NEUTRON SCATTERING AND TRANSPORT STUDIES OF QUANTUM MATERIALS

By

Heda Zhang

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

2022
ABSTRACT

NEUTRON SCATTERING AND TRANSPORT STUDIES OF QUANTUM MATERIALS

By

Heda Zhang

Quantum material is an multi-disciplinary research topic that continues to thrive in recent years. The term Quantum material covers all systems which demonstrate physical phenomena beyond the scope of single-particle, semi-classical/quantum theory. Among many sub-fields of quantum materials, topological systems and strongly correlated systems are two topics which have receive growing attention from the scientific community.

We begin with a discussion on a van der Waals magnet VI$_3$ in chapter three. VI$_3$ hosts ferromagnetism on a honeycomb lattice, which was one of the proposed models for topological magnon bands. There have been ample theoretical studies on ferromagnetic honeycomb lattice. However, there has not been any physical realization of such model. In our study, we show that the is a strong anomalous thermal Hall effect in VI$_3$, the underlying mechanism of which is the non-trivial topological nature of the magnon bands.

In chapter four, we discuss our transport studies on some magnetic topological metals. The non-zero Berry curvature in the reciprocal space of topological metals can lead to anomalous transverse conductivities ($\kappa^A, \sigma^A, \alpha^A$) in the system. We found large anomalous transverse conductivities in TbMn$_6$Sn$_6$ and verified its intrinsic nature through first-principle calculations. Furthermore, we have found large exchange-bias behavior in TbMn$_6$Sn$_6$, which renders it as a promising system for anomalous Nernst effect based thermoelectric device. We will also discuss the topological Nernst effect observed in Fe$_3$Sn$_2$, which is potentially due to the Skyrmion bubble phase revealed by the Lorentz transmission electron microscopic studies.
In chapter five, we discuss our inelastic neutron scattering study on a unique quantum spin chain system in Cu$_2$(OH)$_3$Br. The system hosts alternating ferromagnetic and anti-ferromagnetic spin chains with finite inter-chain couplings. This allows for the coexistence and interactions between magnons and spinons.
# TABLE OF CONTENTS

## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Chapter 1 Introduction</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Strongly correlated systems</td>
<td>2</td>
</tr>
<tr>
<td>1.1.1 What is a strongly correlated system?</td>
<td>2</td>
</tr>
<tr>
<td>1.1.2 High T&lt;sub&gt;c&lt;/sub&gt; superconductor</td>
<td>3</td>
</tr>
<tr>
<td>1.1.3 Quantum spin liquids</td>
<td>5</td>
</tr>
<tr>
<td>1.2 Topological materials</td>
<td>10</td>
</tr>
<tr>
<td>1.2.1 What is topology?</td>
<td>10</td>
</tr>
<tr>
<td>1.2.2 Berry curvature and Haldane model</td>
<td>11</td>
</tr>
<tr>
<td>1.2.3 Berry curvature and anomalous transport</td>
<td>14</td>
</tr>
</tbody>
</table>

## Chapter 2 Experimental techniques

<table>
<thead>
<tr>
<th>2.1 Transport measurements</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.1 Transport coefficients definitions</td>
<td>17</td>
</tr>
<tr>
<td>2.1.2 Hardware</td>
<td>18</td>
</tr>
<tr>
<td>2.1.3 Software</td>
<td>19</td>
</tr>
<tr>
<td>2.1.4 Radiation correction</td>
<td>20</td>
</tr>
<tr>
<td>2.1.5 Thermal Hall effect measurement</td>
<td>21</td>
</tr>
<tr>
<td>2.2 Neutron scattering</td>
<td>24</td>
</tr>
<tr>
<td>2.2.1 Neutron diffraction</td>
<td>25</td>
</tr>
<tr>
<td>2.2.2 Inelastic neutron scattering</td>
<td>26</td>
</tr>
</tbody>
</table>

## Chapter 3 Anomalous thermal Hall effect of VI<sub>3</sub>

<table>
<thead>
<tr>
<th>3.1 Introduction</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2 Results</td>
<td>29</td>
</tr>
<tr>
<td>3.3 The anomalous thermal Hall effect</td>
<td>31</td>
</tr>
<tr>
<td>3.4 Theoretical interpretations</td>
<td>35</td>
</tr>
</tbody>
</table>

## Chapter 4 Electric, thermal and thermoelectric transport studies of magnetic topological metals

<table>
<thead>
<tr>
<th>4.1 Introduction</th>
<th>41</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 Exchange-biased anomalous transport in TbMn&lt;sub&gt;6&lt;/sub&gt;Sn&lt;sub&gt;6&lt;/sub&gt;</td>
<td>43</td>
</tr>
<tr>
<td>4.3 Topological Nernst effect in Fe&lt;sub&gt;3&lt;/sub&gt;Sn&lt;sub&gt;2&lt;/sub&gt;</td>
<td>55</td>
</tr>
</tbody>
</table>

## Chapter 5 Quantum spin chains in Cu<sub>2</sub>(OH)<sub>3</sub>Br

<table>
<thead>
<tr>
<th>5.1 Introduction</th>
<th>69</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2 Results</td>
<td>70</td>
</tr>
<tr>
<td>5.3 Magnon-spinon interactions</td>
<td>78</td>
</tr>
<tr>
<td>5.4 Conclusions</td>
<td>83</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>6.1</td>
<td>Manual for TTO_v2</td>
</tr>
<tr>
<td>6.1.1</td>
<td>The hierarchy of TTO_v2.lvproj and the maine.vi</td>
</tr>
<tr>
<td>6.1.2</td>
<td>Six frequently used options</td>
</tr>
<tr>
<td>6.1.3</td>
<td>Performing a measurement</td>
</tr>
<tr>
<td></td>
<td>BIBLIOGRAPHY</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1.1: Development of superconducting temperatures over the years in different materials. Adapted from [1]. ................................. 4

Figure 1.2: Phase diagram of $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$ under pressure. Adapted from [2]. 5

Figure 1.3: (Left) A single spin-1/2. (Middle) Two-spin system. (Right) Three-spin system with equal anti-ferromagnetic Heisenberg interactions. ............... 7

Figure 1.4: (Left, upper) A graphical representation of the Kitave model, modified from Figure 4 in [3]. The spin is fractionalized into four Majorana fermion. (Left, lower) Pseudocolor plot of the Band gap for $K^x = K^y = K^z = K_0$. A zoom in view of the Dirac-like dispersion near one of the K-points. (Right) Creation of a long-range entangled spin pair through the path indicated by blue dash line. Two vortices (red) were created. ............... 9

Figure 1.5: (Upper, left) A honeycomb lattice with lattice spacing denoted by a. (Upper, middle) Dispersion along $K - \Gamma - K$ and a contour map of the dispersion for the Hamiltonian $H$ with $u = 0$. Berry potential $A(\vec{k})$ and the corresponding Berry curvature $\Omega(\vec{k})$ (scaled) for $M = 0.1t_1$, $t_2 = 0$(Lower, left) and for $M = 0.1t_1$, $t_2 = 0.1t_1$ (Lower, right). 13

Figure 2.1: Front panel of maine.vi. ......................................................... 19

Figure 3.1: (left) Crystal structure of VI$_3$ at room temperature. Vanadium atoms are shown in red and Iodine atoms are shown in purple. (Right) View in the crystal ab-plane showing the Vanadium atoms assembled on a honeycomb lattice. Both figures are generated by VESTA [4]. 29

Figure 3.2: (Upper) The field-cooled magnetic (0.1 T) susceptibility and the absolute value of its temperature derivative of a VI$_3$ sample. (Right) The thermal conductivity of a VI$_3$ sample measured under 0 T and 7 T applied field. The magnetic field is applied along the crystalline c-axis for both figures. 30
Figure 3.3: (Upper) Magnetization and thermal conductivity data measured at 20 K. For the thermal conductivity measurement, the sample is at 21.6 K due to heating. The orange/blue arrow indicates the field sweep direction. (Left) Magnetization data of VI$_{3}$ at selected temperatures from 2 K to 100 K. Each curve has been moved vertically by 3 $\mu_B/V^{3+}$ for clarity. (Right) Change of thermal conductivity in percentage as a function of magnetic field at different temperatures. Each curve has been moved vertically by 3% for clarity.

Figure 3.4: The anomalous thermal Hall effect measurement data at various temperatures between 10 K to 50 K.

Figure 3.5: Thermal measurement data of sample #2 below 10 K. (Left) Change of thermal resistivity. Each curve is shifted vertically by 0.05 K m W$^{-1}$ for clarity. (Middle) Thermal Hall resistivity. Each curve is shifted vertically by 0.015 K m W$^{-1}$ for clarity. (Right, upper) Thermal Hall resistivity obtained by methods described in Section 2.1.5 The black dash lines are scaled magnetization data at each temperature. (Right, lower) Thermal Hall resistivity obtained by methods described in [5].

Figure 3.6: Thermal Hall conductivity ($\kappa_{xy}$, orange/blue) and thermal conductivity ($\kappa_{xx}$, red) measured up to 7 T.

Figure 3.7: Temperature dependence of thermal conductivity (Left) and thermal Hall conductivity (Middle) for different samples. (Right) Magnetic field dependence of thermal Hall conductivity for different samples.

Figure 3.8: (Left) Magnon bands dispersion for $D_z = 0$ meV (red/blue curve) and $D_z = 0.2$ meV (green-white surface). The black dashline represents boundary of Brillouin zone. (Right) Z-component of the Berry curvature ($\Omega^z$) for the upper and lower magnon band.

Figure 3.9: (Upper) Calculated thermal Hall conductivity due to topological magnon with various DMI strength. (Lower) Comparison between experimental data (blue) and theoretical predictions (orange) of thermal Hall conductivity. The difference between experimental and theoretical values are shown as yellow markers. (Right) Berry curvature distribution in the reciprocal space.

Figure 3.10: (Left) Total dispersion of the hybrid magnon-phonon band (g=0.5). (Middle) The absolute value of Berry curvature’s (|$\Omega^z$|) distribution in the reciprocal space. The emergence of a ring-shaped region of Berry curvature is due to the magnon-phonon anti-crossing near $\Gamma$ point. (Right) Comparison between experiment and theoretical values for various magnon-phonon coupling strength.
Figure 4.1: (Left) Crystal and magnetic structure of TbMn\textsubscript{6}Sn\textsubscript{6}. The terbium/manganese/tin atoms are represented by the black/red/blue spheres. The terbium/manganese’s magnetic moments are represented by black/red arrows. (Right) Magnetic susceptibility data of TbMn\textsubscript{6}Sn\textsubscript{6} measured along the crystalline c-axis (red, blue) and a-axis (black). (Lower) The temperature dependence of resistivity ($\rho_{xx}$), thermal conductivity ($\kappa_{xx}$) and Seebeck coefficient ($S_{xx}$) of TbMn\textsubscript{6}Sn\textsubscript{6}. 45

Figure 4.2: (Left) Magnetization data after cooling to the respective temperatures with an applied field of 0.5 T. (3 T $\rightarrow$ -3 T $\rightarrow$ 3 T) (Right) Magnetization data after cooling to 100 K with the respective applied fields. (1.5 T $\rightarrow$ -1.5 T $\rightarrow$ 1.5 T) 47

Figure 4.3: (Left) Temperature and field dependence of the bias-field and magnetization. (Right) Field-reversal and training effect of the exchange-bias behavior. 48

Figure 4.4: (Left) Magnetic field dependence of $\sigma_{xy}$ measured at various temperatures. (Upper, right) Temperature dependence of $\sigma_{xy}^A$. (Lower, right) Fitting result of the anomalous Hall resistivity. 49

Figure 4.5: Field dependence of anomalous thermal Hall conductivity (Left) and anomalous Nernst coefficient (Middle). (Upper, right) Temperature dependence of anomalous thermal Hall conductivity and anomalous Lorentz number. (Lower, right) Temperature dependence of anomalous Nernst coefficient. 50

Figure 4.6: (Upper, left) Band structure and Berry phase ($-\Omega_{xy}$) of TbMn\textsubscript{6}Sn\textsubscript{6}. (Upper, right) Calculated anomalous Hall conductivity. (Lower, left) Berry phase at the Fermi level with kz = 0. (Lower, right) Experimental and theoretical thermoelectric linear response tensor. 52

Figure 4.7: (Left) A illustration of typical design for ANE based thermoelectric device. (Right) Stray field produced by one of the module in the thermopile. 53

Figure 4.8: (Left) Ratio of coercive field ($H_c$) to magnetization (M) as a function of minimum separation distance. The separation distance is plotted in units of sample boundary. For example, at x/(0.5w) = 1 is the sample boundary. (Inset, left) Magnetization of Fe\textsubscript{3}Sn\textsubscript{2} at 2 K. (Right) Summary of the $S_{xy}$ − $M$ scaling for conventional and topological magnets. 54
Figure 4.9: (a) Schematic crystal structure of Fe$_3$Sn$_2$; iron atoms are represented by red spheres forming Kagome planes, tin atoms are represented by blue spheres. (b) Illustration of the experimental set-up. The temperature gradient is indicated by color scale, the heat sink used is oxygen free high conductivity (OFHC) copper, and the heater used is a thin film resistor (1 kΩ) (c) Temperature dependence of longitudinal electrical ($\sigma_{xx}$, black) and thermal ($\kappa_{xx}$, red) conductivities. (d) Temperature dependence of Seebeck (blue) and Nernst (red, 1.5 T) coefficients. Inset shows an expanded view below 160 K.

Figure 4.10: Magnetic field dependence of Seebeck coefficient scaled by temperature $-S_{xx}/T$ (a) and thermal conductivity $\kappa_{xx}$ (b); Magnetic field dependence of Nernst coefficient scaled by temperature $S_{xy}/T$ (c) and thermal Hall conductivity $\kappa_{xy}$ (d). Data were measured at various temperatures.

Figure 4.11: (a) Magnetic field dependence of residual Nernst coefficient measured at various temperatures after subtracting the normal Nernst coefficient ($\propto H$). The magnetization (H∥c) data measured at 300 K is overplotted as the dashed line. The saturated magnetization is about 1.8 $\mu_B$/Fe. (b) Magnetic field dependence of topological Nernst coefficient (left) and Hall resistivity (right) after subtracting out the anomalous contribution ($\propto M$).

Figure 4.12: (a) Residual thermoelectric linear response tensor scaled by temperature $\Delta\alpha_{xy}/T$ after subtracting the normal Nernst coefficient. (b) Normal and anomalous (1.5 T) Nernst coefficient scaled by temperature. (c) Anomalous thermal and electric Hall conductivity (1.5 T) as a function of temperature. (d) Temperature dependence of Total anomalous thermoelectric linear response tensor ($\alpha^A_{xy}$) and its two components ($\alpha^A_1, \alpha^A_2$).

Figure 5.1: Crystal structure and magnetic structure of Cu$_2$(OH)$_3$Br. Crystal structure of Cu$_2$(OH)$_3$Br in the ac (a) and ab (b) plane showing a quasi-two dimensional, distorted triangular lattice of Cu atoms. (c) Temperature dependence of neutron diffraction intensity of an ordering wave vector (0.5 0 0). The inset shows the temperature dependence of heat capacity and magnetic susceptibility measurements. (d) Schematics of spin structure of Cu$^{2+}$ ions with Cu2 spins point along the a-axis while Cu1 spins pointing nearly along the diagonal direction in the ac plane. Exchange interactions of Cu1-Cu1, Cu2-Cu2, and Cu1-Cu2 as well as DM interaction are denoted.
Figure 5.2: Magnetic excitation spectra and the comparison to LSW calculations. (a) The momentum- and energy-resolved neutron scattering intensity map I(E, H) (K = -0.5 and with all measured L values integrated). (b) Intensity map I(E, L) (K = -0.5 and with all measured H values integrated). These two intensity maps show nearly dispersionless magnetic excitations along both H and L directions. (c) Intensity map I(E, K) with both H and L integrated over all measured values to enhance the statistics of the signal. These intensity maps were obtained after using the data measured at T = 100 K as background and subtracting it from the data measured at T = 5 K. (d) The calculated I(E, K) spectra using LSW theory. The white curves in all panels are the calculated dispersions using LSW theory.

Figure 5.3: Electronic structure calculated via first principles DFT. (a) The ground state spin density of the half-filled eg orbital of Cu$^{2+}$ ions and p orbitals of O and Br atoms. Yellow color denotes spin up and cyan color denotes spin down. Cu1 ions with ferromagnetic spin alignment show antiferro-orbital order while Cu2 ions with antiferromagnetic spin alignment show ferro-orbital order. (b) The projected density of states (PDOS) of Cu1, Cu2, Br, and O ions.

Figure 5.4: Magnetic excitation spectra via quantum Monte Carlo simulations. Simulated magnetic excitation spectra (with H = 1) of a system consisting of alternating ferromagnetic and antiferromagnetic quantum spin chains with the interchain coupling J3 = 0 (a), J3 = 0.1J2 (b), and J3 = 0.2J2 (c). (d) Constant energy cuts at E = 8.7 9.7 meV showing the asymmetric spectral intensity about K = 1 induced by non-zero J3. Note that Bose factor but not magnetic form factor of Cu$^{2+}$ ions has been taken into account in the simulation.

Figure 5.5: Magnetic excitation spectra and the comparison with RPA calculations. (a) I(E, K) intensity map obtained after background subtraction with H integrated over [0.85 1.1] and L integrated over all measured values. (b) The RPA calculation of I(E, K) spectra for comparison. Constant energy cuts at E = 10.75 meV (c) and at E = 7.75 meV (d) and their comparison with RPA calculations.

Figure 6.1: The hierarchy of TTO_v2.lvproj

Figure 6.2: The front panel of maine.vi. For the most part, a typical user should only need to access this panel.

Figure 6.3: The front panel of testing module.vi

Figure 6.4: The program hierarchy and the front panel of ScanT_module_stable_III
Figure 6.5: The front panel of log_data_v1.vi
Chapter 1

Introduction

This chapter contains an introduction to quantum material based on my research experience. The word quantum has been so widely used by not only researchers in the scientific community, but also people from all walks of life.\(^1\) The reason behind its popularity is that quantum material is a very broad term, it can encapsulate the essential physics of many different fields of studies. The vague nature of this term made it impossible to define. When two researchers from different fields used the same phrase quantum material, they may be referring to completely different physical phenomena. However, the reason for their usage of the phrase is the same: to convey to the readers in a concise manner that there are new physics at play in the system. Therefore, the only important thing in dealing with quantum materials is to understand the underlying new physics discussed by the authors.

