-plane field, chains of spins rotate to align with field and the soliton lattice (SL) is formed. Further increase of field sends the pitch length of the soliton to infinity (sample dimensions) and the spins polarize ferromagnetically (FM). The white and black dots were taken from field sweeps at fixed temperature and will be discussed shortly.



Figure 3.3: Magnetization as a function of field and temperature for H||ab-plane.



Figure 3.4: Magnetic hysteresis at 2K. H||ab-planes. Sample A.

3.1.1 Magnetocrystalline Anisotropy

There is almost no magnetic hysteresis in this material. Up and down field sweeps are shown in Fig 3.4 at 2K for field applied in the ab-plane. It has been proposed that any hysteresis that is observed may be due to the magnetic kinks in the soliton 'snagging' or pinning to impurities as they are pushed out of the top and bottom of the crystal [10]. There is even less magnetic hysteresis when field is applied along the c-axis.

Magnetization at different temperatures for both field orientations is shown in Fig 3.5. The magnetization is highly anisotropic; note the x-axis scale in (b) is 20 times larger than (a). As field is applied in-plane Fig 3.5.a, spins begin to align with field. The magnetization begins to increase gradually. While there is net magnetization, the pitch length of the helix remains relatively constant [5]. Further increasing the field (0.16 T to 0.18 T at 2K), there is a rapid increase in magnetization and the period of the soliton lattice grows rapidly. Around 0.18 Tesla, the pitch length goes to infinity and the spins are completely polarized. The spins saturate at 2.9 μ_B/Cr_{atom} at 2K. The chromium atoms in $Cr_{1/3}NbS_2$ exist in the trivalent S=3/2 state and a value close to 3 Bohr Magnetons per chromium atom is expected [16].



Figure 3.5: Magnetization vs applied field for various fixed temperatures. Note the difference in x-axis scaling. The c-axis is shown to be the hard axis of magnetization as it takes ~10 times the field to polarize along this direction. Both orientations have same saturated moment ~3 μ_B/Cr at 2K, consistent with Cr being in S=3/2 trivalent state.



Figure 3.6: Magnetic transitions/field orientations from Fig 3.5. Soliton lattice (a) and conical helix (b).

The behavior for fields applied along the c-axis, shown in Fig 3.5.b, is very different. Magnetization increases linearly with field until polarization. This linear transition suggests that when fields are applied along the helix axis, the spins cant up out of the page in a continuous fashion through a conical phase. This is more accurately described as a conical helicoid. With large enough field (H_c^c) the spins polarize. The low temperature saturation value is again close to the 3 μ_B/Cr_{atom} , as expected.

While the saturation values between the two field orientations are very similar, the fields required to polarize are very different. It requires over 10 times the field to reach ferromagnetism along the c-axis (~ 2.5 T) than in the ab-plane (~ 0.2 T). This indicates a strong preference for the magnetic moments to stay in-plane. Thus, the c-axis is the hard axis of magnetization while the ab-plane is the easy plane.

Notice the slope change in Fig 3.5.a always occurs when the magnetization reaches half of its saturated value. Assuming the 'helical' portions of the soliton lattice are still helical, i.e. that their contribution to magnetization is 0, the slope change represents a cross over point in soliton lattice formation. This is the point at which the fraction of the soliton which is ferromagnetic exceeds the fraction that is helical L(H)/L(0) > 2. This field (~ 0.16 T at 4K) will be called H_{SL}^{ab} while the saturation field (~ 0.18 T at 4K) will continue to be referred to as H_c^{ab} . The black dots from the phase diagram separating HM and SL in Fig 3.3 come from this cross over point H_{SL}^{ab} , where the derivative changes slope. The white dots are the fields at which the magnetization saturates, H_c^{ab} . These field scales will become important in angle dependent magnetoresistance.

3.2 Electrical Transport: Magnetoresistance

The relative change in resistivity as a function of field at 2K is shown in Fig 3.7. The resistivity at 0 field is defined to be ρ_0 . The field scales from the soliton lattice (H||ab-plane) and conical transition (H||c-axis), evident in the magnetization, are present here. As spins polarize, spin scattering reduces and the resistivity decreases. After polarization the resistivity is constant in field. In both orientations MR is negative. With field in-plane there is 5% decrease in resistivity from $\rho(H = 0)$ and with field out of plane there is a 15% decrease. Around T_c there is a maximum MR of almost 45% at 7T for Sample A (not shown) and almost 20% for Sample B Fig 3.7.



