

Thermal Conductivity of MXY_3 Magnetic Layered Trichalcogenides

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Amanda Victoria Haglund
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Dedication

I would like to dedicate this dissertation to my large & wonderful & crazy immediate family, the wonderful friends I've made during my time in grad school, and my fantastic ultimate frisbee community for their unconditional love, support and encouragement.

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I would like to thank my advisors, David Mandrus and Veerle Keppens, for their support and encouragement throughout my work as a graduate student, and Philip Rack and Zac Ward for their help as my committee members.

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Abstract

Moore's Law, stating that the number of transistors that can fit on an integrated circuit should double every two years, stood strong for more than 50 years, but is now rapidly reaching its limits. In order to keep up with the need for ever-increasing computer power, focus is shifting towards new materials and technologies. Following the discovery of stable, atomically-thin graphene sheets in 2004, many materials composed of layered sheets have been (re)discovered with great potential to become the "new silicon", including hexagonal boron nitride (h-BN), metal halides such as RuCl_3 , or metal chalcogenides MoS_2 and CrGeTe_3 . With the variety of compositions also comes a multitude of different material properties: from materials exhibiting a metal-insulator transition, to thermoelectrics, and even magnetic semiconductors.

The layers in these materials are considered quasi two-dimensional (2D), as they are just atoms thick and weakly bonded together. Although graphene does not have the required bandgap for transistor applications, with the discovery of a suitable material, devices could be made from an atomically thin layer. However, because the field of single layer materials is so new, there are many materials that have not been completely characterized, leaving their full potential for new applications still unknown.

One particular category of 2D materials that is promising but has much left to be explored is the family of MXY_3 magnetic semiconductors, with $\text{M} = \text{Cr, Mn, Fe, Co, Ni}$; $\text{X} = \text{P, Si, Ge}$; and $\text{Y} = \text{S, Se, Te}$, along with CrPS_4 . While much is known about the materials' magnetic and electronic behavior, thermal conductivity has only been partially characterized for CrGeTe_3 and CrSiTe_3 . To better understand the behavior of this class of materials, single crystals of each material have been synthesized, characterized, and their in-plane thermal conductivity temperature dependence measured. By measuring one property across an entire class of

materials, behavioral trends can be more easily analyzed and understood and perhaps applied to future layered materials. At the same time, important intrinsic material properties are being provided, which will be useful for future applications of these materials.

Table of Contents

Chapter 1. Introduction: Background & Motivation.....	1
1.1 Materials of Interest	2
1.2 Materials Background	3
1.2.1 Crystal Structure	3
1.2.2 Magnetic Structure.....	5
Chapter 2. Crystal Growth and Characterization.....	8
2.1 Material Synthesis	8
2.1.1 Vapor Transport Crystal Growth	8
2.1.2 Flux Crystal Growth	13
2.2 Characterization	16
2.2.1 Powder X-ray Diffraction	16
2.2.2 Energy Dispersive X-ray Spectroscopy	16
2.2.3 Magnetization	22
Chapter 3. Thermal Conductivity Measurements	28
3.1 Thermal Conductivity Measurement Methods.....	28
3.2 Thermal Conductivity Measurement Setup.....	30
3.2.1 Temperature & Measurement Control.....	30
3.2.2 Sample Preparation	32
3.2.3 Thermocouple Construction.....	33
3.2.4 Final Setup Preparation.....	33
3.3 Running the Measurements.....	35
3.4 Calculations & Corrections	36
3.4.1 Determining Temperature Differential Across the Sample	36
3.4.2 Heater Resistance Correction.....	37
3.4.3 Correction for Thermal Voltage Variations.....	38
3.4.4 Radiation Loss Corrections.....	38
3.4.5 Final Calculations for Thermal Conductivity	40
Chapter 4. Results and Discussion.....	41
4.1 Thermal Conductivity: General Behavior	41
4.2 Literature: CrSiTe ₃ Thermal Conductivity.....	42

4.3	Literature: CrGeTe ₃ Thermal Conductivity	43
4.4	Thermal conductivity: Experimental Data – Analysis and Discussion.....	45
4.4.1	Thermal conductivity: CrSiTe ₃	46
4.4.2	Thermal conductivity: CrGeTe ₃	46
4.4.3	Thermal conductivity: MnPS ₃ & MnPSe ₃	49
4.4.4	Thermal conductivity: FePS ₃ & FePSe ₃	52
4.4.5	Thermal conductivity: NiPS ₃	55
4.4.6	Thermal conductivity: CrPS ₄	57
4.4.7	Thermal Conductivity: Overall Behavior	57
Chapter 5. Summary & Conclusions		60
Bibliography		61
Vita.....		65

List of Tables

Table 1-1: Crystal structure and space groups for magnetic semiconducting compounds [17].	4
Table 1-2: Some magnetic properties of the layered compounds studied in this work.	6
Table 2-1: Source materials for MPX_3 crystals.	10
Table 2-2: CVT growth details for MPX_3 compounds.	11
Table 2-3: $CrPS_4$ crystal growth source materials.	13
Table 2-4: $CrSiTe_3$ and $CrGeTe_3$ flux growth source materials.	15
Table 2-5: $CrSiTe_3$ and $CrGeTe_3$ self-flux growth details.	15
Table 2-6: Space group and crystal structure for all studied materials.	21
Table 2-7: EDX molar ratio results for single crystal samples.	22
Table 2-8: Magnetic ordering, easy-axis orientation and ordering transition temperatures of experimental vs. literature values.	27