The quantum materials that will be discussed in this thesis can be cast into two main categories: strongly correlated systems and topological materials \([6]\). Atomic, molecular and optical systems will not be discussed in this thesis.

\(^1\) Even Ponzi schemes have to do quantum nowadays, can you imagine, a quantum Ponzi scheme
1.1 Strongly correlated systems

1.1.1 What is a strongly correlated system?

In condense matter physics, a physical system is composed of atoms assembled in certain geometric orders called lattice. The atoms are made of nuclei and electrons. The electrons surrounding the nuclei have different spatial density profile which are called orbitals (or electron clouds). An electron possesses both a spin of 1/2 Bohr magneton ($\mu_B$) and a charge of $1.6 \times 10^{-19}$ coulombs (C). When considered in isolation, each of the four degrees of freedoms (lattice-spin-charge-orbital) of an atom may be understood using quantum mechanics. However, atoms in a physical system inevitably interacts with each other. The correlated here refers to correlations within and between these four degrees of freedom among atoms in a physical system. When this correlation becomes strong enough that a physical system starts to demonstrate behaviors beyond what known theory can explain, an adjective strongly is added in front. Collecting these concepts together, we arrive at a loose definition of strongly correlated systems from my perspective.

The reason I qualify the aforementioned definition with ‘loose’ is two-fold: first, I could not find a more strict definition which would also cover the entire body of work on the subject. Second, I could not find a single consensus on the definition of a strongly correlated system from existing literature. The same sentiment was expressed in a manuscript posted on arXiv in the year 2020 called The Future of the Correlated Electron Problem\(^2\) [7]. In the manuscript, the authors wrote in the first paragraph of the first chapter:

\(^2\)“This manuscript is the result of the vigorous discussions and deliberations that took place at Johns Hopkins University during a three-day workshop January 27, 28, and 29, 2020 that brought together six senior scientists and 46 more junior scientists.”
There is no consensus on the role of strong electron correlations in solids. Moreover, at present, there is no agreed single definition as to what constitutes the correlated electron problem. As such, for the purposes of this manuscript, we adopt the following working definition: a correlated electron problem is one in which interactions are so strong or have a character such that theories based on the underlying original “bare” particles fail even qualitatively to describe the material properties.

The authors here further explain what “beyond known theory” means: the breakdown of “bare”, single particle physics. For example, the celebrated Fermi liquid theory fails to explain the metal-insulator transition in many transition metal oxides. To correctly predict the band structure of these systems, the electron-electron correlation effect (i.e., the Coulomb repulsion of d-electrons) needs to be taken into account.

1.1.2 High T\textsubscript{c} superconductor

Although there is no consensus on the definition of strongly correlated systems, most condensed matter researchers may agree that the discovery of high T\textsubscript{c} superconductors in Ba-La-Cu-O system \cite{8} provided strong motivations for the following theoretical and experimental investigations in the study of strongly correlated systems. Looking in hindsight, the exciting nature of this discovery is not simply that the T\textsubscript{c} (superconducting temperature) is high, but that the highest T\textsubscript{c} was found in such a ‘dirty’ system. Following simple physical intuitions, one would try to avoid introducing any scattering centers when searching for superconductors (e.g., lattice defects, magnetic impurities, etc.), as these scattering centers may prohibits the electrons from traversing freely through the system\footnote{The Bardeen-Cooper-Schrieffer (BCS) theory explains superconductivity as the condensation of Cooper pairs at low temperatures, which was the most accepted explanation at the time. In this sense, superconductivity is a coherent quantum state and cannot be thought of as electrons traversing freely through the system with no scattering.} and cause high electric resistance.
As remarked by B. Keimer et al in [1]: “... the copper oxides would have seemed the least likely materials in which to look for superconductivity: at room temperature they are such poor conductors that they can hardly be classified as metals ...”.

The discovery forced researchers to break from the paradigm of the BCS-theory and pointed to the new direction of cuprates. Since then, cuprates with higher and higher superconducting temperatures have been gradually identified (Figure 1.1), culminating in finding HgBaCaCuO system with $T_c = 165 \text{ K}$ under pressure.

After the discovery of cuprates, the importance of electron correlations has been gradually realized and accepted by the condense matter physics community. With electron correlations taken into account, we have seen even stranger tale of superconductivity in recent years. Unless you are a mad scientist, when trying to search for new superconductors, you should typically start with a conductor. However, superconductivity was observed in an organic Mott insulator $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$ under external pressure [2]. The pressure needed there was no more than 0.4 GPa, which is an incredibly small input for such a titanic response.

---

4“Woah, We’re halfway there; Woah, livin’ on a prayer. - Mr. Bovine Joni” - Frank Reynolds

5After all, the clue is in the name: a superconductor is a ‘super’ conductor. But as we shall see later, just like superman is not a ‘super’ man but an alien, an unconventional superconductor may be something of a completely different nature than a typical superconductor.

6For reference, diamond anvil cells generally can reach between 10 GPa to over 100 GPa.
which many researchers were drawn: that the simultaneously activation of the four degrees of freedom can result in complex energy landscapes, where many potential ground states may be in close proximity to each other. The implication of this is that when some parameters were tuned (e.g., temperature, field, pressure, chemical, etc), one may obtained a phase diagram such as the one on the right panel of Figure 1.2.

Although searching for superconductivity by simply tuning some parameters of a Mott insulator [9] may have seemed highly implausible, it was not without a supporting theory. In fact, the resonating valence bond (RVB) theory [10], which motivated the work on $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$, predates the experiment by nearly two decades. The RVB theory was intended to explain the high-$T_c$ superconductivity of La$_2$CuO$_4$, it caused a surging interests in another field of study called quantum spin liquids (QSL).

1.1.3 Quantum spin liquids

What does ‘liquid’ in quantum spin liquid refer to? The ‘liquid’ here refers to a situation wherein a system of interacting spins does not develop magnetic long-range order (‘solid’), even as the system temperature approaches absolute zero. Magnetic frustration plays an

\footnote{In my opinion, quantum spin liquid can be considered as a sub-field of strongly correlated system, where the spin degree of freedom play the main role.}
Important role in preventing the onset of magnetic long-range order, but it is not the defining feature of a QSL. In recent years, more and more theoretical and experimental investigations on candidate QSL materials suggest that, a more appropriate description of QSL should be a spin system whose ground state possesses long-range entanglement [11].

We begin our discussions with an isolated spin-1/2 system (Figure 1.3, left). In a spin-1/2 system, any spin wave function can be written as the superposition of two eigenstates \{ |↑⟩, |↓⟩ \}. In this way, one may obtain a geometrical interpretation of spin wave function in terms of a vector which can point to any direction on the globe. Moving on to two spin-1/2 systems (Figure 1.3, middle). In this case, the eigenstates can be shown to be singlet \([(|↑⟩−|↓⟩)/√2] \) and triplet. I will not go into details about singlet/triplet but only point out that the singlet state is a maximally entangled state. Here, the concept of entanglement needs be introduced. Entanglement refers to the phenomenon when the state of a quantum mechanical system cannot be written as the direct product states of it constituting sub-systems. This abstract concept can be quantified, for example by the Von Neumann entropy. However, we will take a more intuitive approach to see why the singlet state is maximally entangled. Imaging taking a single particle measurement of either of the spins in the singlet state, for any quantization axes (σₓ, σᵧ, σᶻ) chosen, the expectation value along that axis would have been zero. What this means is that there is no information to be gained by any single-particle measurement, and that all the information resides in the entanglement of the two spins in the singlet (i.e., they points to opposite directions).

---

8In my opinion, while the geometric interpretation makes for a good pedagogical analogy, it masks the peculiarity of superposition. For example, a spin which points to the equator is in fact pointing to both the north and the south pole instead. It is in a superposition state, to which we could find no classical analogy (you could not have the cake and eat it too). When we draw a vector pointing to the equator, we were given a very tangible and ordinary physical picture, when in fact the state to which it represents is highly intangible and extraordinary.

9From this definition, we immediately see that entanglement is impossible without superposition.
Finally, we consider a three-spin system with equal anti-ferromagnetic (AFM) Heisenberg interactions and discuss magnetic frustrations (Figure 1.3, right).\footnote{I should add that the solution of triangular lattice AFM-Heisenberg model is the 120° configuration.} If we were given two known spins configured as shown, the spin on top would have been ‘frustrated’ in the sense that it could not find a preferred direction to point to, in order to lower the total energy. From this example, we see that magnetic frustration is one specific realization of the more abstract concept \textit{degeneracy}.

![Figure 1.3: (Left) A single spin-1/2. (Middle) Two-spin system. (Right) Three-spin system with equal anti-ferromagnetic Heisenberg interactions.](image)

In microscopic systems, such degeneracy can be easily handled; However, in a physical system consisting of avogadro’s number of particles, the proliferation of ground state degeneracy to a macroscopic level could lead to long-range entanglement and novel quasiparticles. To see this, consider the example (triangular lattice) shown as the bottom row of Figure 1.3. Two degenerate ground state $\psi_1$ and $\psi_2$ with 3 pairs of spin-singlets\footnote{Although I have drawn arrows here to represent the spin direction, we should recall from our previous discussion that singlet is a maximally entangled state and each individual spin points to no definitive direction.} (indicated by the gray
dashline) were show, the superposition with equally weighted $\psi_1$ and $\psi_2$ is also a ground state ($\psi_3$). However, the entanglement has now grown in dimensions: a pair of singlet is now separated by twice the lattice constant. While the example here is only for a 9-spin system, it is not a hard exercise to see that the same principle could work for lattices of any size. This is the essential idea of resonating valence bond (RVB) theory, that the superposition of a highly degenerate ground states set could lead to entangled spin singlets separated by macroscopic distance.

An exact solvable model of QSL can be found in the celebrated Kitaev model [3]. The model consists of spins (S=1/2) on a honeycomb lattice with nearest neighbor anisotropic exchange-interactions (Figure 1.4). To understand the Kitaev model, we first note that a plaquette operator $W_p = \sigma_1^x\sigma_2^y\sigma_3^z\sigma_4^x\sigma_5^y\sigma_6^z$ takes on value of ±1, commutes with each other and the Hamiltonian. Therefore, eigenstates of the Hamiltonian can be labeled by the locally conserved ‘flux’ through each plaquette. A plaquette with $W_p = -1$ is a ‘vortex’, and the ground state is the superposition of any spin configurations which are vortex-free\(^\text{12}\). The spin Hamiltonian can be re-written in a form consisting of 4 Majorana operators: three of which are immobile ($b_j^{x,y,z}$) and control the phase gain while the itinerant ($c_j$) one hops through that bond. The dispersion relation for the itinerant Majorana fermion was $\epsilon(\vec{q}) = 2|K_x e^{iq_1 \cdot n_a} + K_y e^{iq_2 \cdot n_b} + K_z|$, which become gapless at K-pionts. Entanglement is a strange concept because of its implication of non-locality. It is interesting to consider the creation of a long-range entangled spin pair as depicted in Figure 1.4. In the Kitave model, entanglement between the spin pair does not need to rely on ‘action at a distance’; Instead, the entanglement is the result of a path operator (local at each lattice site) which connects

\(^\text{12}\)An alternative description of the ground state is the superposition of the classical spin configurations shown as red, blue and green. The idea is very similar to the RVB model.
the entangled spin pair. The spectrum for a more general gapped phase and non-Abelian Anyons of the Kitave model has been discussed in length in [3]. I should not need to further belabor the rich physics behind this deceivingly simple model [3, 12, 13].

Figure 1.4: (Left, upper) A graphical representation of the Kitave model, modified from Figure 4 in [3]. The spin is fractionalized into four Majorana fermion. (Left, lower) Pseudocolor plot of the Band gap for $K^x = K^y = K^z = K_0$. A zoom in view of the Dirac-like dispersion near one of the K-points. (Right) Creation of a long-range entangled spin pair through the path indicated by blue dash line. Two vortices (red) were created.
1.2 Topological materials

1.2.1 What is topology?

Like many young researchers drawn to the concept of topological insulators (TIs), my first attempt to understand the topic was to read the review paper by M. Z. Hasan and C. L. Kane [6]. At the beginning of this paper, a picture of an orange and a donut was shown to illustrate the concept of topology. However, this was not the ‘answer’ to what I was hopping for: I can see that there are different numbers of holes in them, but how do I make the connection between ‘holes’ to non-trivial band topology?

To see the connection, we must first understand Topology on an elementary level. We begin by introducing manifolds: a topological space that locally resembles Euclidean space near each point. For example, a piece of (infinitely thin) A4 paper is a 2D-manifold; And just like we can artistically fold a piece of paper into a swan or a frog (origami), we can continuously deform a manifold into almost any other manifolds. A question we can ask is: can we classify manifolds into different groups, such that manifolds within one group can be continuously deformed into each other, but not to manifolds outside the group? One such way to categorize manifolds was by using the genus (g) as the index for different groups.

A more formal way to calculate the genus of a surface than ‘counting the number of holes’,

---

13During the Nobel Prize announcement event, a cinnamon bun, a donut and a pretzel were used to demonstrate the concept of topology... but I believe they were just too hungry.
14To get a sense of manifolds, consider the following: a circle is a 1D-manifold, a Lemniscate (∞) is not a manifold but a Mobius strip is a 2D-manifold.
15The task description here clearly indicates that this is a task for group theory. In fact, there have been efforts of high-throughput calculations using symmetry-indicators to identify new topological materials. It is very helpful to get a basic understand of group theory in CMP by reading the textbook: Applications of Group Theory to the Physics of Solids [14]. I particularly recommend the lecture notes by Daniel Arovas [15] for both deeper knowledge and some great jokes. (As written in the preface: “These lecture notes are intended to supplement a graduate level course in group theory applied to condensed matter physics. Or one can skip all the math and just read the jokes.”)
16Technically, the genus is defined for a connected, orientable surface.
was by integrating the Gaussian curvature (K) over the surface.\textsuperscript{17} The genus is a topological invariant: its value will remain the same during any deformations which does not change the compactness of the surface.

Returning to the context of condense matter physics: we can use the Berry curvature, integrated over the first Brillouin zone as an index, to categorize different insulators into trivial and topological groups. The integrated value scaled by a factor of $1/2\pi$ is the Chern number, which always takes on integer value. We discuss the application of this topological invariant by studying its application on the Haldane model.

### 1.2.2 Berry curvature and Haldane model

The adiabatic theorem \cite{16} states that, a system will remain in its instantaneous eigenstates (up to a phase), if the process is slow enough and does not admit any eigenstates mixing. Applying this theorem to a system whose Hamiltonian depends on some external parameters $H(\vec{p})$, we see that there can be a phase shift after an adiabatic evolution along a close path $C$ in the parameter space. The phase shift between the initial and final state is the Berry’s phase \cite{17}. The concept can be generalized to Berry potential/connection $A(\vec{p}) = \langle u(\vec{p}) | i\nabla | u(\vec{p}) \rangle$. The curvature of Berry potential $\Omega = \nabla \times A(\vec{p})$ is the Berry curvature. The advantage of introducing Berry potential and curvature is that we can write them as scalar and vector fields in the parameter space, without the need to consider any specific loops or path. We can directly visualize these concepts by studying the Haldane model \cite{18}.

The Haldane model is a two-dimensional tight-binding model on a Honeycomb lattice (Figure 1.5, upper left). The Hamiltonian matrix writes $H(\vec{k}) = \begin{bmatrix} u & h \\ h^* & -u \end{bmatrix}$, where $h = 2t_1 * $\textsuperscript{17}They are related through the Gaussian-Bonnet theorem for a closed surface, $\int_S K = 4\pi(1 - g)$
\[ \sum_j e^{i\vec{k} \cdot \vec{a}_j} \] and \( u = M + 2t_2 \sum_j \sin (\vec{k} \cdot \vec{b}_j) \). By solving the eigenvalue problem \( \det |H - \lambda I| = 0 \), we obtain the spectrum \( \lambda = \pm \sqrt{|h|^2 + u^2} \). When \( u = 0 \), the spectrum reaches its maximum value at \( \Gamma \) and become gapless at \( K \). A dispersion along \( K - \Gamma - K \) and a contour map of the spectrum are shown in Figure 1.5 (upper, middle). We further consider two ways of gapping out the model Hamiltonian to obtain an ‘insulator’. The first way was to add a site specific potential energy \( \pm M \), and the second way was to add an imaginary hopping energy \( (it_2) \) between second-nearest neighbors, whose sign depends on the hopping direction. Either method would produce a gap at \( K \) points, thereby ensuring that no eigenstates mixing would be allowed within the Brillouin zone. We can calculate the Berry potential and its curvature. The lower panel of Figure 1.5 shows the numerical results for the upper band (\( E > 0 \)). The black arrow represents the vector field of Berry potential \( A(\vec{k}) \), the pseudo-color map represents the Berry curvature \( \Omega(\vec{k}) \), both of which have been multiplied by a \( k \)-dependent scaling factor \( |\lambda| \sqrt{(|h|^2 + (|\lambda| + u)^2)(|h|^2 + (|\lambda| - u)^2)} \).

For the case of \( M = 0.1t_1 \), \( t_2 = 0 \) (Figure 1.5, lower left), two types of vortices with opposite curling directions emerge near \( K \)-points. The Chern number for this ‘insulator’ phase is \( C = 0 \) (i.e., a trivial insulator). If we add in the second-nearest neighbor imaginary hopping integral \( t_2 = 0.1t_1 \), only one type of vortex arise (Figure 1.5, lower right), and the corresponding Chern number (for the positive energy branch) is +1.

---

\(^{18}\)This is done because the magnitude of Berry potential/curvature increase drastically near the smallest band gap points. Without the scaling factor, the plots in Figure 1.5 will be strongly emphasized only near each of the \( K \)-points.
Figure 1.5: (Upper, left) A honeycomb lattice with lattice spacing denoted by a. (Upper, middle) Dispersion along $K - \Gamma - K$ and a contour map of the dispersion for the Hamiltonian $H$ with $u = 0$. Berry potential $A(\vec{k})$ and the corresponding Berry curvature $\Omega(\vec{k})$ (scaled) for $M = 0.1t_1$, $t_2 = 0$ (Lower, left) and for $M = 0.1t_1$, $t_2 = 0.1t_1$ (Lower, right).

The model can be further generalized by allowing the second-nearest neighbor hopping integral to have arbitrary phase: $t_2 \ast e^{i\phi}$. The Chern number ($C$) is a topological invariant, in the sense that it does not vary continuously with changing $M$, $t_2$ or $\phi$. As shown in the phase diagram from [18]: $\phi$ will control boundary between trivial and topological phase and there does not exist any intermediate value for the Chern number.