Figure 3.7: Magnetoresistance for H||ab-plane and H||c-axis at 2K. The decrease in resistivity for field along c-axis is almost three times greater.

The anisotropy in field scales is expected, but the discrepancy in the MR for fields beyond polarization is very surprising. With field out of plane, there is a three fold decrease in the resistivity compared with field in-plane. This is in contrast to other materials with easy and hard axes of magnetization. From the magnetization curves it is apparent that the spins prefer to stay in-plane. When they are pulled out of the plane there is a possibility to support excitations such as magnons, which should increase resistivity. In fact, in some materials the MR is positive along the hard axis [17]. The magnitude of the change in resistivity with H||c is surprising even without comparison to the H||ab value. That magnitude of MR is only recovered close to T_c . Around T_c there are many competing energies, spin fluctuate frequently, and a large MR is expected.



Figure 3.8: Anisotropy in magnetoresistance: H||ab-plane (left), and H||c-axis (right). Curves are offset 0.02 for clarity.

Magnetoresistance at different temperatures is shown in Fig 3.8. Current and field direction relative to helical axis are indicated. As temperature increases the mean free path of the conduction electrons decrease, as a result the electrons experience less of the magnetic texture and the anisotropy lessens. However, the anisotropy is still visible at 20 K. At higher temperatures, the field scales from magnetization (evidenced by the shoulders in ρ), are still present but the high field anisotropy is gone. In fact, at temperatures above 50 K the drop in resistivity is greater for fields in-plane than fields out-of-plane, as one might expect.

3.3 Anisotropic Magnetoresistance

To further explore the unusual low temperature magnetocrystalline anisotropy in the MR, we investigate the MR angular dependence of field when there are both c-axis, and ab-plane components. The field was fixed at some intermediate angle θ relative to the ab-plane as shown in the inset of Fig 3.9. Then, field was swept up to 3 T while measuring resistivity. The results are shown in Fig 3.9. It takes a large out of plane component of field to start to see changes in the transport, again indicating a strong preference for moments to stay in-plane. As angle is increased further, for $72^{\circ} < \theta < 90^{\circ}$, two field scales begin to emerge.

These two fields, H_{k1} and H_{k2} , are plotted in Fig 3.10.a. They are identified as the field at which the magnitude of $\frac{d\rho}{dH}$ achieves a minimum (just to right of each shoulder). The fit in Fig 3.10.a is $1/\cos(\theta)$. Notice that the component of magnetic field in the ab-plane is $\cos(\theta)$. The fitting parameters H_{k1}^0 and H_{k2}^0 (which scale $1/\cos(\theta)$) from 3.10.a are plotted in 3.10.b along with the magnetization when the field is completely in-plane (Fig 3.5.a). The field scales in the resistivity, H_{k1} and H_{k2} , are scaling with the Helimagnetic \rightarrow Soliton Lattice (H_{SL}^{ab}) and Soliton Lattice \rightarrow Ferromagnetic (H_c^{ab}) transitions. This indicates a soliton lattice robust enough to withstand large c-axis components of spin: a conical soliton lattice. Moreover, with a large c-axis component of H, transport measurements become more sensitive to changes in magnetic structure in the ab planes i.e. there is only one field scale evidenced in MR when field is completely in-plane ($\theta=0$).



Figure 3.9: Magnetoresistance at 4K for different angles with respect to the ab-plane. Inset depicts field angle with respect to ab-planes. H_{k1} and H_{k2} taken just to the right of each shoulder.



(a) Field scales from Fig 3.9 plotted against $1/\cos(\theta)$. (b) Magnetization H||ab-plane ($\theta=0$) at 4K with fitting They curves are scaled by $H_{k_1}^0$ and $H_{k_2}^0$. parameters $H_{k_1}^0$ in blue and $H_{k_2}^0$ in red.

Figure 3.10: The field scales from Fig 3.9 go as $1/\cos(\theta)$. The fitting parameters H_{k1}^0 and H_{k2}^0 match the field scales from magnetization H_{SL}^{ab} and H_{c}^{ab} .

3.4 Electrical Transport: Hall Effect

There are two main contributions to the Hall voltage. The normal Hall voltage can be understood classically in terms of the Lorentz force $F = q\vec{v} \times \vec{B}$. As charge carries move in perpendicular electric and magnetic fields, they are forced to one edge of the material, until a Hall field big enough to oppose the Lorentz force is achieved. This phenomenon has been well understood for over a century and been used to determine charge carrier type and density.