Up to this point, we have seen the analogy between band topology and ‘mathematical’ topology. They both feature a topological invariant which remains a constant during smooth transformations. We have not seen any connection between the topological invariant to anomalous transport phenomena. While an orange and a donut have different genus, there is no physical implication for this difference. In condense matter physics, the bulk-boundary
correspondence dictates that there must exist a chiral edge state between two gapped bands with different topological invariants. For the Haldane model with $|M| < 3\sqrt{3}|t_2\sin(\phi)|$, the valence and conduction band has opposite C and a chiral edge state connecting them. The opposite situation is found for the case of $|M| > 3\sqrt{3}|t_2\sin(\phi)|$. The existence of such chiral edge state is why an insulator with $C = 0$ is trivial, but an insulator with $C \neq 0$ is topological.

1.2.3 Berry curvature and anomalous transport

Berry curvature also plays an essential role in anomalous transports. Using the Kubo formula, it was found that electrons acquire an ‘anomalous velocity’ (perpendicular to electric field) due to the presence of non-zero Berry curvature. As such, the Berry curvature acts like an synthetic gauge field\textsuperscript{19} in the reciprocal space. As an extreme case demonstration (for example, the TaAs system), this synthetic gauge field permits the existence of pairs of monopoles and anti-monopoles called Weyl points.\textsuperscript{20} Surface state called fermi arcs connects Weyl points of opposite chirality and has been experimentally observed (right figure [19]).

\textsuperscript{19}The Berry potential/curvature are related as $\Omega = \nabla \times A$. The Berry curvature interacts with an electron through $v \times \Omega$. For anomalous transport studies, the Berry curvature is a synthetic gauge field which acts as if it were a ‘magnetic’ field.

\textsuperscript{20}It should be noted that the divergence of any curl field is identically zero, i.e. $\nabla \cdot (\nabla \times A) = 0$. For the case of Weyl physics, the Berry curvature is directly calculated from Berry phase, rather than Berry connection, which is shown to be $|\Omega| = \frac{|\vec{k}|}{|k|\delta}$. 

14
The scope of this thesis and beyond - An introduction to the general theme of this paper, i.e. quantum materials is given in chapter one. Relevant experimental techniques used in this thesis (and related published papers) are discussed in chapter two. In chapter three, we introduce our work on a van der Waals ferromagnet VI₃. Transport data and theoretical calculations of two magnetic topological metals (TbMn₆Sn₆, Fe₃Sn₂) are discussed in chapter four. Finally, the inelastic neutron scattering experiment results on a unique quantum spin chain system Cu₂(OH)₃Br is presented in chapter five. For future students of our lab, a manual for the transport measurement software can be found in chapter six (the appendix). Not all original studies I carried out during my graduate research life has been included in my thesis. This is not a verdict on the quality of these works. To interested readers, please see the published versions of these works for detail discussions on YMn₆Sn₆ [20], DyPtBi [21].
Chapter 2

Experimental techniques

This chapter contains detailed information regarding the experimental techniques that I used during my time as a graduate student. There are two main sections: transport characterization and neutron scattering. The focus will be on the thermal and thermoelectric measurement system.
2.1 Transport measurements

A transport measurement quantifies the response of a system to an external drive. For example, an electrical resistance measurement quantifies the voltage drop across a system per unit current. These responses allow us to infer some physical properties of the system. Anomalous transport behavior refers to the situation wherein the system develops a response perpendicular to the direction along which the drive is applied. As discussed in chapter one, such anomalous response allows us to infer information regarding the Berry phase in the system’s band structure.

2.1.1 Transport coefficients definitions

We begin by defining the transport coefficients. For an electrical measurement, we measure the resistance and Hall resistance of a material. The resistance is defined as \( R_{xx} = \frac{V_2 - V_1}{I} \), and the Hall resistance is defined as \( R_{xy} = -\frac{V_3 - V_1}{I} \), where \( I \) is the current passing through the sample. The resistivity (\( \rho \)) are calculated by \( \rho_{xx} = \frac{1}{w} \cdot R_{xx}, \rho_{yx} = -t \cdot R_{xy} \), and the conductivity (\( \sigma \)) by \( \sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^{2} + \rho_{yx}^{2}} \approx \rho_{xx}^{-1}, \sigma_{xy} = \frac{\rho_{yx}}{\rho_{xx}^{2} + \rho_{yx}^{2}} \), where \( t \) is the sample thickness. For a thermal measurement, the definition is identical to the electrical measurements through a simple mapping analogy: \( \{ V \rightarrow T, I \rightarrow P, R \rightarrow R, \rho \rightarrow w, \sigma \rightarrow \kappa \} \). For a thermoelectric measurement, we measure the Seebeck (\( S_{xx} \)) and Nernst (\( S_{xy} \)) coefficients of a material. The Seebeck coefficient is obtained by \( S_{xx} = -\frac{V_2 - V_1}{T_2 - T_1} \). The Nernst coefficient is obtained by \( S_{xy} = \frac{(V_3 - V_1)}{w(T_2 - T_1)l} \).
2.1.2 Hardware

<table>
<thead>
<tr>
<th>Physical Property Measurement System (PPMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity option (PPMS)</td>
</tr>
<tr>
<td>Keithley 2182A nanovolt meter</td>
</tr>
<tr>
<td>Keithley 6220 current source</td>
</tr>
<tr>
<td>Keithley DMM6500 multimeter</td>
</tr>
<tr>
<td>Type-E thermocouple (chromel-constantan)</td>
</tr>
<tr>
<td>Cernox (CX-1070)</td>
</tr>
</tbody>
</table>

The table on the left lists the Hardware for our transport measurements. The Physical Property Measurement System (PPMS) is a commercially available cryostat. We use the PPMS chamber to obtain the desired temperature and magnetic field for our measurements. The software to control PPMS was provided to us.

Third-party control of the PPMS system is very simple: one can use the .vi files from Quantum design, or use the SCPI¹ commands directly.

The Keithley 2182A nanovolt meters were used to measure voltage signals. This meter has very good performance, with noise level typically at 5 nV to 10 nV. The Keithley 6220 current source was used to generate a current through a resistive heater during the measurement.² The Keithley DMM6500 multimeter was used to read out voltage drop across the resistive heater during thermal/thermoelectric measurements.

We use two types of thermometer for our measurements depending on the temperature range we aim to cover. We use Cernox for low temperature region (2 K - 150 K) and type-E thermocouple for high temperature region (20 K to 400 K).

¹Standard Commands for Programmable Instruments
²In retrospect, this meter has far superior performance than necessary.
2.1.3 Software

The hardware were controlled by a Labview project called TTO_v2. A typical user would only need to access the maine.vi program to take measurements. A manual of TTO_v2 is included in the appendix.

Figure 2.1: Front panel of maine.vi.
2.1.4 Radiation correction

During thermal conductivity measurements, the black body radiation may become an issue and needs to be calibrated. As an example, the figure on the right shows the thermal conductivity ($\kappa$) of Fe$_{3-x}$GeTe$_2$. The red and blue curves show clear bifurcation beginning at 100 K. The black body radiation follows $P \propto A\epsilon T^4$, where $P$ is the radiating power, $A$ is the surface area of a sample, and $\epsilon$ is a material dependent emissivity constant ($0 < \epsilon < 1$). During the experiment, the sample’s temperature [defined as $T = (T_1 + T_2)/2$] is elevated to a higher value than the environment. The power loss through radiation would be $P_{\text{loss}} = CT^3(T_{\text{samp}} - T_{\text{env}}) = CT^3\Delta T$, where $C$ is a experiment dependent constant. Given the cubic proportionality between radiation power loss and temperature, we can carry out a calibration routine to infer the material dependent constant $C$. After a thermal conductivity measurement experiment, we keep every contacts on the sample except the connection to the heat sink. The puck was then put back into the chamber for calibration process: from 250 K to 300 K at 10 K step size, a constant heating power $P_{\text{heat}}$ was applied to the sample. After the sample temperature stabilized (this can take several minutes), the temperature rise $\Delta T$ was then recorded. Note that at this point, it was only an assumption that the majority of the heating power was dissipated through radiation channel ($P_{\text{heat}} = P_{\text{loss}}$), rather than through the wires connected to the sample. We then plot the $P_{\text{heat}}/\Delta T$ as a function of temperature (black dots) and fit the

$\text{III usually manually chose a power which raise the sample temperature by 10 K.}$
measured data by a cubic function \((CT^3, \text{orange curve})\). If a good fit can be obtained, the assumption holds true. We extract the constant \(C\) and subtract out a component from the total applied power using \(P_{\text{act}} = P_{\text{tot}} - CT^3\). This constant \(C\) needs to be obtained for each experiment.

As a final remark, it is only necessary for a radiation calibration if the sample being measured is extremely thin and the thermal conductivity of the sample is relatively low. For a bar shape sample, the relative importance of \(P_{\text{loss}}/P_{\text{tot}} \propto 1/t\), where \(t\) is the sample thickness. So the thinner a sample is, the more prominent radiation effect will become. Secondly, if the thermal conductivity of a sample is high, a large total power can propagate through the sample to the sink without substantially heating up the sample. In this case, the relative importance of radiation heat loss can also be omitted.

### 2.1.5 Thermal Hall effect measurement

The thermal Hall effect (THE) of insulating compounds is one of the most challenging transport measurements. The thermal Hall effect is the thermal counterpart of Hall effect. It refers to the production of a temperature difference \((\Delta T_{yx}/\bar{e}_y)\) perpendicular to the heat current direction \((\bar{J}/\bar{e}_x)\) in the presence of a magnetic field \((\bar{H}/\bar{e}_z)\). The difficulty is mainly due to \(\Delta T_{yx}\) being a very weak signal. Consider an illustration as shown in section 2.1.1. While \(T_1\) and \(T_3\) appear to be exactly perpendicular to the heat current direction in the schematic, this is impossible to achieve in a real experiment device. This means that the measured \(\Delta T_{yx} = T_3 - T_1\) actually contains two components, i.e. \(\Delta T_{yx} = \delta T_{yx} + \delta T_{xx}\). The \(\delta T_{yx}\) is the intrinsic signal we wish to measure, and the \(\delta T_{xx}\) is a component along the heat current direction we wish to separate out. For the magnetic materials that we are interested in, a method for separating these two components is available.
As an example, the figure on the right shows our data taken on FeCl$_2$. The longitudinal and transverse thermal resistivity ($w_{xx} = \frac{\Delta T_{xx} \omega_T}{T} = \frac{T_2 - T_1}{T}, w_{xy} = \frac{\Delta T_{xy}}{\rho T} = \frac{\rho T_3 - \rho T_1}{T}$) data were collected during two field sweeps: $\{9 \, T \rightarrow -9 \, T, -9 \, T \rightarrow 9 \, T\}$. The sweeping directions were indicated by blue and red colors. In principle, we expect the intrinsic signal $\delta T_{xy}$ to be odd with respect to the field direction $[\delta T_{xy}(H) = -\delta T_{xy}(-H)]$. We plot the odd components of $w_{xx}^{\text{odd}} = w_{xx}(H) - w_{xx}(-H)$ and $w_{xy}^{\text{odd}} = w_{xy}(H) - w_{xy}(-H)$ as the upper and lower panels in the right figure. From the lower panel, we see that the signal in $w_{xy}$ channel is largely dominated by an odd component. However, from the upper panel, we see that there is also an odd component in the $w_{xx}$ channel. What this implies is that we could not simply take the odd component in $w_{xy}$ as the intrinsic thermal Hall signal. A second observation we can make is by comparing the hysteresis behavior of this odd component in the longitudinal and transverse channels. By averaging the odd components of $w_{xx}$ during a field ramp-up and ramp-down curve, we obtained the black curves shown in the upper panel. We see that by this procedure, we can get rid of the major part of the odd component in the $w_{xx}$ channel. Therefore, we can apply this method to the $w_{xy}$ channel, by averaging the $w_{xy}^{\text{odd}}$ during a field ramp-up and ramp-down process.
Why does this procedure matter? The left column in the following figure shows the raw data recorded during a measurement on CrI$_3$. While we can see the asymmetric feature from $w_{yx}$ data if we squint at the curves, one may inevitably question the ‘intrinsic’ nature of this signal. For example, the middle column shows the odd component of the raw data. If we only measure them during field ramps from -1 T to 1 T (i.e., we only have the orange curve), I would seriously doubt the measured signal of $-w_{\text{odd}yx}$, since there may be some unwanted signal due to misalignment of temperature leads. However, if we carry out the aforementioned procedure, the resulted signal $w^{\text{Ass}}$ were shown in the right column, which gave us much more confidence in the intrinsic nature of the thermal Hall signal.

Another test that we routinely carry out to verify the intrinsic nature of the thermal Hall signal was a power test. In principle, we expect the thermal Hall resitivity $w_{yx} = \frac{\Delta T_{yx}}{P}$ to not depend on the applied power. A power test at $T = 20$ K for CrI$_3$ is shown on the right. We see that the $-w^{\text{Ass}}_{yx}$ signal is independent of the applied power.
2.2 Neutron scattering

Neutron is a charge neutral particle with $S = 1/2$. Neutrons can interact with a system and the quasi-particle excitations in the system through scattering. Such scattering experiments allow one to infer information on the structural, magnetic and dynamical properties of a system. Different experimental techniques covers different length, time and energy scales where interesting physical phenomena could take place, as shown by the following figure\(^4\).

In this thesis, we focus on neutron scattering and inelastic neutron scattering.

\[^4\text{https://europeanspallationsource.se/science-using-neutrons}\]
2.2.1 Neutron diffraction

In a neutron diffraction experiment, a beam of neutron with wavelength $\lambda$ is guided to shine on the sample. Neutrons are then scattered off by the nuclei and the electrons’ spins. The underlying principle for a neutron diffraction experiment is the well-known Bragg’s law. When the neutron wavelength, lattice spacing and the diffraction angle satisfy the relation: $n\lambda = 2d\sin(\theta)$, the scattered waves (neutrons) interferes with each other constructively. The result is a strong peak in the diffracted intensity, called Bragg peaks. Since neutron carries a magnetic moment, there will also be Bragg peaks due to the magnetic lattice. We can solve the magnetic structure of a material by refining these magnetic Bragg peaks.

The figure on the rights shows a photo of the neutron diffractometer DEMAND\textsuperscript{5} at Oak Ridge National Lab (ORNL). The instrument mainly consists of incoming beam guide, a sample holder and an area detector. We can cover different $\theta$ by rotating the detector, and cover different Bragg peaks (with different lattice spacing $d$) by rotating the sample. A schematic of the scattering plane (horizontal plane in this case) is also shown.

\textsuperscript{5}Dimensional Extreme Magnetic Neutron Diffractometer, https://neutrons.ornl.gov/hb3a/publications
2.2.2 Inelastic neutron scattering

In an inelastic neutron scattering experiment, a beam of neutron with incident momentum and energy \((\vec{q}_i, E_i)\) is guided to shine on a sample. Different from a diffraction experiment, the scattered neutrons beam intensity were recorded as a function of their energy and momentum change \(I(\Delta \vec{q}, \Delta E)\). The following figure shows a photo of the neutron spectrometer HYSPEC\(^6\) at ORNL and its simplified conceptual schematic. Pulses of neutron beams with initial energy and momentum \((E_i, \vec{q}_i)\) are sent through the beam guide to shine on the sample. The scattered beam first passes through a grid of radial collimators, such that the direction of its momentum is known \(\frac{\vec{q}_f}{|\vec{q}_f|}\). When neutrons are recorded by the detector, its energy \((E_f)\) and momentum’s magnitude \((|\vec{q}_f|)\) are recorded and calculated. Combining these data, we can construct an intensity map as a function of energy and momentum transfer \(I(E_f - E_i, \vec{q}_f - \vec{q}_i)\).

\(^6\)Hybrid Spectrometer, https://neutrons.ornl.gov/hyspec
Chapter 3

Anomalous thermal Hall effect of VI$_3$

3.1 Introduction

The concept of non-trivial band topology originated from, but was not limited to, the pioneering studies on electron systems. The concept has been generalized to photon, phonon and magnon systems. One of the earliest experimental work on topological magnon was the observation of thermal Hall effect ($\kappa_{xy}$) in Lu$_2$V$_2$O$_7$ [22]. Although not stated explicitly, the theoretical calculations of this paper attributed the observed $\kappa_{xy}$ to the Berry curvature of magnon bands. There have been rising interests in topological magnons due to its potential in offering dissipation-free spin transport channels [23].

We discuss the theoretical backgrounds of a Chern type topological magnon ‘insulator’\textsuperscript{1} by examining a ferromagnet with Kagome lattice. A kagome lattice is shown on the right, it is a 1/6 depleted triangular lattice. Each atom has four nearest neighbors. The center at each nearest neighbor bond (red pentagon) is not a center of inversion for the kagome lattice. This allows for a nearest neighbor Dzyaloshinskii-Moriya (DM) in-

\textsuperscript{1}Magnon population follows the Bose-Einstein statistics, there is no well-defined metallic/insulator phases.
interaction in the kagome lattice. The DM interaction is an anti-symmetric exchange interaction, in that it involves the cross product of two neighbor spins, which is described as 

\[ \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j). \]

In the Haldane model we discussed in section 1.2.2, the second-neighbor imaginary hopping was an artificial construct, which may or may not be realized in a physical system. Here, the DM interaction is a physical realization of this imaginary hopping term. For ferromagnetic kagome lattice with nearest neighbor Heisenberg interaction, the magnon dispersion along \( M - \Gamma - K - \Gamma \) is shown in the figure on the left. Without the DM interaction (solid lines), the magnon band feature a flat top band (blue) and a Dirac-like band touching at K. By adding in a finite DM interaction at \( \vec{D} = (0, 0, 1J) \), all three bands become gapped. The corresponding Berry curvature, Chern number and the magnon edge states has been reported in [24]. Experimentally, the topological magnon bands of this model is proposed to be realized in Cu(1,3-bdc) [25, 26]. There are many theoretical models for topological magnon bands, and more experimental evidence are emerging. One of these theoretical models involves a magnetic honeycomb lattice with second-nearest neighbor DM interactions. The two-dimensional van der Waals magnets in transition-metal chalcogenides [27] often hosts a honeycomb lattice.

The intensity of currently available neutron beams is insufficient for the direct observation of magnon edge states. The thermal Hall effect was proposed to be one of the indirect way

---

2 As appose to Heisenberg/Ising type, which involves \(-J \vec{S}_i \cdot \vec{S}_j\)

3 The DM interaction is represented by a pseudovector, the exact form of which needs to be determined by analyzing the space group symmetry of a material.
for observing the magnon edge states. These magnon edge states can act as heat carriers for anomalous transverse thermal transports. We aim to study the anomalous thermal Hall effect in VI₃ and understand its potential connection to topological magnons.

3.2 Results

Crystal structure - VI₃ crystallize in the space group R-3 (No. 148) at room temperature. Its crystal constants and crystal angles are \( a = b = 6.8325 \, \text{Å}, \quad c = 19.6776 \, \text{Å} \) and \( \alpha = \beta = 90^\circ, \quad \gamma = 120^\circ \). The crystal structure can be visualized in Figure 3.1. Recent experiment has revealed a further lowering of crystal symmetry at lower temperatures [28, 29].

Figure 3.1: (left) Crystal structure of VI₃ at room temperature. Vanadium atoms are shown in red and Iodine atoms are shown in purple. (Right) View in the crystal ab-plane showing the Vanadium atoms assembled on a honeycomb lattice. Both figures are generated by VESTA [4].

Basic physical properties - VI₃ is a ferromagnetic insulator. Field cooled magnetic susceptibility (\( \chi_c \)) data on a bulk sample is shown in the left panel of Figure 3.2. The Curie temperature determined by a peak in \( \left| \frac{d\chi}{dT} \right| \) is \( T_c = 50 \, \text{K} \). We have also measured the thermal conductivity (\( \kappa_{xx} \)) of VI₃ as shown in the right panel of Figure 3.2. The sudden increase of \( \kappa_{xx} \) around 77 K is due to the structural transition at this temperature [28, 29]. For
0T applied field, there is small anomaly in $\kappa_{xx}$ near the Curie temperature. The thermal conductivity of VI$_3$ is strongly influenced by the applied field.$^4$

![Graph of magnetic susceptibility and thermal conductivity](image)

Figure 3.2: (Upper) The field-cooled magnetic (0.1 T) susceptibility and the absolute value of its temperature derivative of a VI$_3$ sample. (Right) The thermal conductivity of a VI$_3$ sample measured under 0 T and 7 T applied filed. The magnetic field is applied along the crystalline c-axis for both figures.

For the magnetization data shown in the left panel of Figure 3.3, we see that VI$_3$ has Ising-type magnetic anisotropy, with an easy axis along the crystalline c-axis direction. The magnetic moment from our measurement is about 1.5 $\mu_B$/V$^{3+}$ below the Curie temperature. In the upper panel of Figure 3.3, we show both $\kappa_{xx}$ and M measured at $T = 20$ K. At high fields, $\kappa_{xx}$ increases monotonically. The increase of $\kappa_{xx}$ at high fields (also shown by the data in Figure 3.2) indicates strong inelastic magnon-phonon scattering process. At low fields, there are two small dips in $\kappa_{xx}$ coinciding with magnetization switching. A more detail profile of the low field behavior of $\kappa_{xx}$ is shown in the right panel of Figure 3.3. The $\kappa_{xx}$ clearly shows hysteresis behavior due to the switching of magnetic domains.

To summarize, VI$_3$ is a ferromagnetic insulator with Ising-type magnetic anisotropy, whose thermal conductivity is strongly influenced by the its internal magnetization.

$^4$In this chapter, unless stated otherwise, the magnetic field will be applied along the crystalline c-axis.
Figure 3.3: (Upper) Magnetization and thermal conductivity data measured at 20 K. For the thermal conductivity measurement, the sample is at 21.6 K due to heating. The orange/blue arrow indicates the field sweep direction. (Left) Magnetization data of VI$_3$ at selected temperatures from 2 K to 100 K. Each curve has been moved vertically by 3 $\mu_B/V^{3+}$ for clarity. (Right) Change of thermal conductivity in percentage as a function of magnetic field at different temperatures. Each curve has been moved vertically by 3 % for clarity.

3.3 The anomalous thermal Hall effect

The first curve - We aimed to investigate the potential magnon edge states in VI$_3$ using thermal Hall effect (THE) measurements. At the time, this was easier said than done.
First, we had no experience in measuring THE of an insulating compound. There are many
details which we need to learn through experimenting. Secondly, surveying through existing
experimental data\(^5\), we expect the thermal Hall signal \(\kappa_{yx}\) to be very weak and hard to detect.
Thirdly, there have only been a handful of insulating materials with reported thermal Hall
effect. To actually observe THE in a material may requires an extensive search through
many candidates.

\[\begin{align*}
\Delta T_x(T) & = 1.16 \\
\mu_0 H(T) & = -0.5, -0.3, -0.1, 0.1, 0.3, 0.5 \\
\text{T} = 40 \text{ K}, \text{P} = 520 \, \mu \text{W}
\end{align*}\]

Allow me to introduce the first curve, measured on a piece of VI\(_3\) sample, whose
sample dimensions we forgot to measure, and no photo was taken before it was re-
moved from the chamber. The experiment began at 2:48 p.m., January 29\(^{th}\), 2021.
During the cooling process, one of the temperature contact leads had fallen off. Luck-
ily, it was the temperature lead at \(T_2\), so we could process to measure thermal Hall effect.
Prior to measuring VI\(_3\), we have gone through only two materials: a vanadium oxide com-
pound and MnPSe\(_3\). We have learned two things from this experiment: first, the sample is
hygroscopic. Second, there is a very strong\(^6\) thermal Hall signal in VI\(_3\).

\textit{Anomalous thermal Hall effect} - We proceed to synthesize new batches of VI\(_3\) single
crystals and repeat the thermal Hall experiment on three samples. The data presented in
Figure 3.4 was obtained on sample \#2, with dimensional parameters at \(l = 1.19 \text{ mm}, w =
1.33 \text{ mm} \) and \(t = 0.084 \text{ mm}\). The anomalous nature of the observed signal is worth point

\(^5\)Please see Figure 4 in [30] for a summary of thermal Hall effects in insulators.
\(^6\)Easily measurable even by beginners.
out. The ‘anomalous’ here refers to the thermal Hall conductivity ($\kappa_{xy}$) being scaled with magnetization (M), rather than the applied magnetic field ($\mu_0 H$). Such behavior is critical for technological applications and has rarely been reported.

Figure 3.4: The anomalous thermal Hall effect measurement data at various temperatures between 10 K to 50 K.

Below 10 K - Below 10 K, the effect of temperature contact mis-alignment (Section 2.1.5) becomes more apparent. In the left panel of Figure 3.5, we see clear hysteresis behavior in $\Delta w_{xx}$. The signal in $\Delta w_{xx}$ is inevitably also detected by the $w_{yx}$ channel due to small mis-alignment of temperature leads (Middle panel, Figure 3.5). As a result, the $w_{yx}$ curves show unwanted additional signals as temperature decreases. We adopted two methods to obtain the intrinsic value from the raw measurement data. The first way was described in Section 2.1.5. We applied this method to both $w_{yx}$ and M, the data is shown in the upper right panel of Figure 3.5. This method will get rid of any hysteresis behavior and allow us to get the amplitude of the anomalous thermal Hall resistivity. The second method is described
in [5], the data is shown in the lower right panel of Figure 3.5. Both methods yield identical results.

Figure 3.5: Thermal measurement data of sample #2 below 10 K. (Left) Change of thermal resistivity. Each curve is shifted vertically by 0.05 K m W$^{-1}$ for clarity. (Middle) Thermal Hall resistivity. Each curve is shifted vertically by 0.015 K m W$^{-1}$ for clarity. (Right, upper) Thermal Hall resistivity obtained by methods described in Section 2.1.5 The black dash lines are scaled magnetization data at each temperature. (Right, lower) Thermal Hall resistivity obtained by methods described in [5].

**High field data** - The thermal Hall conductivity ($\kappa_{xy}$) has also been measured up to 7 T. The orange and blue curve in Figure 3.6 shows $\kappa_{xy}$ data measured for a typical hysteresis loop and up to 7 T at 21.5 K. The decrease of $\kappa_{xy}$ at high fields can be fitted by a parabolic function $\kappa_{xy} = \kappa_{xy}^0 + C(\mu_0 H)^2$, where was found to be $C = -5.546 \times 10^{-5}$ W m$^{-1}$ K$^{-1}$ T$^{-2}$. On the other hand, $\kappa_{xx}$ continue to increase with the applied field. These data suggests that the magnons in VI$_3$ is responsible for the observed thermal Hall effect.

**Sample dependence** - We have measured the thermal Hall effect on three pieces of VI$_3$ samples. We have observed experimental results with the same behavior, but different mag-
Figure 3.6: Thermal Hall conductivity ($\kappa_{xy}$, orange/blue) and thermal conductivity ($\kappa_{xx}$, red) measured up to 7 T.

The thermal conductivity of three samples are shown on the left panel of Figure 3.7. $\kappa_{xx}$ display similar anomalies at the structural (78 K) and magnetic (50 K) transitions. The thermal Hall conductivity plateaus in a wide temperature range (middle, Figure 3.7) and has the hysteresis loop (right, Figure 3.7) for all three samples.

Figure 3.7: Temperature dependence of thermal conductivity (Left) and thermal Hall conductivity (Middle) for different samples. (Right) Magnetic field dependence of thermal Hall conductivity for different samples.

### 3.4 Theoretical interpretations

**Magnon band structure and Berry curvature** - We begin with a theoretical investigation of the band structure and potential Berry curvature of the magnons in $\text{VI}_3$. The system's
Hamiltonian writes,

\[
H = \sum_{\gamma=1,2,3} J_\gamma \sum_{i,j} \vec{S}_i \cdot \vec{S}_j + \sum_{\langle i,j \rangle} \vec{D}_{ij} \cdot (\vec{S}_i \times \vec{S}_j) - K \sum_i S_{i,z}^2 - B \sum_i S_i^z
\]  

(3.1)

We have included up to third-nearest neighbor Heisenberg interactions \((J_\gamma)\), second-nearest neighbor Dzyaloshinskii-Moriya interaction (DMI, \(\vec{D}_{ij}\)), easy-axis single-ion anisotropy (K) and an external magnetic field (B). The exchange parameters used in our calculations are adapted from [31] tabulated here,

<table>
<thead>
<tr>
<th>J_1</th>
<th>J_2</th>
<th>J_3</th>
<th>D</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.746 meV</td>
<td>-0.169 meV</td>
<td>-0.210 meV</td>
<td>[-0.05, 0.95] meV</td>
<td>1.12 meV</td>
</tr>
</tbody>
</table>

The magnon band dispersion and the corresponding Berry curvature \((\Omega^z)\) are shown in Figure 3.8. Without DMI \([\vec{D}_{i,j} = (0,0,0)\) meV\], the two magnon bands have a linear touching point at K, as shown by the blue and red lines. With finite DMI \([\vec{D}_{i,j} = (0,0,0.2)\) meV\], the magnon bands become fully gapped. The corresponding Berry curvature \((\Omega_z)\) are shown on the right panel, where the upper half represents \(\Omega^z\) for the upper band and lower half represents that of the lower band. The Chern number for these two bands are found to be +1 and -1, respectively.

**Thermal Hall conductivity** - More importantly, we aim to calculate the thermal Hall conductivity \((\kappa_{xy})\) due to the topological magnons. We adopt the method described in [32]:

\[
\kappa_{xy} = -\frac{k_B^2 T}{\hbar A} \sum_n \int_{\vec{k}} c_2(\rho_n) \, \Omega_{n,z}(\vec{k})
\]  

(3.2)

\[
c_2(\rho_n) = (1 + \rho_n) \left( \log \frac{1 + \rho_n}{\rho_n} \right)^2 - (\log \rho_n)^2 - 2Li_2(-\rho_n)
\]  

(3.3)
Wherein $\rho_n$ is Bose-Einstein distribution function for the n-th band, and $Li_2$ is the polylogarithm function of order two. The temperature dependence of $\kappa_{xy}$ was taken into account by a mean-field method described in [33, 5]. In the upper panel of Figure 3.9, we show the calculated results of $\kappa_{xy}$ for various DMI strength. The calculated results show that $\kappa_{xy}$ has a broad peak behavior as a function of temperature, and its magnitude should be on the order of $10^{-2}$ W m$^{-1}$ K$^{-1}$. When compared with the experimental, we found that although the calculated data (with $D = 0.2$ meV) follows the same trend as the experimental data, there are two main discrepancies: one near the Curie temperature and another at the low temperatures region (lower panel, Figure 3.9). The difference of between experimental (blue) and theoretical (orange) values are shown as yellow markers. Near the magnetic phase transition, our mean-field approach is no longer valid. The magnetic short-range correlations may be responsible for the difference peaking at $T_c = 50$ K. In the lower temperature region, we found that $\kappa_{xy}^{exp}$ rises much faster than $\kappa_{xy}^{the}$. The slow increase of $\kappa_{xy}^{the}$ below 10 K was
because non-zero $\Omega_z$ are mainly located at K-points and along K-M-K lines in the reciprocal space (Right panel, Figure 3.9). Magnons have relatively high energy and low population density $\rho_n$ at these locations. Referring back to Equation 3.2, we see that some ‘activation’ temperature is necessary for Berry curvature to take effect in the magnon system. With this observation, we investigate a potential mechanism which could give rise to non-zero $\Omega_z$ located at lower energy positions.

![Figure 3.9](image)

**Figure 3.9:** (Upper) Calculated thermal Hall conductivity due to topological magnon with various DMI strength. (Lower) Comparison between experimental data (blue) and theoretical predictions (orange) of thermal Hall conductivity. The difference between experimental and theoretical values are shown as yellow markers. (Right) Berry curvature distribution in the reciprocal space.

**Magnon-phonon coupling** - We consider the coupling between an out-of-plane phonon and in-plane magnon as described in [5], where $g$ controls the coupling strength. The dispersion of the hybrid magnon-phonon band is shown in the left panel of Figure 3.10. There are anti-
crossing regions near Γ-point and K-point due to magnon-phonon coupling. Furthermore, we have found that substantial Berry curvature emerging at the anti-crossing regions near Γ. The ring-shape region of Berry curvature near Γ is located at much lower energy and may be responsible for the observed $\kappa_{xy}$ at low temperatures. In the right panel of Figure 3.10, we show the comparison between experiment and theoretical values for various magnon-phonon coupling strength (g) [5]. We see that as the magnon-phonon coupling strength increases, the lower temperature region of $\kappa_{xy}^{th}$ also increase, approaching the experimental values of $\kappa_{xy}^{exp}$. At present, we only considered an out-of-plane phonon mode, which couples to the in-plane magnons on a leading order. Future experiments to resolve the phonon spectrum may be an interesting study.

![Figure 3.10](image)

Figure 3.10: (Left) Total dispersion of the hybrid magnon-phonon band (g=0.5). (Middle) The absolute value of Berry curvature’s ($|\Omega|^2$) distribution in the reciprocal space. The emergence of a ring-shaped region of Berry curvature is due to the magnon-phonon anti-crossing near Γ point. (Right) Comparison between experiment and theoretical values for various magnon-phonon coupling strength.

In conclusion, we report the observation of an anomalous thermal Hall effect (THE) with $\kappa_{xy} \approx 1 \times 10^{-2} W K^{-1} M^{-1}$ in an insulating van der Waals ferromagnet VI$_3$. The thermal Hall signal persists in the absence of an external magnetic field and flips sign upon the switching of the magnetization. By combining the theoretical calculations, we show that VI$_3$ exhibits a dual nature of the THE, i.e., dominated by topological magnons hosted by
the ferromagnetic honeycomb lattice at higher temperatures and by phonons induced by the magnon-phonon coupling at lower temperatures. Our results not only position VI$_3$ as the first ferromagnetic system to investigate both anomalous magnon and phonon THEs, but also render it as a potential platform for spintronics/magnonics applications.
Chapter 4

Electric, thermal and thermoelectric transport studies of magnetic topological metals

4.1 Introduction

Berry curvature and itinerant electrons - A charged particle experience a force \( \vec{F} = q(\vec{E} + \vec{v} \times \vec{B}) \) due to the presence of electromagnetic fields. From Maxwell’s equations, we see that the magnetic B-field has zero divergence (\( \nabla \cdot \vec{B} = 0 \)), meaning that there exists a magnetic vector potential (\( \vec{A} \)), such that \( \vec{B} = \nabla \times \vec{A} \). Together with the electric potential (\( \vec{E} = -\nabla \phi \)), (\( \phi, \vec{A} \)) forms the electromagnetic potential. Although (\( \phi, \vec{A} \)) is a gauge field which cannot be measured directly, it has directly measurable effect on the phase of wave functions. This is known as the Aharonov-Bohm (AB) effect [34]. The AB-effect is a special application of the more general concept as Berry’s phase [17]. In this sense, we can draw an analogy between magnetic fields and Berry curvature. The Berry potential is a gauge field representing the ‘phase gradient’ of a wave function in a parameter space, i.e., \( \vec{A}(\vec{r}) = i \langle \phi(\vec{r})|\nabla_{\vec{r}}|\phi(\vec{r}) \rangle \). As discussed in Section 1.2.2, the Berry curvature is the curl of Berry potential \( \vec{\Omega}(\vec{r}) = \nabla_{\vec{r}} \times \vec{A}(\vec{r}) \). Given the analogy, we can ask the following question: Does the Berry curvature exert a force
on charged particles? And does it have a measurable physical effect?

To the first question, Berry curvature does not directly exert a force on a charged particle. This is quite obvious since the gauge field (Berry connection, $\mathbf{A}$) does not directly couple to the charge. However, a more subtle point is that Berry curvature has a measurable physical effect for electrons in a crystalline lattice: the anomalous Hall effect (AHE) [35]. While $\mathbf{Ω}$ does not couple to the charge directly, the Bloch electron group velocity acquires an ‘anomalous’ term ($q\mathbf{E} \times \mathbf{Ω}$) due to the Berry curvature [35, 36, 37]. The ‘anomalous’ velocity give rise to an intrinsic contribution ($\sigma^{int}$) to the total anomalous Hall conductivity ($\sigma_{xy}$) and has been studied extensively.