Discovered only a short time after the normal Hall effect, the origin of the anomalous Hall effect (AHE) is still debated. However, there is thought to be three main contributions to the AHE: side jump, skew scattering, and intrinsic deflection [18]. Side jump and skew scattering are both due to the presence of impurities. Intrinsic deflection is as its name implies, an intrinsic effect related to the magnetization that occurs in ferromagnetic materials. The anomalous Hall conductivity σ_{yx} is proportional to the magnetization, M. Picking up a factor of ρ^2 when converting from conductivity to resistivity, the transverse resistivity becomes

$$\rho_{ux} = R_H B + \mu_0 \rho^2 S_H M \tag{3.1}$$

 \mathbf{R}_{H} and \mathbf{S}_{H} are referred to as the normal and anomalous Hall coefficients respectively.

The Hall resistivity ρ_{yx} at different temperatures is shown in Fig 3.11. The field is parallel to the c-axis. This transverse resistivity is odd with respect to field; for clarity only positive field values are shown. At 200 K, above T_c, the normal Hall effect dominates. As temperature lowers and the material begins to magnetize the AHE becomes significant. Below T_c, there is sharp kink in the signal marking the ferromagnetic saturation of the conical phase. This feature remains until around 20K where the kink turns into a dip.



Figure 3.11: ρ_{yx} vs. field at various temperatures. H||c-axis.

In Fig 3.12.a the slope from 3T-7T has been subtracted from the ρ_{yx} for a clearer picture. The curves for temperatures above 20 K resemble the magnetization curves, from Fig 3.5.b, as expected from Eq 3.1. The 2K and 20K curves do not. This is the same temperature and field regime in which the unexpected anisotropy in MR is observed. Because the traces of ρ_{yx} with a linear subtraction resemble the magnetization traces, they can be fit using Eq 3.1.



Figure 3.12: Hall signal with linear subtraction (a) resembling the magnetization curves and a typical fit to Eq 3.1 (b).

Fitting the Hall traces using Eq 3.1 results in the normal and anomalous coefficients given in Fig 3.13. Values from 2K and 20K are not shown as a good fit could not be achieved due to the 'dip' feature. A typical fit is shown in 3.12.b. The normal Hall coefficient R_H is positive, meaning the charge carries are 'hole like' over the entire temperature range. The charge carrier density n is extracted from the normal Hall coefficient $R_H = \frac{1}{ne}$. The carrier concentration n is relatively constant across temperature with a value at 200 K of $n \sim 9 \cdot 10^{20}$ holes/cm³. Throughout the helical phase S_H is constant in temperature indicating that the ρ_{yx} 's dependence on T and H can be completely attributed to the Magnetization's dependence on T and H (Fig 3.5.b). In the Hall data, no chiral topological signal was observed. The topological signal is identified with a sharp increase in ρ_{yx} over a short field range [15].



Figure 3.13: The normal and anomalous Hall coefficients \mathbf{R}_H and \mathbf{S}_H vs temperature.

3.5 Thermal Transport: Thermopower and Thermal Conductivity

The Thermoelectric, or Seebeck effect, describes the generation of an electric field in conductors due to the application of a temperature gradient. Charge carriers thermally diffuse across the material from hot to cold until the generation of an electric field large enough to oppose diffusion. Sign convention dictates that $S = \Delta V/(-\Delta T)$. Therefore, materials with S>0 have hole like charge carries and materials with S<0 have electron like carries.

The Seebeck coefficient as a function of temperature is shown in Fig 3.14. It decreases from a maximum of $32 \ \mu V/K$ at 300 K to $0 \ \mu V/K$ as we approach 0K. There is a kink around the magnetic transition and a steep decrease from 50K to 4K. The positive Seebeck coefficient supports the evidence from Hall data of hole dominated transport over the entire temperature range. This data, taken on the 133 T_c sample, is in contrast to data reported earlier this year on the 120 T_c sample [10]. They report an increase in S from T_c down to ~ 50K. The sharp drop below 50 K is the same temperature region the interesting behavior was observed in the MR and Hall data. The anomalous low temperature behavior, consistent across measurements, gives credibility to the data reported here.

To better understand this discrepancy the thermal conductivity κ was extracted from the thermopower data. It is shown in Fig 3.15. Thermal conductivity has both electron and phonon contributions. The electrical contribution to thermal conductivity can be estimated from the empirical Wiedemann-Franz law as $\kappa_e = LT/\rho$ where ρ is the resistivity, T is the temperature and $L=2.44 \times 10^{-8} W \Omega K^{-2}$ is the Lorenz number [19] . κ_e achieves a maximum of only 4.5 mW/cmK at 250 K (out of 190 mW/cmK), indicating the majority of heat transfer in this material is from phonons. As T \rightarrow 0, phonons freeze out and the conductivity drops to 0.