This mechanism can also give rise to an anomalous thermoelectric conductivity ($\alpha_{xy}$) [38]. The thermoelectric conductivity measures the anomalous current density driven by a temperature gradient ($\alpha_{xy} = j_x/\partial_y T$, $A m^{-1} K^{-1}$). The electric and thermoelectric conductivity tensor are correlated, as expressed in the Mott relation $\alpha_{xy}/T = \frac{\pi^2 k_B^2}{3e} \frac{d\sigma_{xy}}{dE}|_{\epsilon=\epsilon_f}$. For the study of topological metals, $\alpha_{xy}$ serves as a complementary tool to measure the Berry curvature distribution in the reciprocal space: $\alpha_{xy}$ is only sensitive to the Berry curvature in the vicinity of Fermi level. Experimentally, there have been rising interests in the anomalous Nernst effect (ANE) of magnetic topological metals. The Seebeck ($S_{xx}$) and Nernst ($S_{xy}$) coefficients have been defined in Section 2.1.1. We can write these coefficients in a compact form as a 2-rank tensor $\bar{S} = \begin{pmatrix} S_{xx} & S_{xy} \\ S_{yx} & S_{yy} \end{pmatrix}$, the formula $\bar{\alpha} = \bar{\sigma} \bar{S}$ relates the thermoelectric conductivity, conductivity and thermoelectric coefficients.

**Anomalous Nernst effect based thermoelectric device** - Another reason for the rising interests in ANE of magnetic topological metals is its potential applications in energy conversion device [39, 40]. There are two main merits of the ANE based device compared to its Seebeck
based counterparts. First, the voltage gradient and temperature gradient are orthogonal to each other, allowing more freedom in device design. Secondly, given the same figure of merit value (zT), Nernst effect based devices can achieve much higher energy conversion efficiency. For the development of ANE based devices, the greatest obstacle thus far is the extremely low zT value.\footnote{It should be noted that the Nernst effect of Cd$_3$As$_2$ can reach zT = 0.7 at 350 K \[41\]. However, a sizable magnetic field (3 T) is required for obtaining such large zT value.}

### 4.2 Exchange-biased anomalous transport in TbMn$_6$Sn$_6$

*Introduction*\footnote{This section is adapted from \[42\].} - TbMn$_6$Sn$_6$ belongs to a family of the RMn$_6$Sn$_6$ (R = rare earth, Y, Sc, Lu) compounds. The manganese atoms in these compounds form a double-layer Kagome lattice structure. The unique Kagome lattice can give rise to flat bands and Dirac points in the band structure. The former provides an ideal platform for studying strongly correlated phenomena, while the latter is an interesting topological object by its own right. In particular, TbMn$_6$Sn$_6$ stands out as a ferrimagnet with out-of-plane magnetization where Tb moment aligns antiferromagnetically with Mn moment. As a result, the electronic band structure of TbMn$_6$Sn$_6$ exhibits spin polarized Dirac dispersion with a Chern gap. The massive Dirac bands near the Fermi energy can give rise to anomalous electric and heat transport phenomena.

*Crystal/magnetic structure and basic physical properties of TbMn$_6$Sn$_6$ - TbMn$_6$Sn$_6$ (TMS)* crystallize in space group P6/mmm (No. 191), with lattice constants $a = b = 5.522 \ \text{Å}$, $c = 9.004 \ \text{Å}$ and crystal angles $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The terbium atoms are arranged in a triangular lattice, while the manganese atoms are arranged in a kagome lattice. The
magnetic structure of TMS has been determined from a previous powder neutron diffraction experiment [43]. Both the terbium’s and manganese’s magnetic moments are ferromagnetic within the ab-crystal plane. Along the crystalline c-axis, the terbium and manganese spins are anti-ferromagnetic to each other (left panel, Figure 4.1). TMS undergoes a spin-reorientation process near 310 K as shown by the inset in the right panel of Figure 4.1. The magnetic moments switch from an in-plane configuration at higher temperature to an out-of-plane one at lower temperature [43]. The bifurcation between field cooled and zero-field cooled susceptibility may be attributed to formation of anti-aligned ferrimagnetic domains [44]. The temperature dependence of some basic physical properties of TMS (lower panel, Figure 4.1) shows typical behavior for a magnetic metal.
Figure 4.1: (Left) Crystal and magnetic structure of TbMn$_6$Sn$_6$. The terbium/manganese/tin atoms are represented by the black/red/blue spheres. The terbium/manganese’s magnetic moments are represented by black/red arrows. (Right) Magnetic susceptibility data of TbMn$_6$Sn$_6$ measured along the crystalline c-axis (red, blue) and a-axis (black). (Lower) The temperature dependence of resistivity ($\rho_{xx}$), thermal conductivity ($\kappa_{xx}$) and Seebeck coefficient ($S_{xx}$) of TbMn$_6$Sn$_6$. 
Exchange-bias behavior of TbMn₆Sn₆ - Exchange-bias was first discovered by W. H. Meiklejohn and C. P. Bean [45], which was described as the following: ‘The exchange anisotropy is a unidirectional anisotropy in that it produces one easy direction of magnetization.’ A typical magnetization curve of TbMn₆Sn₆ is shown in the right figure (field-cooled), demonstrating a clear exchange-bias (EB) behavior. The necessary ingredients for EB are: i) an uncompensated magnetic moment and ii) a mechanism for its pinning. This is typically realized by patterning thin layers of ferromagnetic/anti-ferromagnetic heterostructures. Exchange-Bias behavior has also been observed in single-phase, single-crystalline materials.

Exchange-bias behavior has rarely been observed in single-crystalline magnetic topological metals. In a ferromagnetic Weyl semimetal Co₃Sn₂S₂, exchange-bias behavior has been observed and proposed to originate from the coexisting ferromagnet/spin glass orders. In TbMn₆Sn₆, a ferrimagnetic metal hosting a Chern gap, we have observed huge exchange-bias behavior. In the left panel of Figure 4.2, the magnetization of TMS after cooling to the respective temperatures with an applied field of 0.5 T were shown. The coercivity and exchange-bias field were found to increase in magnitude as temperature decreases. In the right panel of Figure 4.2, the magnetization of TMS after cooling to 100 K with the respective cooling fields were shown. The coercivity and exchange-bias field were found to increase with the cooling field. The coercive fields are signified by a switch in magnetization and the bias-field \( H_{EB} \) is defined as the average of the coercive fields \( H_{EB} = \frac{H_{c1} + H_{c2}}{2} \). The exchange-bias field of TMS has reached considerable magnitudes.
Figure 4.2: (Left) Magnetization data after cooling to the respective temperatures with an applied field of 0.5 T. (3 T → -3 T → 3 T) (Right) Magnetization data after cooling to 100 K with the respective applied fields. (1.5 T → -1.5 T → 1.5 T)

The exchange-bias field’s temperature and field dependence have been summarized in the left panel of Figure 4.3. One of the key challenges in ANE-based thermoelectric device design was the stray field problem during miniaturization. The stray field originating from neighboring magnetic thermoelectric material sets the upper limit for thermopile density. Exchange-bias can provide a solution to this issue if the exchange-bias field is strong enough. In Figure 4.3, we see that the exchange-bias field can exceed the magnetization below 120 K. In reality, it is only necessary for the exchange-bias field to be comparable to magnetization. We also see that the exchange-bias field increases with the cooling-field, saturating at \( \mu_0 H_{FC} = 0.7 \) T. This effect could be further increased by increasing the sweeping field range. In the right panel of Figure 4.3, we see the filed-reversal and training effect (hysteresis loop.
depends on the number of repeating measurements, [46]) of the exchange-bias behavior. The potential mechanism for the exchange-bias behavior may be a co-existing spin-glass phase in the system [42].

![Figure 4.3: (Left) Temperature and field dependence of the bias-field and magnetization. (Right) Field-reversal and training effect of the exchange-bias behavior.](image)

\[ M, \mu_0 H_{EB} \]

Anomalous transports - In Figure 4.4 we summarize the AHE effect\(^3\) in TbMn\(_6\)Sn\(_6\). In the left panel, the field dependence of \(\sigma_{xy}\) were shown. In the intermediate temperature range (e.g., \(T = 240\) K), we observe the effect of magnetic metastable states as sudden jumps in \(\sigma_{xy}\). The single-ion anisotropy of Tb/Mn and the inter-layer exchange interactions may be responsible for the complex energy landscapes and the metastable states. The ordinary contribution (\(\sigma^0_{xy} \propto \mu_0 H\)) to the total Hall conductivity (\(\sigma_{xy}\)) only become visible at much lower temperature (e.g., 100 K). The temperature dependence of the anomalous Hall

\[^3\text{All transport data shown from this point on have been trained by repeating field sweeping sequence three times.}\]
conductivity \( \sigma_{xy}^A = \sigma_{xy} - \sigma_{xy}^o \) was shown in the upper right panel. The anomalous Hall conductivity decrease with temperature, indicating the there is a skew-scattering component \( \rho_{yx}^{sk} \propto \rho_{xx} \) in the total anomalous Hall signal. We extract the intrinsic AHE component \( \rho_{xy}^{int} \propto \rho_{xx}^2 \) by fitting the total Hall resistivity as \( \rho_{yx} = A\rho_{xx} + B\rho_{xx}^2 \) as shown in the lower right panel. The red line is the fitting curve and the blue dash lines are the 95% confidence bound. The intrinsic component was found to be 131 ± 20 (Ω cm)^{-1}. This value is consistent with a previous report [47].

Figure 4.4: (Left) Magnetic field dependence of \( \sigma_{xy} \) measured at various temperatures. (Upper, right) Temperature dependence of \( \sigma_{xy}^A \). (Lower, right) Fitting result of the anomalous Hall resistivity.

We have also measured the anomalous thermal Hall effect and anomalous Nernst effect of TbMn₆Sn₆ as shown in Figure 4.5. The field dependence of \( \kappa_{xy}^A \) and \( S_{xy}^A/T \) at a few selected
temperatures were shown in the left and middle panels of Figure 4.5. Similar features were observed in these measurements. The temperature dependence of $\kappa_{xy}^A$ is shown in the upper-right panel of Figure 4.5, which also decreases with temperature. We show the anomalous Lorentz number ($L_A = \kappa_{xy}^A / \sigma_{xy}^A T$) in units of the Lorentz number ($L_0 = 2.44 \times 10^{-8} \text{ V}^2 \text{K}^{-2}$) as the blue markers. $L_A^A$ remains close to the Lorentz number in the measured temperature range. The anomalous Nernst coefficient monotonically increases with temperature.

![Figure 4.5: Field dependence of anomalous thermal Hall conductivity (Left) and anomalous Nernst coefficient (Middle). (Upper, right) Temperature dependence of anomalous thermal Hall conductivity and anomalous Lorentz number. (Lower, right) Temperature dependence of anomalous Nernst coefficient.](image)

**Theoretical interpretations** - We investigate the band structure and its Berry phase by carrying out density functional theory (DFT) calculations on TbMn$_6$Sn$_6$. The DFT calculations are done within the generalized gradient approximation (GGA) framework. The Berry phase were evaluated by an effective Hamiltonian, obtained through projecting the Bloch wave functions into Wannier functions. In the upper left panel of Figure 4.6, we show...
the band structure as well as its Berry phase ($-\Omega_{xy}$). With spin-orbit interactions (SOC) taken into account, there are multiple anti-crossing points with non-zero Berry phase near the Fermi level. We further calculate the anomalous Hall conductivity due to Berry phase using the Kubo formula, as shown in the upper right panel of Figure 4.6. The calculated result is $\sigma_{xy} = 120$ (Ω cm)$^{-1}$, close to the intrinsic value extracted from the experiment data at $\sigma_{xy}^{inc} = 131 \pm 20$ (Ω cm)$^{-1}$. A surface plot of Berry phase at the Fermi level with $kz = 0$ is shown in the lower left panel of Figure 4.6. The Berry phase at Fermi level was dominated by contributions from the anti-crossings at K-points, as suggested by a previous scanning tunneling microscopy (STM) study. However, we found TbMn$_6$Sn$_6$ to be a multi-band system beyond the simple kagome model base on our DFT results. In the lower right panel of Figure 4.6, a comparison between the experimental and theoretical thermoelectric linear response tensor is shown. Compared to the calculated results (blue line), the experiment data (blue markers) shows a much faster rise of $\alpha_{xy}^A / T$ as temperature decreases. It has been shown that skew-scattering may contribute significantly to the total $\alpha_{xy}^A$ for magnetic topological metals. The orange curve shows the ‘adjusted’ theoretical results, by multiplying a temperature dependent variable $\beta = \sigma_{xy}^A / \sigma_{xy}^{inc}$ to the calculated results. The ‘adjusting’ factor $\beta$ takes into account the effect of skew-scattering in a naive manner. At the lower temperature region, the effect of skew-scattering is more prominent as a result of the enhanced conductivity ($\sigma_{xx}$), and the experiment data approaches the adjusted theoretical predictions.

The stray field problem - Previous discussions on the The stray field problem has remained qualitative. Numerical evaluation of the stray field (demagnetization field) produced by the candidate magnetic topological metals will provide crucial insight for application purposes. For an anomalous Nernst effect based thermoelectric device, a typical thermopile consists
of neighboring modules with alternating magnetization (Left, Figure 4.7). Here, the direction of magnetization plays the same role as the n-type/p-type materials in Seebeck based thermoelectric device. The problem with such design is that the stray field produced by one module will always work against its neighboring module. As a result, there needs to be sufficient separation between each module, causing a lower energy conversion density.

The magnetic stray field produced by a bar-shape sample has been analytically solved [48]. Using the analytical formulas, I performed numerical evaluation of the magnetic stray field as shown in Figure 4.7. A module with length, width and thickness at $l = 6 \, \mu\text{m}$, $w = 3 \, \mu\text{m}$, $t = 2 \, \mu\text{m}$ were assumed (Black solid box in Figure 4.7). The magnetization
of the module is assumed to be parallel to y-axis, with strength at \( M_0 \). Following results are carried out at \( z = 0.5 \, \mu m \). The in-plane stray fields are indicated by black arrows with \( \vec{H} = (H_y, H_x) \), the color indicates the out-of-plane stray field component \( (H_z) \). In the design shown in the left panel of Figure 4.7, the y-component of the stray field is the main concern. Two spatial profiles of \( H_z \) at \( (x=0 \, \mu m, \text{cut along y-axis}) \) and \( (y = 2 \, \mu m, \text{cut along x-axis}) \) were also shown in Figure 4.7. From the spatial profile at \( y = 2 \, \mu m \), we see that \( H_y \) is limited to \([-l/2, l/2]\) (i.e., confined to the sample length). The stray field also decreases rapidly along the y-axis direction, with field strength reaching one-tenth of \( M_0 \) at \( y = 2.2 \, \mu m \).

Figure 4.7: (Left) A illustration of typical design for ANE based thermoelectric device. (Right) Stray field produced by one of the module in the thermopile.

The separation distance \( (x) \) between neighboring modules depends on the magnetization and the coercive field of the candidate material. For topological magnets with no hysteresis
(inset of left panel in Figure 4.8, Fe$_3$Sn$_2$), the stray field is a very serious problem since very little field is required to begin the flipping process of neighboring modules. For topological magnets with hysteresis, the ratio between its magnetization and coercive field will determine the separation distance. In Figure 4.8, the $H_c/M$ is shown as a function of separation distance. The black dash line indicates sample boundary at $x = 0.5w$. In TbMn$_6$Sn$_6$, both the coercive field and bias-field can exceed magnetization and the minimum separation approaches zero (i.e. they could be patterned as close as desired). The same claim holds for Mn$_3$Sn and Mn$_3$Ge, with magnetization at $M \approx 20$ Oe and coercive field at $\mu_0 H_c \approx 50$ Oe.

![Graph](image)

Figure 4.8: (Left) Ratio of coercive field ($H_c$) to magnetization ($M$) as a function of minimum separation distance. The separation distance is plotted in units of sample boundary. For example, at $x/(0.5w) = 1$ is the sample boundary. (Inset, left) Magnetization of Fe$_3$Sn$_2$ at 2 K. (Right) Summary of the $S_{xy} - M$ scaling for conventional and topological magnets.

Another important factor is the ANE coefficient magnitude ($S_{xy}$), and there is an trade-off between the two issues. While materials with large $S_{xy}$ and small $M$ is ideal, they are extremely rare. In conventional ferromagnets, the two are typically governed by a scaling constant between $0.05 \mu VK^{-1}T^{-1}$ to $1 \mu VK^{-1}T^{-1}$. For topological magnets, this scaling can be surpassed. A summary plot of $S_{xy} - M$ is shown in Figure 4.8.
In conclusion, we report the prominent AHE, ANE and ATHE behavior of TbMn$_6$Sn$_6$ which is ferrimagnetic Kagome metal hosting a Chern gap near the Fermi level. We show that these anomalous transverse conductivities are associated with large Berry phase in the reciprocal space. Furthermore, we find that TbMn$_6$Sn$_6$ exhibits an exchange-bias feature in both magnetization and transverse conductivity measurements. This, combined with the large ANE, places TbMn$_6$Sn$_6$ as a promising system for transverse thermoelectric devices based on the Nernst effect.

4.3 Topological Nernst effect in Fe$_3$Sn$_2$

*Introduction*\(^4\) - Thermoelectricity is the study of conversion between thermal and electric signals \([50]\). Well-known thermoelectric effects include Seebeck \((S_{\alpha\alpha})\), Nernst \((S_{\alpha\beta})\), Peltier \((\Pi_{\alpha\alpha})\) and Ettingshausen \((\Pi_{\alpha\beta})\) \([50]\). In thermoelectric material research, the primary focus has been on exploring materials hosting ever larger longitudinal thermoelectric coefficients \((S_{\alpha\alpha} \text{ and } \Pi_{\alpha\alpha})\). Although devices with desirable energy efficiency can already be built from these materials, such devices share an unfortunate bottleneck in their designs: miniaturization problem. This can be naturally circumvented by utilizing the transverse thermoelectric effects \([51]\). Recently, there have been reviving interests in the anomalous Nernst effect (ANE) from the condensed matter community, following the pioneering study by D. Xiao et al \([52]\) which showed that Berry phase in the band structure could induce anomalous thermoelectric transport.

In contrast to the normal Nernst effect which is proportional to the applied magnetic field, anomalous Nernst signal emerges when charge carriers acquire an anomalous transverse

\(^4\)This section is adapted from [49].
velocity in the presence of a longitudinal temperature gradient and a finite Berry phase [52].

In this respect, ANE is a thermoelectric counterpart of the anomalous Hall effect (AHE), both of which are associated with the Berry curvature in the momentum space [53]. On the one hand, ANE and AHE are intimately related to each other via anomalous thermoelectric linear response tensor $\alpha^A$. On the other hand, compared to AHE which probes the Berry curvature of the whole Fermi sea, ANE is sensitive to the Berry curvature near the Fermi surface. As a result, ANE may become the dominant term of the total Nernst signal in topological semimetals with an enhanced Berry curvature near the Fermi energy. For instance, large ANE has been observed in Dirac and Weyl semimetals, such as Co$_3$Sn$_2$S$_2$ [54], Cd$_3$As$_2$ [55], Co$_2$MnGa [56], which offer promising applications as the new generation of thermoelectric energy conversion devices. In addition to the normal and anomalous Nernst effect, a third potential contribution to the Nernst signal is coined as topological Nernst effect (THE). THE is by far the most elusive phenomenon among these three possible contributors. Up to date it has been only observed in MnGe [57] and Gd$_2$PdSi$_3$ [58], both of which were attributed to Berry phase in real space associated with non-zero spin chirality arising from the field-induced magnetic skyrmion lattice.

In this section, we report comprehensive electrical, thermal and thermoelectric measurement results on Fe$_3$Sn$_2$, a three-dimensional frustrated ferromagnetic Kagome metal hosting massive Dirac fermion [59]. We show that anomalous thermal and thermoelectric response are present in Fe$_3$Sn$_2$, in addition to the previously reported AHE. We find that Fe$_3$Sn$_2$ exhibits TNE in the low field regime above 120 K, which is attributable to the skyrmion bubble phase revealed by Lorentz transmission electron microscopy (TEM) [60, 61]. Furthermore, we observe prominent thermal Hall effect and large anomalous Nernst signal (2.1 $\mu$V/K at room temperature), a value that is comparable to the largest ANE observed thus
The corresponding anomalous thermoelectric linear response tensor \( \alpha^A \) is found to increase with temperature, reaching a value of around 1 A/m K at room temperature. These features highlight the synergic effects of Berry phase in both real and momentum space in Fe\(_3\)Sn\(_2\).

Results - Fe\(_3\)Sn\(_2\) crystalize in the trigonal crystal system, space group R-3m (No. 166), with crystal constants at \( a = b = 5.338 \) Å, \( c = 19.789 \) Å and crystal angles at \( \alpha = \beta = 90^\circ \), \( \gamma = 120^\circ \). The crystal structure of Fe\(_3\)Sn\(_2\) is shown in Figure 4.9 (a), wherein iron atoms are represented by red spheres and tin atoms are represented by blue spheres. The iron atoms form a double-layer kagome lattice, which hosts topological flat bands and Dirac fermions [64, 65, 59]. Neutron powder diffraction measurement showed that while Fe\(_3\)Sn\(_2\) is ferromagnetic, its spin Hamiltonian is frustrated within the Kagome plane, which resulted in non-collinear spin structures [66]. Recently, skyrmion bubble states were directly observed in Fe\(_3\)Sn\(_2\) by Lorentz TEM [61]. Regarding its electronic properties, large anomalous Hall conductivity \( \sigma_{xy}^A \) was observed, which contains a nearly temperature-independent, intrinsic anomalous Hall conductance \( \sigma_{xy}^{int} \) on the order of 0.27 e\(^2\)/h per Kagome bi-layer (250 Ω\(^{-1}\) cm\(^{-1}\)). In addition, ARPES study revealed the existence of two Dirac points at \( E = -70 \) meV and \( E = -180 \) meV below the Fermi energy, which were argued to be responsible for the intrinsic anomalous Hall conductance [59].

Fe\(_3\)Sn\(_2\) single crystals were grown using the chemical vapor transport (CVT) method [59]. Magnetic susceptibility measurements of Fe\(_3\)Sn\(_2\) were carried out using a Superconducting Quantum Interference Device (SQUID) magnetometer from Quantum Design. Resistivity and Hall effect measurements were conducted using a Physical Property Measurement System (PPMS) from Quantum Design. Thermoelectric measurements were performed using a homemade sample puck designed to be compatible with the PPMS cryostat. For tempera-
Figure 4.9: (a) Schematic crystal structure of Fe$_3$Sn$_2$; iron atoms are represented by red spheres forming Kagome planes, tin atoms are represented by blue spheres. (b) Illustration of the experimental set-up. The temperature gradient is indicated by color scale, the heat sink used is oxygen free high conductivity (OFHC) copper, and the heater used is a thin film resistor (1 kΩ). (c) Temperature dependence of longitudinal electrical ($\sigma_{xx}$, black) and thermal ($\kappa_{xx}$, red) conductivities. (d) Temperature dependence of Seebeck (blue) and Nernst (red, 1.5 T) coefficients. Inset shows an expanded view below 160 K.

ature below 40 K, calibrated Cernox sensors were used to measure the temperature gradient, while type-E (Chromel-Constantan) thermocouples were used for temperature above 10 K up to room temperature. The thermoelectric voltage was measured using K2182A Nanovoltmeters. An illustration of the experimental set up is shown in Figure 4.9 (b). The sample is attached to a piece of oxygen-free high conductivity copper used as the heat sink using silver epoxy. A heater (1 kΩ resistor) is attached to the other end of the sample and applies heat.
current $J_Q$ parallel to the a-axis. The magnetic field is applied along the out-of-plane direction (c-axis). The (Nernst/|Seebeck coefficients are obtained by (anti-)symmetrizing the thermoelectric voltages measured in the presence of positive and negative field separately.

We first present temperature dependence of electronic and thermal transport properties of the Fe$_3$Sn$_2$ sample measured in this experiment. Figure 4.9 (c) shows the longitudinal electrical conductivity ($\sigma_{xx}$, black) and thermal conductivity ($\kappa_{xx}$, red) measured as functions of temperature. The sample exhibits metallic transport behavior down to $T = 2$ K with a residual resistance ratio $[RRR = \rho(300K) / \rho(2K)]$ of 46.7, indicating good crystal quality. And $\kappa_{xx}$ shows a characteristic broad peak around $T = 26$ K, which arises from the competition between the Umklapp phonon scattering dominating at high temperature and the phonon scattering by defects dominating at low temperature. Note that the measured $\kappa_{xx}$ is slightly larger than the value calculated based on the Wiedemann-Franz law [67, 68], suggesting the loss of heat current due to inelastic phonon scattering. In Figure 4.9 (d) we present the temperature dependence of Seebeck ($S_{xx} = \frac{-\partial_x U}{\partial_x T}$) coefficient, wherein $U$ is the thermoelectric voltage and $T$ is the measured temperature. A sign change of $S_{xx}$ at $T = 110$ K can be clearly seen in the inset of Figure 4.9 (d). The sign change of $S_{xx}$ has been described previously by Q. Du et al [60]. It is the result of two competing components in the total $S_{xx}$: the electron diffusion contribution (negative, dominant at high temperature) and the phonon drag contribution ($\propto T^{2.67}$, positive, dominant at low temperature) [60]. Overall, these features in the temperature dependence of $\sigma_{xx}$, $\kappa_{xx}$, and $S_{xx}$ are similar to the observations in recent reports [60, 66, 59], affirming good quality of our sample. In Figure 4.9 (d) we also plot the first measurement of Nernst coefficient $[S_{xy} = \frac{\partial_y U}{\partial_x T}]$ of Fe$_3$Sn$_2$ as a function of temperature. Here the sign of Nernst coefficient follows the Bridgman’s “Ampere current” conventions [69, 55], that is, the vector cross product of magnetic
field ($\vec{B}$) and heat current ($\vec{J}_Q$) is parallel to the Nernst electric field ($\vec{E}_N$). One can see that $S_{xy}$ changes the sign at $T = 145$ K. As to be discussed later on based on the field dependent $S_{xy}$ measurements, such a sign change in $S_{xy}$ arises from the competition between the normal Nernst effect and the anomalous Nernst effect.

Next, we discuss the field dependence of longitudinal thermoelectric and other thermal responses of Fe$_3$Sn$_2$. Figure 4.10 (a-b) show the field dependent $-S_{xx}/T$ and $\kappa_{xx}$ measured at various temperatures, respectively. Interestingly, both these two longitudinal quantities exhibit similar field dependent behaviors: there is a broad peak in the low field region at low temperatures (below 200 K) while both longitudinal quantities are nearly field independent at high temperatures (also seen in Fig. S1(b-c) [49]). Similar feature in thermopower behavior was observed recently [60], although the signal reported is not as clear as the data shown in Figure 4.10 (a). The broad peak feature was presented as a signature of skyrmion bubbles existing in Fe$_3$Sn$_2$, since the gained entropy associated with the formation of skyrmion bubble lattice enhances $S_{xx}$ by providing an extra driving force to the thermal diffusion of conduction electrons [60]. The formation of skyrmion bubbles in the low field region is presumably responsible for the broad peak observed in $\sigma_{xx}$ as presented in Fig. S1(a) [49], via the spin-scattering process, a feature that is consistent with an early report [70]. Intriguingly, as shown in Figure 4.10 (b) and Fig. S1(c-d) [49], $\kappa_{xx}$ (H) shows a hump feature in low field region at 100 K < $T$ < 250 K while it monotonically decreases at low field prior to near saturation at $T$ < 100 K. Such a field dependent $\kappa_{xx}$ suggests that various quasiparticles of this system, including phonon, electron, magnon, and skyrmion, play a non-negligible role in thermal transport in different field-temperature regions. For instance, the hump feature in the low field region at 100 K < $T$ < 250 K can be related to the skyrmions either by serving as heat carrier or via the electron/phonon-skyrmion interaction.
Now we focus on the transverse responses \( (S_{xy}, \kappa_{xy}) \) and their relation to the Berry phase of Fe\(_3\)Sn\(_2\), as shown in Figure 4.10 (c-d). In addition to the normal term that is linearly proportional magnetic field, for topological materials there is an anomalous contribution to the transverse electric, thermoelectric and thermal responses that arises from an intrinsic mechanism associated with the Berry curvature. Compared to the vast amount of studies of AHE [53], ANE has only recently emerged as another sensitive probe in identifying topological semimetals [54, 56, 55, 71, 72, 73, 52, 74], and anomalous thermal Hall effect has only been observed in a few topological semimetals recently [75, 76]. Figure 4.10 (c) presents the field dependence of \( S_{xy} / T \) measured at various temperatures. Similar to the \( \sigma_{xy} \) shown in Fig. S2(a-b) [49], at high temperatures the Nernst signal is dominated by an anomalous contribution (\( \propto M \)), which saturates near 0.8 T. At lower temperatures, the contribution from normal Nernst effect (\( \propto H \)) dominates in the high field regime, as evidenced by the linearly increasing negative value at high field. Interestingly, in the low field region, a clear broad hump emerges at \( 100 \text{ K} < T < 200 \text{ K} \), the origin of which will be discussed next. Note that the competition between normal Nernst effect and ANE leads to the sign change at \( T = 145 \text{ K} \) in \( S_{xy} \) measured at 1.5 T magnetic field as plotted in Figure 4.10 (d). The field dependent thermal Hall effect \( \kappa_{xy} (H) \) is shown in Figure 4.10 (d). Only anomalous thermal Hall component is present, which increases with temperature and reaches a value of around 0.086 W/mK. Anomalous thermal Hall effect have been observed in other topological materials such as Mn\(_3\)Sn, Co\(_2\)MnGa [75, 76]. The anomalous transverse thermal response is the result of Berry curvature summed over the inverse of thermal de Broglie length of electrons \( (\lambda = h/\sqrt{2\pi m k_B T}) \) [76]. AHE feature has also been observed in Fe\(_3\)Sn\(_2\) previously [77, 59] and is shown in Fig. S2 [49]. All these (electric, thermoelectric, thermal) transverse transport coefficients are dominated by anomalous contributions.
Figure 4.10: Magnetic field dependence of Seebeck coefficient scaled by temperature $-S_{xx}/T$ (a) and thermal conductivity $\kappa_{xx}$ (b); Magnetic field dependence of Nernst coefficient scaled by temperature $S_{xy}/T$ (c) and thermal Hall conductivity $\kappa_{xy}$ (d). Data were measured at various temperatures.

**Topological Nernst** - The origin of the hump feature observed in Nernst measurement at the low field region shown in Figure 4.10 (c) presents a puzzle. By performing linear fitting using the high field data, we subtract the contribution from the normal Nernst effect. The obtained $\Delta S_{xy}/T$ is shown in Figure 4.11 (a). The broad hump feature at low temperatures (e.g., $T = 120$ K) is clearly confined to magnetic field smaller than 1 T. Note that 1 T is the upper limit of skyrmion bubble phase observed in the Lorentz TEM experiment [61, 78]. This observation should not be coincidental; instead, this feature is the result of
electron-skyrmion interactions [79]. Since the skyrmion bubble phase persists up to room temperature, we anticipate that there should be topological contribution in the observed Nernst signal even though $\Delta S_{xy}$ is dominated by the anomalous term at high temperature. To verify this conjecture, the magnetization data $M(H)$ measured at $T = 300$ K is overplotted in Figure 4.11 (a) as thick black dashed line [additional magnetization data measured at various temperatures are shown in Fig. S4(b) [49]]. By comparing $\Delta S_{xy}/T(H)$ and $M(H)$ curves measured at 300 K, it is clear that there is a topological contribution to the observed Nernst signal in the low field region. Assuming the proportionality of anomalous Nernst signal to the magnetization at the same temperature, we further subtract the anomalous Nernst contributions to extract the topological Nernst signal $S_{xy}^{T}/T$ which is shown in the left panel of Figure 4.11 (b). To the best of our knowledge, there have only been two clear-cut reports on TNE, one on MnGe ($T_{N}$=150 K) and another on Gd$_2$PdSi$_3$ ($T_{N}$ 22 K). Compared to the two previous reports [58, 57], Fe$_3$Sn$_2$ is a high-temperature frustrated ferromagnet, whose skyrmion phase region expands well above room temperature [60, 61].

Considering the skyrmion bubble lattice in Fe$_3$Sn$_2$, topological Hall effect (THE) is also anticipated. Indeed, THE has recently been reported by Li et al [77]. In order to study the thermoelectric linear response tensor (to be discussed latter on), in the right panel of Figure 4.11 (b) we plot the topological Hall resistivity $\rho_{yx}^{T}$ after subtracting the both normal Hall effect and AHE components (see Fig. S2 [49]), which is consistent with the previous report [77]. Remarkably, $S_{xy}^{T}/T$ and $\rho_{yx}^{T}$ seem to have a simple scaling constant between them (0.137 A/m K$^2$) in the temperature range between 200 K to 300 K. The unit of this constant is the same as that of thermoelectric linear response tensor divided by temperature, $\alpha/T$. This simple proportionality suggests a common origin for the two observed topological responses in electric and thermoelectric sectors of Fe$_3$Sn$_2$, which is presumably attributed to non-zero
Berry curvature arising from the non-zero spin chirality of the skyrmion spin structure. In contrast, the two topological responses $S_{xy}^T / T$ and $\rho_{yx}^T$ at lower temperatures ($T = 150$ K and 120 K) exhibit rather different behaviors. At $T = 150$ K, there is a sign change in TNE, while THE maintains the same sign. At $T = 120$ K, $\rho_{yx}^T$ is barely detectable, whereas the $S_{xy}^T / T$ still shows a broad peak with a positive amplitude of around 0.4 nV/K$^2$. As noted in the introduction and many other review papers [80, 52], the ‘drive’ for thermoelectric response is a temperature gradient, a macroscopic, statistical force; on the other hand, the ‘drive’ for electrical response is a voltage gradient, a microscopic, electro-mechanical force. Thus, the difference in behavior of $S_{xy}^T$ and $\rho_{yx}$ at low temperature is naturally anticipated. To fully understand these topological responses, especially the thermoelectric topological response $S_{xy}^T$, one needs to take into account the electron-skyrmion interactions in the Boltzmann transport theory, which calls for future theoretical investigation.

Figure 4.11: (a) Magnetic field dependence of residual Nernst coefficient measured at various temperatures after subtracting the normal Nernst coefficient ($\propto H$). The magnetization ($H \parallel c$) data measured at 300 K is overplotted as the dashed line. The saturated magnetization is about 1.8 $\mu_B$/Fe. (b) Magnetic field dependence of topological Nernst coefficient (left) and Hall resistivity (right) after subtracting out the anomalous contribution ($\propto M$).

The observation of both anomalous and topological components in Hall effect and Nernst
effect measurements, together with the simple scaling between TNE and THE at high temperature, raises an intriguing issue regarding the thermoelectric linear response tensor $\bar{\alpha}$, a revealing quantity in the study of magnetic topological semimetals which incorporates anomalous contributions from both AHE and ANE [73]. In a typical thermoelectric measurement set-up, there is no electric current flowing through the material, i.e., $\vec{J} = \bar{\sigma} \vec{E} + \bar{\alpha} (-\nabla T) = 0$.

By defining another tensor $S = \begin{pmatrix} S_{xx} & S_{xy} \\ S_{yx} & S_{yy} \end{pmatrix} = \begin{pmatrix} E_x/\partial_x T & E_y/\partial_x T \\ E_x/\partial_y T & E_y/\partial_y T \end{pmatrix}$, one obtains $\bar{\alpha} = \bar{\sigma} \bar{S}$ [55]. Specifically, here we measure the in-plane thermoelectric linear response tensor $\alpha_{xy} = \sigma_{xx} S_{xy} + \sigma_{xy} S_{xx} = \alpha_1 + \alpha_2$ [54]. By replacing $S_{xy}$ with $\Delta S_{xy} = S_{xy} - S_{xy}^0$ and $\sigma_{xy}$ with $\Delta \sigma_{xy} = \sigma_{xy} - \sigma_{xy}^0$, where $S_{xy}^0$ and $\sigma_{xy}^0$ represent normal Nernst coefficient and Hall conductivity respectively, we plot the residual thermoelectric linear response tensor $\Delta \alpha_{xy}/T$ in Figure 4.12 (a). At high temperature, $\Delta \alpha_{xy}/T$ is dominated by the anomalous part $\alpha_{xy}^A/T$, which is directly proportional to the integrated Berry curvature at the Fermi surface [73]. In contrast, at low temperature $\Delta \alpha_{xy}/T$ is dominated by the topological contribution, $\alpha_{xy}^T$, which is a manifestation of Berry curvature in real space due to the underlying skyrmion bubble phase [81].