The thermal conductivity from the contradicting paper agrees well over the entire temperature range. Given their agreement, the difference in Seebeck coefficients is surprising.



Figure 3.14: Thermopower at 0 applied field.



Figure 3.15: Thermal Conductivity at 0 applied field.

3.6 Strain: A Novel Measurement

Traditionally, mechanical stress has been applied to samples isotropically though the use of a pressure cell. In this experiment, planar strain was applied in the ab-planes using a piezoelectric, as explained in Chap 2.2.2. The sample was stretched parallel to the direction of current. As a consequence, the sample was compressed in the perpendicular direction around a half as must as it was stretched. Because the geometry of the sample is becoming thinner and longer, a zeroth order approximation would expect the resistance to increase. This is not the case for $Cr_{1/3}NbS_2$. Resistivity decreases with strain over the entire temperature range. The relative change in resistivity as a function of strain is shown in Fig 3.16. Both stretching and relaxation sweeps are shown and there is small observed hysteresis. This hysteresis is likely due to the adhesive.

The relative change in resistivity divided by the strain as a function of temperature is shown in Fig 3.17. Interestingly there is a minimum at T_c .



Figure 3.16: Change in resistivity vs strain at different temperatures. 0 applied field.



Figure 3.17: Resistance change with strain as a function of temperature. 0 applied field.

As a comparison and as a test of the experimental method, the same measurement was made on a sample of TaSe₂. TaSe₂ is a dichalcogenide like NbS₂. Unlike $Cr_{1/3}NbS_2$, TaSe₂ is not magnetic; it goes through a Charge Density Wave transition instead of a magnetic transition. However, TaSe₂ does have a similar transition temperature of ~120K. Resistivity as a function of temperature is shown in Fig 3.18.a. The relative change in resistivity divided by the strain at different temperatures is shown in Fig 3.18.b

Above T_c TaSe₂ has a small increase in resistivity with strain. As the temperature is decreased through T_c the sign switches and there is a large decrease in resistivity with strain. Interestingly, while the transitions have completely different origins, both samples have negative values below 120K (although $Cr_{1/3}NbS_2$ is negative over the entire range).



Figure 3.18: Strain induced resistivity change in $TaSe_2$.

Chapter 4

Conclusions

Various electric and thermal properties of the helimagnet $Cr_{1/3}NbS_2$ are reported. In this material, a high level of structural anisotropy pins the helical magnetic ground state along the crystallographic c-axis, inducing a high level of magnetic anisotropy. This creates two distinct pathways to the ferromagnetic regime: the conical helix, and the soliton lattice. In turn, this results in anisotropies in bulk transport properties. When field is applied along the hard axis of magnetization (T<<T_c), the decrease in resistivity is three times greater than when field is applied in the easy plane. This difference is very rare for materials with a hard axis of magnetization. Additionally, for fields with an ab-plane component as well as a large c-axis component of field, it seems likely that a conical soliton lattice is forming. At the same time, for these intermediate field orientations, the electrical transport becomes more sensitive to the magnetic transitions into and out of the soliton phase. An unusual low temperature field dependence of the Hall resistivity is reported in the same temperature range as the unexpected anisotropy in the magnetoresistance. A sharp decrease in the Seebeck coefficient occurs in this same temperature range. Additionally, a negative relation between resistivity and planer strain, peaking at T_c , is observed. In this material, changes in temperature (near T_c), as well as the application of magnetic fields, lead to large reductions in the resistivity through a reduction in spin degrees of freedom. Therefore, it seems likely that strain is in some way reducing spins degrees of freedom as well. By way of crystallographic change, small amounts of strain may be significantly altering the magnetic texture. There was no evidence of nontrivial spin textures observed. A high crystalline anisotropy, leading to a large magnetic anisotropy, likely suppresses topologically complex spin textures from forming in this material.

4.1 Future Work

Moving forward, we search for an explanation to the low temperature anisotropy in the magnetoresistnace, as well as the unusual field dependence of the Hall effect. In the meantime, we will continue to investigate mechanical strain as a new tool to explore the relationship between transport properties and spin and lattice degrees of freedom. With this approach, some insight may be gained into magneto-phonon coupling. In the near future we will explore sample properties as the c-axis thickness approaches the pitch length of the helix by measuring thin films of $Cr_{1/3}NbS_2$ (thickness < 1µm).

Chapter 5

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