Finally, we present the evolution of thermoelectric quantities extracted at 1.5 T (above the saturation field) as function of temperature, as shown in Figure 4.12 (b-d). In Figure 4.12 (b), we see that the normal Nernst coefficient and the ANE coefficient have opposite trends. Generally speaking, the ordinary Nernst effect positively correlates with carrier mobility [50]. Thus, the normal Nernst effect becomes stronger as the carrier mobility increases at low temperature. On the other hand, the ANE is independent of carrier mobility, in some cases even amplified by disorder in the system [54]. This is because the intrinsic contributions of $S_{xy}^A$ is not affected by defects but depends on the integrated Berry curvature in the
Figure 4.12: (a) Residual thermoelectric linear response tensor scaled by temperature $\Delta \alpha_{xy}/T$ after subtracting the normal Nernst coefficient. (b) Normal and anomalous (1.5 T) Nernst coefficient scaled by temperature. (c) Anomalous thermal and electric Hall conductivity (1.5 T) as a function of temperature. (d) Temperature dependence of Total anomalous thermoelectric linear response tensor ($\alpha_{xy}^A$) and its two components ($\alpha_{xy}^A, \alpha_{xy}^A$).

momentum space near the Fermi level [54]. Thus, $S_{xy}^A$ is sensitive to both Fermi energy and temperature via the Fermi distribution function. It is likely that, within the measurement temperature range, the enhanced thermal fluctuation or the closer energy spacing between the field-induced Weyl nodes and the chemical potential with the increase of temperature leads to larger contribution from the Berry curvature [62, 73]. As a result, here $S_{xy}^A$ continues to increase linearly even up to 300 K, suggesting that an even larger Nernst signal is anticipated at high temperatures, which is consistent with the presence of two Dirac points
revealed by ARPES with one of them positioning at $E = -70\text{meV}$ below the Fermi energy [59]. The increase of $S_{xy}^A$ as a function of temperature has been recently observed in other magnetic topological semimetals [54, 72]. In Figure 4.12 (c) we plot the temperature dependence of $\sigma_{xy}^A$ and anomalous thermal Hall conductivities ($\kappa_{xy}^A$) extracted at 1.5 T. Similar to $S_{xy}^A/(T)$, both $\sigma_{xy}^A$ and $\kappa_{xy}^A$ increase with temperature, suggesting a common mechanism of all these three anomalous electronic, thermoelectric and thermal responses in this system. Figure 4.12 (d) presents the temperature dependence of thermoelectric linear response tensor $\alpha_{xy}^A$ and its two components $\alpha_1^A = \sigma_{xx} S_{xy}^A$ and $\alpha_2^A = S_{xx} \sigma_{xy}^A$. Note that the signs of $\alpha_1^A$ and $\alpha_2^A$ are determined by the transverse and longitudinal components of Seebeck coefficients respectively, which needs to be taken into account when calculating the total $\alpha_{xy}^A$ [54, 74]. Recent theory study by Papaj and Fu [71] predicted $\alpha_{xy}^A|_{T=80K} = 0.67 \text{A/mK}$ for Fe$_3$Sn$_2$, whereas our experiment showed that $\alpha^A$ reaches this value at $T = 240 \text{K}$. This inconsistency may be associated with the level of disorder used in theoretical calculation compared to the actual value in our sample [71]. To put these data in perspective, we note that among high-temperature magnetic semimetals, the largest ANE was observed in Co$_2$MnGa, with $S_{xy}^A|_{T=300K} \approx 6 \text{µV/K}$ and $\alpha_{xy}^A|_{T=300K} \approx 2.8 \text{A/m K}$. In comparison, the Fe$_3$Sn$_2$ sample measured here has $S_{xy}^A|_{T=300K} \approx 2.1 \text{µV/K}$ and $\alpha_{xy}^A|_{T=300K} \approx 1 \text{A/m K}$. These results place Fe$_3$Sn$_2$ as one of the materials with large anomalous thermoelectric coefficients.

**Conclusions** - In conclusion, we have observed a large anomalous Nernst signal ($2.1 \text{µV/K}$ at 300 K) in Fe$_3$Sn$_2$, a value that is comparable to the largest value reported thus far. The temperature and field dependence of this Nernst signal was investigated: it is the manifestation of Berry curvatures both in real and reciprocal space. At high temperature, the Nernst signal is dominated by the anomalous contribution, the magnitude of which is proportional to the integrated Berry curvature near the Fermi surface in the momentum space. At lower
temperatures, the Nernst signal is dominated by a topological term, restricted to the low field region where the skyrmion bubble phase is present, associated with the Berry curvature in real space generated by the underlying skyrmion lattice. This study demonstrates an effective strategy of investigating topological materials by measuring their transverse thermal and thermoelectric responses at different temperatures and magnetic fields.
Chapter 5

Quantum spin chains in Cu$_2$(OH)$_3$Br

This chapter is adapted from Coexistence and Interaction of Spinons and Magnons in an Antiferromagnet with Alternating Antiferromagnetic and Ferromagnetic Quantum Spin Chains [82].

5.1 Introduction

In conventional magnets with magnetic long range order (LRO), low-energy excitations are carried by spin waves, represented by massless bosons called magnons with $S = 1$ [83]. However, in one-dimensional (1D) antiferromagnetic quantum spin systems, quantum fluctuations destroy LRO in the ground state. Such systems cannot be described using mean-field theory such as the standard Landau-Ginzburg-Wilson theory [84]. As a result, the low-energy excitations in these systems behave quite differently from their higher-dimensional counterparts. One of the prototypical systems is the Heisenberg antiferromagnetic quantum spin-1/2 chain, where the low-energy excitations are carried by pairs of deconfined spinons [85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98]. In contrast to magnons, spinons possess fractional spin $S = 1/2$ which could be thought of as propagating domain walls [87, 88]. On the other hand, materials hosting ferromagnetic quasi-1D spin-1/2 chains are quite rare and the magnetic quasiparticles of ferromagnetic quantum spin chains are magnons [99, 100]. Importantly, interaction between different quasiparticles has been an exciting research topic.
In many cases, such interactions often lead to novel electronic and magnetic phenomena. For instance, electron-phonon interaction plays an essential role in the formation of Cooper pairs in conventional superconductors [101], while magnons have been proposed as the glue for Cooper pairs in unconventional superconductors [102]. In some metallic magnets, it has been found that electron-skyrmion interactions give rise to topological Hall effect [103], which provides a new route for spintronic applications. However, up to date there is no report on the interaction between two different types of magnetic quasiparticles. In this chapter, we report our observation of the coexistence and interaction of spinons and magnons in a quasi-1D antiferromagnetic insulator \( \text{Cu}_2(\text{OH})_3\text{Br} \) using inelastic neutron scattering measurements. These two different magnetic quasiparticles arise from the peculiar orbital ordering and spin structure of \( \text{Cu}_2(\text{OH})_3\text{Br} \), which consists of nearly decoupled, alternating antiferromagnetic and ferromagnetic chains of \( \text{Cu}^{2+} \) ions with spin-1/2. The antiferromagnetic chains support spinons and the ferromagnetic chains support magnons. Using both quantum Monte Carlo (QMC) simulations and Random Phase Approximation (RPA) calculations, we demonstrate evidence of magnon-spinon interactions via the weak but finite interchain couplings. To the best of our knowledge, such an interaction between two different magnetic quasiparticles has not been investigated even in theory due to the unusual nature of the spin structure. Our study thus opens up a new research arena and calls for further experimental and theoretical studies.

5.2 Results

Figure 5.1 (a, b) depict the crystal structure of \( \text{Cu}_2(\text{OH})_3\text{Br} \), which is indicative of quasi-two-dimensional nature with the neighboring Cu-Cu distance along the c-axis much larger than
those in the ab plane. The Cu\(^{2+}\) magnetic ions in the ab plane form a distorted triangular lattice with two inequivalent Cu sites: Each Cu1 site has 4 Cu-O bonds and 2 Cu-Br bonds while each Cu2 site has 5 Cu-O bonds and 1 Cu-Br bond. As will be discussed later, the differences in the local geometry (caused by the ordering of Br ions) of these two Cu sites are crucial: they determine the nature of orbital ordering (partially occupied d orbitals) of Cu1 and Cu2 and the sign of nearest-neighbor intra-chain exchange interactions between Cu moments, Cu1-Cu1 and Cu2-Cu2.

Heat capacity and magnetic susceptibility measurements [inset of Figure 5.1 (c)] on a single crystal sample reveal a paramagnetic-antiferromagnetic phase transition at \( T_N \approx 9.0 \) K, in agreement with previous reports [104, 105]. The main panel of Figure 5.1 (c) plots the temperature dependence of neutron diffraction intensity of ordering wave vector (0.5 0 0), affirming the antiferromagnetic nature of the magnetic long-range ordered state. The magnetic structure determined by Rietveld refinement (FullProf) [106] (Fig. S1 [82]) is presented in Figure 5.1 (d). Along the b-axis, Cu1 spins align ferromagnetically with spins oriented nearly along the diagonal direction in the ac-plane, while Cu2 spins align anti-ferromagnetically with spins oriented along the a-axis. The nearest-neighbor spins of both Cu1 and Cu2 sites along the a-axis are antiparallel, as suggested by the ordering wave vector. The ordered moment for Cu1 and Cu2 sites are \( \approx 0.737(6) \) \( \mu B \) and \( \approx 0.612(2) \) \( \mu B \) respectively; both of these values are smaller than the full saturation value of 1 \( \mu B \) for spin-1/2, resulting from strong quantum fluctuation.

To investigate the nature of the spin dynamics, we performed inelastic neutron scattering measurements on co-aligned single crystals in the (H K 0) scattering plane using the HYSPEC time-of-flight spectrometer at Spallation Neutron Source [107]. Intriguingly, we find that this system shows quasi-1D nature of the exchange interactions as seen in the momentum-
Figure 5.1: Crystal structure and magnetic structure of Cu$_2$(OH)$_3$Br. Crystal structure of Cu$_2$(OH)$_3$Br in the ac (a) and ab (b) plane showing a quasi-two dimensional, distorted triangular lattice of Cu atoms. (c) Temperature dependence of neutron diffraction intensity of an ordering wave vector (0.5 0 0). The inset shows the temperature dependence of heat capacity and magnetic susceptibility measurements. (d) Schematics of spin structure of Cu$^{2+}$ ions with Cu2 spins point along the a-axis while Cu1 spins pointing nearly along the diagonal direction in the ac plane. Exchange interactions of Cu1-Cu1, Cu2-Cu2, and Cu1-Cu2 as well as DM interaction are denoted.

energy-resolved neutron scattering intensity maps presented in Figure 5.2 (a-c). The nearly dispersionless behavior of the excitation spectrum along both H [Figure 5.2 (a)] and L [Figure 5.2 (b)] directions indicates weak coupling between Cu spins along both a- and c-axes.
In contrast, the $I(E, K)$ intensity map (integrated over all $H$ and $L$) presented in Figure 5.2 (c), shows unusual excitation features with well-defined magnon dispersion and broad continuum above $\approx 5$ meV. These observations, combined with the refined spin structure shown in Figure 5.1 (d), demonstrate that this system consists of nearly-decoupled, alternating ferromagnetic and antiferromagnetic chains. To the best of our knowledge, Cu$_2$(OH)$_3$Br is the only system discovered thus far to exhibit the coexistence of quasi-1D ferromagnetic and antiferromagnetic quantum spin chains.

As an initial attempt to understand the magnetic excitations of this system, we performed Linear Spin Wave (LSW) calculations using SpinW [108]. The model magnetic Hamiltonian ($H$) [82] consists of nearest neighbor Heisenberg-Ising type exchange couplings with intrachain interactions ($J_1$ and $J_2$), interchain interaction ($J_3$, $J_4$) and Dzyaloshinskii-Moriya (DM) interaction ($D$) [Figure 5.1 (d)]. The dominant interactions are $J_1$ (ferromagnetic), $J_2$ (antiferromagnetic) whereas $J_3$ and $J_4$ are antiferromagnetic and small. The LSW fitting spectra are shown in Figure 5.2 (c, d) and the fitting parameters are $J_1 = -2.6$ meV, $J_2 = 9.9$ meV, $J_3 = 1.2$ meV, $J_4 = 0.3$ meV and $D = 1.0$ meV. The anisotropy parameter of interchain interactions is are $\Delta F = 0.173$ for $J_1$ and $\Delta AF = 0.045$ for $J_2$, and the DM term is on the interchain bonds between Cu1 and Cu2 [82]. The good agreement between the experimental data and the LSW results reassures us that this system indeed is composed of quasi-1D ferromagnetic and antiferromagnetic alternating chains. The lower-energy branches associated with ferromagnetic chains have an energy gap of $\approx 1.2$ meV at the zone center (e.g. $K = 0$), while the higher-energy branches associated with antiferromagnetic chains have an energy gap of $\approx 4.2$ meV at the zone center (e.g., $K = -1$). These spin gaps arise from anisotropic exchange interactions and finite interchain coupling and the spectral gap in the ferromagnetic branch around 3.5 meV at $K = -0.5$ and -1.5 arises from the DM interaction.
Figure 5.2: Magnetic excitation spectra and the comparison to LSW calculations. (a) The momentum- and energy-resolved neutron scattering intensity map $I(E, H)$ ($K = -0.5$ and with all measured $L$ values integrated). (b) Intensity map $I(E, L)$ ($K = -0.5$ and with all measured $H$ values integrated). These two intensity maps show nearly dispersionless magnetic excitations along both $H$ and $L$ directions. (c) Intensity map $I(E, K)$ with both $H$ and $L$ integrated over all measured values to enhance the statistics of the signal. These intensity maps were obtained after using the data measured at $T = 100$ K as background and subtracting it from the data measured at $T = 5$ K. (d) The calculated $I(E, K)$ spectra using LSW theory. The white curves in all panels are the calculated dispersions using LSW theory.
As discussed in the introduction, the excitations of (quasi-) 1D spin-1/2 antiferromagnets are spinons instead. As a result, one expects a broad continuum produced by pairs of spinons, which cannot be described within the framework of LSW theory [89]. Indeed, we do observe a broad continuum above 5 meV as shown in Figure 5.2 (c), similar to the spinon continuum feature observed in the prototypical quasi-1D antiferromagnet KCuF3 [90, 94]. This again affirms quasi-1D nature of Cu$^{2+}$ spins of Cu$_2$(OH)$_3$Br.

The measured magnetic excitations and their comparison within LSW theory raise two important questions. First, what is the underlying mechanism that leads to ferromagnetic and antiferromagnetic alternating chains in this system? Second, how do the two different types of magnetic quasiparticles interact with each other?

In order to shed light on the magnetic interactions and the resultant unique spin structure of Cu$_2$(OH)$_3$Br, we performed first-principles density functional theory (DFT) based calculations. The total energy calculated with different long-range ordered magnetic states is listed in Fig. S4 [82], with the lowest energy spin configuration agreeing with the experimental observation. Using only an isotropic Heisenberg model with nearest neighbor intra- and interchain couplings, the intra-chain (J1 and J2) and the interchain chain (J3 and J4) couplings, illustrated in Figure 5.1 (d), were calculated. Their values are listed in Fig. S5 [82]. One can see that the intra-chain interactions indeed dominate, with J1 being ferromagnetic and J2 antiferromagnetic. The weaker interchain couplings J3 and J4 are both antiferromagnetic. The theoretical results are in qualitative agreement with the exchange parameters obtained from LSW fitting. Note that spins of neighboring Cu1 and Cu2 with antiferromagnetic J4 are not energetically favorable, while neighboring spins with antiferromagnetic J3 are energetically favorable. The non-zero magnetic interaction J4 leads to frustration, which facilitates the decoupling of Cu1 and Cu2 chains.
To understand the nature of these exchange interactions, in Figure 5.3 (a) we present the ground state spin density profile. The t2g orbitals of Cu$^{2+}$ ions are completely filled while there is a single hole in the eg manifold, which splits due to local crystal field. The spin density shows the half-filled eg orbital, which has (x2-y2)-like character in a local coordinate axis system. Interestingly, all the Cu eg orbital lobes extend towards the oxygen p orbitals but not towards the Br ions. This can be understood by the weaker crystal field associated with Br ions, which have -1 charge as opposed to -2 for the oxygen ions. The resulting crystal field pushes the Cu eg orbital with electron clouds extending towards oxygen ions to higher energies, a characteristic of the hole occupying this orbital and spin density associated with it. The crystal field, combined with the geometry and local coordinate of these two Cu sites, leads to antiferro-orbital orientational order for Cu1 chains and ferro-orbital orientational order for Cu2 chains. Such an unusual orientational ordering of the active magnetic orbital, which can be considered as an improper orbital order imposed by the strongly asymmetric crystal field of the anions, gives rise to anion-mediated exchange interactions that are dominated by Cu-O-Cu exchange pathways, considering that only O orbitals e-bond with the half-filled Cu eg orbitals. This is supported by nearly zero spin density on the Br ions as illustrated in Figure 5.3 (a), which indicates that Br does not hybridize with the spin-polarized Cu orbitals, and hence does not contribute to superexchange. The projected density of states (DOS) of Br, O and the hole (i.e. the unoccupied states) of Cu$^{2+}$ ions are shown in Figure 5.3 (b). Consequently, antiferro-orbital order along Cu1 chains leads to ferromagnetic spin coupling ($J_1 < 0$) whereas ferro-orbital order leads to antiferromagnetic spin coupling along the Cu2 chains ($J_2 > 0$) [109].
Figure 5.3: Electronic structure calculated via first principles DFT. (a) The ground state spin density of the half-filled eg orbital of Cu$^{2+}$ ions and p orbitals of O and Br atoms. Yellow color denotes spin up and cyan color denotes spin down. Cu1 ions with ferromagnetic spin alignment show antiferro-orbital order while Cu2 ions with antiferromagnetic spin alignment show ferro-orbital order. (b) The projected density of states (PDOS) of Cu1, Cu2, Br, and O ions.
5.3 Magnon-spinon interactions

Next, we discuss magnon-spinon interaction via the weak interchain couplings (J3, J4) between neighboring AFM/FM chains. In the absence of interchain couplings, the system would host deconfined spinons propagating in the AFM chain and well-defined magnons propagating in the FM chain. With gradual increase of interchain couplings, the quasi-1D nature of the system is progressively destroyed and magnetic long-range order develops. It is known that in quasi-1D antiferromagnets composed of identical spin chains, such as KCuF3 [91], there is an energy threshold which separates spinons and magnons. Above this threshold, spinons are deconfined; below this threshold, the spinon continuum turns into classical magnons because of the finite interchain couplings and resulting in long-range order [110, 95]. Thus, in these systems, magnetic excitations are carried either by unbound spinons or classical magnons in different energy regimes, and they do not interact. In contrast, due to the coexistence of both ferromagnetic and antiferromagnetic chains in Cu2(OH)3Br, the corresponding magnon and spinon excitations can coexist in the same energy range and interact with each other through the finite interchain couplings.

To better understand the effects of interchain couplings, we have used the Algorithms for Lattice Fermions (ALF) implementation [111] of the finite temperature auxiliary field quantum Monte Carlo to carry out numerical simulations of the dynamical spin structure factor of a system consisting of ferromagnetic and antiferromagnetic spin-1/2 chains [82, 112, 113]. While this algorithm is formulated for fermionic systems, it can also be used to simulate non-frustrated spin systems [113]. For simplicity, we only consider intra-chain couplings (J1 = -1.6 meV, J2 = 5.3 meV) and antiferromagnetic interchain coupling J3 while keeping J4 = 0 (non-zero J4 would introduce magnetic frustration and a negative sign problem).
Figure 5.4 presents the simulated spectra without taking into account the magnetic form factor of Cu$^{2+}$. There are several important features to point out. First, both well-defined magnon dispersion and spinon continuum, which are associated with ferromagnetic chains and antiferromagnetic chains respectively, are clearly seen, consistent with the experimental observation shown in Figure 5.2 (c). Second, by introducing non-zero J3, the magnetic excitations associated with antiferromagnetic chains are pushed up to higher energy and a gap opens which increases with J3. This gap opening is the result of molecular field arising from the neighboring ferromagnetic chains. Third, compared to the decoupled spin chains, non-zero J3 introduces asymmetric spectral intensity centered about K = 1, as shown by the constant energy cut (at E = [7.7 9.7] meV) presented in Figure 5.4 (d), which suggests that the interchain coupling induces redistribution of spectral weight.

To obtain further insights on the effects of interchain couplings and the resultant magnon-spinon interactions, we perform Random Phase Approximation (RPA) calculations and compare the results with the INS excitation spectra. For this purpose, we adopt and generalize the RPA approach for coupled antiferromagnetic chains [114]. In the presence of interchain interaction, we obtain generalized susceptibilities $\chi_{RPA}^{F,AF}(\vec{k}, \omega)$ for the two types of chains.

$$\chi_{RPA}^{F,AF}(\vec{k}, \omega) = \frac{1 - J_\perp(\vec{k}) \cdot \chi_{1D}^{AF,F}(\vec{k}_\parallel, \omega) \cdot \chi_{1D}^{F,AF}(\vec{k}_\parallel, \omega)}{1 - [J_\perp(\vec{k})]^2 \cdot \chi_{1D}^{AF}(\vec{k}_\parallel, \omega) \cdot \chi_{1D}^{F}(\vec{k}_\parallel, \omega)}$$

(5.1)

$$J_\perp(\vec{k}) = 4(J_3 + J_4) \cos\left(\frac{k_\perp a}{2}\right) \sin\left(\frac{k_\parallel b}{4}\right)$$

(5.2)

where $\chi_{1D}^{F,AF}(\vec{k}_\parallel, \omega)$ are the susceptibilities of non-interacting chains and $J_\perp(\vec{k})$ is the Fourier transforms of the interchain couplings. Here $k_\parallel$ is the component of the wave vector $\vec{k}$ along the chain direction (b-axis), and $k_\perp$ is perpendicular to the chain direction (a-
Figure 5.4: Magnetic excitation spectra via quantum Monte Carlo simulations. Simulated magnetic excitation spectra (with $H = 1$) of a system consisting of alternating ferromagnetic and antiferromagnetic quantum spin chains with the interchain coupling $J_3 = 0$ (a), $J_3 = 0.1J_2$ (b), and $J_3 = 0.2J_2$ (c). (d) Constant energy cuts at $E = [8.7, 9.7]$ meV showing the asymmetric spectral intensity about $K = 1$ induced by non-zero $J_3$. Note that Bose factor but not magnetic form factor of Cu$^{2+}$ ions has been taken into account in the simulation.

We use a Lorentzian function for $\chi_{1D}^F(\vec{k}_\parallel, \omega)$ and the Muller Ansatz [89] expression for $\chi_{1D}^{AF}(\vec{k}_\parallel, \omega)$. Detailed description of the generalized RPA approach is documented in the Supplemental Materials [82].

Figure 5.5 (a, b) present the measured excitations with $H$ integrated over $[0.85, 1.15]$
and the corresponding RPA results, respectively. In addition to the two-spinon continuum that is clearly observed in RPA calculations [Figure 5.5 (b)], which is consistent with the experimental data shown in Figure 5.5 (a), one can see a clear modification of the spectral intensity caused by the interchain couplings. For instance, a constant energy cut at $E = 10.75$ meV is plotted in Figure 5.5 (c), together with the RPA calculations with (red) and without (black) interchain couplings. One can see that RPA with the inclusion of interchain couplings captures the redistribution of the spectral weight with the intensity at $K = -0.5$ larger than that at $K = -1.5$. This difference cannot be accounted for by magnetic form factor. Note that $J_\perp(\vec{k})$ is negative when $K$ is in the range of $[-1, 0]$ and positive when $K$ is in the range $[-2, -1]$. This difference in the sign leads to the asymmetry in the spectral weight about $K = -1$, which is consistent with the QMC simulation results shown in Figure 5.4 (b-d). If we reduce the constant energy cut to $E = 7.75$ meV [Figure 5.5 (d)] and focus on the two peaks closest to $K = -1$, again the RPA spectrum with interchain couplings introduces asymmetry. The agreement near $K = -1.25$ is very good but not so good for $K = -0.75$. Further comparison between experimental data and RPA calculation results are discussed in the Supplemental Materials [82].
Figure 5.5: Magnetic excitation spectra and the comparison with RPA calculations. (a) I(E, K) intensity map obtained after background subtraction with H integrated over [0.85 1.1] and L integrated over all measured values. (b) The RPA calculation of I(E, K) spectra for comparison. Constant energy cuts at E = 10.75 meV (c) and at E = 7.75 meV (d) and their comparison with RPA calculations.
5.4 Conclusions

In summary, we have discovered that magnons and spinons coexist in Cu$_2$(OH)$_3$Br, which uniquely consists of quasi-1D ferromagnetic and antiferromagnetic quantum spin chains. Magnons and spinons interact with each other via weak but finite interchain couplings, which opens the gap of the spinon continuum and gives rise to a redistribution of the spectral weight. This study highlights a new toy model and research paradigm to study the interaction between two different types of magnetic quasiparticles.
Appendix

6.1 Manual for TTO_v2

TTO_v2.lvproj is a Labview project located on the PPMS computer at C:\Users\PPMS\Desktop\Thermal Transport\2182_test\TTO_v2.

A screen shot of TTO_v2.lvproj is shown above. Although there are many .vi files in the project, a typical user would only need to access the maine.vi (highlighted) file.
6.1.1 The hierarchy of TTO_v2.lvproj and the maine.vi

The hierarchy structure of TTO_v2.lvproj is shown in the following figure. There are six options typically used for measurement purposes as highlighted by the orange boxes. They can all be called by the maine.vi file. For a typical user, one would need to write a sequence file, supply the path to maine.vi and click ‘run’.

![Figure 6.1: The hierarchy of TTO_v2.lvproj](image_url)

**maine.vi** - The following figure shows a screen shot of the maine.vi file. There are three interactive levers one can click. Clicking lever one will load the sequence file from the path indicated by the text area under ‘Sequence’.

C:\Users\PPMS\GDfu\proj\TTO_data\VI3\exp02102021\seqt.

The loaded sequence will be displayed in the text area on the bottom left (red box). Clicking lever two will run the loaded sequence. The maine.vi will not be responsive before a sequence is finished. You will be able to stop the program by clicking the red stop button below the menu bar at the top. Clicking lever three will run the *testing module.vi*. Clicking View (menu bar) → VI Hierarchy will prompt a window with the content shown in Figure 6.1. Double clicking any icons in the prompt window will open the front panel of the module.
Figure 6.2: The front panel of maine.vi. For the most part, a typical user should only need to access this panel.
6.1.2 Six frequently used options

testing module.vi - This module is represented by the icon Testing module in Figure 6.1. This module should be used at the beginning of each measurement to examine if all contacts are made properly and all meters are connecting correctly.

An example is shown by the following figure. The left window in the first row shows the PPMS system temperature and temperature one/two/three as green dots and red/green/blue lines, respectively. The selection box with Cernox/Thermocouple determines which sensor testing module.vi will use. Selecting Cernox, the reading from the three resistance bridge channels of PPMS will be used. Selecting Thermocouple, the readings from the three voltage meters will be used. The relation is tabulated here.

<table>
<thead>
<tr>
<th></th>
<th>Cernox</th>
<th>Thermocouple</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>bridge 1</td>
<td>Vl</td>
</tr>
<tr>
<td>T2</td>
<td>bridge 2</td>
<td>Vr</td>
</tr>
<tr>
<td>T3</td>
<td>bridge 3</td>
<td>Vu</td>
</tr>
</tbody>
</table>

The middle window in the first row shows the longitudinal ($\Delta T_{xx}$) and transverse ($\Delta T_{yx}$) temperature difference. These two quantities needs to be defined before each run. The left and right window in the second row and the right window in the first row shows the readings from the left, right and upper voltage meters (you will know what they are when you go into the lab).

Clicking the lever under Clear will clear all data points. Clicking the lever next to I(mA) will turn on/off the current source, there by generating a pulse. If one of the contacts was loose, there will not be much response (for example, no temperature change) after turning on the current, then it will be necessary to take the sample out and remake the contacts.
The pulse in the screen shot is produced by the following actions: run the testing module → click the lever next to I(mA) → wait → click the lever next to I(mA) again → wait → click the stop button on the lower right. (Note that Vu is not connected in this example)

Figure 6.3: The front panel of testing module.vi.
**ScanT\textunderscore continuous\textunderscore module\textunderscore v2\textunderscore vi** - This module is represented by the icon *ScanT Conti* in Figure 6.1. This module is used for measuring the thermal conductivity and Seebeck/Nernst coefficients as functions of temperature. The module is invoked by writing the following sentence in your sequence file.

\[
\text{scanT, T1, T2, Trate, not\_test\_cur==0, curr, dT\_target,raise\_per\_K(in mk), mode (0-SN, 1-Pi)}
\]

Example: `scanT,10,305,3,0,0.5,0,0,0`

ScanT is the keyword telling *maine.vi* to call *ScanT\textunderscore continuous\textunderscore module\textunderscore v2\textunderscore vi*. T1 is the initial temperature, T2 is the final temperature and Trate is the temperature ramping rate. For the first data point measured at T1, the program assumes the user does not know what is the appropriate current to use. The program will try to find the appropriate current if not\_test\_cur is set to any value other than zero. The program will use the curr supplied by the user as the initial current for this finding procedure. The current for all following measurements are handled by the program. The dT\_target,raise\_per\_K(in mk) are obsolete quantities which can be set to any value (I usually put zeros there since they are harmless). The mode should always be supplied with a zero. The example shown here translate to the following: A temperature scan from 10 K to 305 K at a ramping rate of 3 K/minute will be performed (10,305,3). An initial current of 0.5 milliampere will be used and no initial testing procedure will take place (0,0.5). We measure the Seebeck/Nernst coefficients (mode==0).

**ScanT\textunderscore continuous\textunderscore res\textunderscore v2\textunderscore vi** - This module is represented by the icon *ScanT Resist* in Figure 6.1. This module is used for measuring the resistivity as a function of temperature. This module is invoked by writing the following sentence in your sequence file. This module is very similar to the previous module. The not\_test\_cur field should always be supplied with a zero.
The example shown here translate to the following: A temperature scan from 10 K to 305 K at a ramping rate of 3 K/minute will be performed (10,305,3). A current of 5 milliampere will be used and no initial testing procedure will take place (0,5). We measure the resistivity (mode==0).

*ScanT* module *stable III*\(^1\) - This module is represented by the icon *Stable ScanT III* in Figure 6.1. This module is used for measuring the thermal conductivity and Seebeck/Nernst coefficients as functions of temperature. This module is invoked by writing the following sentence in your sequence file.

<table>
<thead>
<tr>
<th>scanTs, T1, T2, Tstep, test_cur==1, curr, dT_target, mode (0-constant current, 1-polynomial)</th>
</tr>
</thead>
<tbody>
<tr>
<td>scanTs,30,120,3,1,0,2,0,0</td>
</tr>
</tbody>
</table>

ScanTs is the keyword telling *maine.vi* to call *ScanT* module *stable III*. In ‘stable’ mode, the program will set the temperature and wait for it to stabilize before each data point was taken. T1 is the initial temperature, T2 is the final temperature and Tstep is the temperature difference between each data point. The current testing procedure will take place if test_cur is set to one (and not take place otherwise). The dT_target is an obsolete quantity which can be set to any value (I usually put zeros there since they are harmless). The mode should always be supplied with a zero, the ‘1-polynomial’ option is obsolete. The example shown here translate to the following: A series of measurements at [30 K, 33 K, 36 K ... 120 K]

\(^1\)It will be necessary for the user to select the temperature sensor from the front panel of this .vi file.
will be performed (30,120,3). An initial current of 0.2 milliampere will be used and initial
testing procedure will take place (1,0.2). We use the same current for all measurement points
(mode==0).

*ScanT.module_stable.II* - This module is represented by the icon *Stable ScanT lowT* in
Figure 6.1. This module performs the same functions as the previous module, except that it
is intended for measurements at lower temperatures (2 K to 50 K). This module is invoked
by writing the following sentence in your sequence file.

```
scanTsl, T1, T2, Tstep, test_cur==1, curr, dT_target
scanTsl,2,40,2,1,0.2,0,0
```

*Thermal_hall_module.II*\(^2\) - This module is represented by the icon *Thermal Hall Module*
in Figure 6.1. This module performs a magnetic field scan at fixed temperatures. This
module is invoked by writing the following sentence in your sequence file.

```
th, H1, H2, Hrate, loop=1, curr, dT_target, test_cur==0, mode (0-SN, 1-Pi)
th,3,-3,100,1,0.5,0,0,0
```

th is the keyword telling *maine.vi* to call *ScanT.module_stable.III*. H1 is the initial field,
H2 is the final field and Hrate is the magnetic field ramping rate in units of Oe/s. The
program will take another measurement from the final field back to the initial field if loop
is set to one. The curr is the initial current (mA) the program will use. The current testing
procedure will take place if test_cur is set to zero (and not take place otherwise). The
dT_target is an obsolete quantity which can be set to any value. The mode should always
be supplied with a zero, the ‘1-Pi’ option is obsolete. The example shown here translate to
the following: A magnetic field scan 3 T → -3 T → 3T will be performed. An initial current
of 0.5 milliampere will be used and initial testing procedure will take place.

\(^2\)It will be necessary for the user to select the temperature sensor from the front panel of this .vi file.
6.1.3 Performing a measurement

Performing a measurement includes the following steps: making contacts on sample → connecting meters → selecting temperature sensors → defining measured quantities → writing a sequence → run sequence.

Selecting temperature sensors - For a thermal/thermoelectric measurement, we sometimes need to test for the ‘appropriate’ heating power, which does not heat up the sample substantially. The program can handle this task, but we need to tell the program what readings to use by configuring the temperature sensor. We need to do this step only when we are using either of the two options (Section 6.1.2): the ScanT_module_stable_III and the Thermal_hall_module_II. To do this, open the project hierarchy → double click the module (For example, Stable ScanT III) → select ‘Thermocouple/Cernox’ → right click on the edge of the highlighted selection box → Data Operations → Make current value Default.

Figure 6.4: The program hierarchy and the front panel of ScanT_module_stable_III

Defining measured quantities - There are six quantities which ‘need’ to be defined: $\Delta T_{xx,t}$,
When making contacts on the sample, it may not be easy to make them exactly as the layout in section 2.1.1. In this case, we will be allowed to make the contacts in the most convenient way possible, and define the measured quantities such that the measurement will make sense. To do this, double click log_data_v1.vi (right above maine.vi, see Section 6.1) → click ‘E’ while holding down Ctrl on keyboard → click any of the boxes will prompt a selection menu, allowing the user to change definitions (example shown here is consistent with the layout in section 2.1.1 → click ‘S’ while holding down Ctrl on keyboard (to save). T1/T2/T3 means the temperature readings from cernox sensor-1/2/3. Th1/Th2/Th3 means the temperature readings from thermocouples-1/2/3. T_{heatup} and T_{heatup,c} means the temperature difference between the hot-end (depend on how the contacts are made) and system read from thermocouple/cernox, respectively.

Figure 6.5: The front panel of log_data_v1.vi
**Writing a sequence** - A Sequence is a text file made up of a series of commands. The following table tabulates all commands. Each command should be typed as a newline in the sequence file. The ‘waitd’ command is used to conserve helium. Ramping the magnetic field will cause the dewar pressure to increase substantially. Between measurements, we can wait for the compressor to catch-up and lowers the dewar pressure before proceeding using this command. Do so will allow a helium tank to last for months. I usually set the threshold value to 4.3 kpsi.

<table>
<thead>
<tr>
<th>Command</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘ ’</td>
<td>do nothing.</td>
</tr>
<tr>
<td>‘nf’</td>
<td>create a new file to record data from following measurements.</td>
</tr>
<tr>
<td>‘wait,XXX’</td>
<td>wait for XXX seconds.</td>
</tr>
<tr>
<td>‘waitd,XXX’</td>
<td>wait for the dewar pressure to settle below XXX kpsi.</td>
</tr>
<tr>
<td>‘set,1,Tset,rate,wait’</td>
<td>to set the temperature (indicated by ‘1’) to ‘Tset’ (K), at a rate of ‘rate’ K/minute. Wait ‘wait’ seconds before proceeding to the next line.</td>
</tr>
<tr>
<td>‘set,2,Hset,rate’</td>
<td>to set the magnetic field (indicated by ‘2’) to ‘Hset’ (T), at a rate of ‘rate’ Oe/second.</td>
</tr>
</tbody>
</table>

Commands to invoke the six options described in Section 6.1.2.
BIBLIOGRAPHY
BIBLIOGRAPHY


[31] BingBing Lyu, YiFan Gao, Yujun Zhang, Le Wang, Xiaohua Wu, Yani Chen, Jiasheng Zhang, Gaomin Li, Qiaoling Huang, Naipeng Zhang, Yuanzhen Chen, Jiawei Mei, Hugen Yan, Yue Zhao, Li Huang, and Mingyuan Huang. Probing the ferromagnetism and spin wave gap in vi₃ by helicity-resolved raman spectroscopy. *Nano Letters*, 20(8):6024–6031, 2020.