List of Figures

Figure 1-1: Example MnPS_3 crystal structure, along (a) the c-axis of MnPS_3 structure and (b) parallel to the ab-plane showing the van der Waals gap between layers.....	4
Figure 1-2: CrPS_4 crystal structure, (a) parallel to the ab-plane, showing the rectangular grid of Cr atoms, and (b) perpendicular to the ab-plane.....	4
Figure 1-3: Magnetic ordering of transition metals in the ab-plane. Filled and empty circles indicate opposite directions of magnetic moment on transition metal sites: (a) FM, (b) Néel AFM, (c) stripy AFM, (d) zigzag AFM.....	6
Figure 2-1: Chemical vapor transport process for growing single crystals from a solid ($A_{s,\text{poly}}$), using a transport agent (X_g), while under a temperature gradient $T_2 > T_1$. Figure based on [30]. .	9
Figure 2-2: Single crystals of MPX_3 materials grown by CVT.....	12
Figure 2-3: Single crystals of CrPS_4 grown by auto-transport.	13
Figure 2-4: Flux grown single crystal samples of CrGeTe_3 and CrSiTe_3	15
Figure 2-5: Experimental powder XRD pattern for MnPS_3 in black, with red marks indicating peak positions from a known MnPS_3 pattern [37]. Inset shown for better clarity due to density of peaks.	17
Figure 2-6: Experimental powder XRD pattern for MnPSe_3 in black, with red marks indicating peak positions from a known MnPSe_3 pattern [38]. Inset shown for better clarity due to density of peaks.	17
Figure 2-7: Experimental powder XRD pattern for FePS_3 in black, with red marks indicating peak positions from a known FePS_3 pattern [37]. Inset shown for better clarity due to density of peaks.	18

Figure 2-8: Experimental powder XRD pattern for FePSe ₃ in black, with red marks indicating peak positions from a known FePSe ₃ pattern [38]. Inset shown for better clarity due to density of peaks.	18
Figure 2-9: Experimental powder XRD pattern for NiPS ₃ in black, with red marks indicating peak positions from a known NiPS ₃ pattern [29]. Inset shown for better clarity due to density of peaks.	19
Figure 2-10: Experimental powder XRD pattern for CrPS ₄ in black, with red marks indicating peak positions from a known CrPS ₄ pattern [14]. Inset shown for better clarity due to density of peaks.	19
Figure 2-11: Experimental powder XRD pattern for CrSiTe ₃ in black, with red marks indicating peak positions from a known CrSiTe ₃ pattern [39]. Inset shown for better clarity due to density of peaks.	20
Figure 2-12: Experimental powder XRD pattern for CrGeTe ₃ in black, with red marks indicating peak positions from a known CrGeTe ₃ pattern [15]. Inset shown for better clarity due to density of peaks.	20
Figure 2-13: Single crystal SEM image of NiPS ₃ with EDX analysis points.....	21
Figure 2-14: Magnetic susceptibility of MnPS ₃ vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T. Easy axis c-axis, Table 2-8.....	23
Figure 2-15: Magnetic susceptibility of MnPSe ₃ vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T. Easy axis ab-plane, Table 2-8.....	23
Figure 2-16: Magnetic susceptibility of FePS ₃ vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T. Easy axis c-axis, Table 2-8.....	24

Figure 2-17: Magnetic susceptibility of FePSe ₃ vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T. Easy axis c-axis, Table 2-8.	24
Figure 2-18: Magnetic susceptibility of NiPS ₃ vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T. Easy axis c-axis, Table 2-8.	25
Figure 2-19: Magnetic susceptibility of CrPS ₄ vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T.	25
Figure 2-20: Magnetic susceptibility of CrSiTe ₃ vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T.	26
Figure 2-21: Magnetic susceptibility of CrGeTe ₃ vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T.	26
Figure 3-1: Diagram of various steady-state thermal conductivity measurement methods: (a) absolute technique measurement by total power from heater (b) comparative technique measurement by comparing heat flow with a reference (c) radial heat flow method for lower heat loss of higher-temperature measurements, measures by heat flow from inside sample (d) parallel thermal conductance measurement by subtracting holder conductance to give sample values. ..	29
Figure 3-2: Sample stage, cold finger, radiation shield, and vacuum shield.	31
Figure 3-3: Sample prepared for installation in cryostat.	32
Figure 3-4: Prepared sample installed on sample stage.	34
Figure 4-1: Phonon thermal conductivity as governed by the Debye approximation [42].	41
Figure 4-2: Linear and log thermal conductivity dependence on temperature for CrSiTe ₃	47
Figure 4-3: Linear and log thermal conductivity dependence on temperature for CrGeTe ₃	48
Figure 4-4: Linear and log thermal conductivity dependence on temperature for MnPS ₃	50
Figure 4-5: Linear and log thermal conductivity dependence on temperature for MnPSe ₃	51

Figure 4-6: Linear and log thermal conductivity dependence on temperature for FePS_3	53
Figure 4-7: Linear and log thermal conductivity dependence on temperature for FePSe_3	54
Figure 4-8: Linear and log thermal conductivity dependence on temperature for NiPS_3	56
Figure 4-9: Linear and log thermal conductivity dependence on temperature for CrPS_4	58

List of Abbreviations

2D – Two dimensional

AFM – Antiferromagnetic

FM - Ferromagnetic

CVT – Chemical vapor transport

XRD – X-ray diffraction

EDX – Energy dispersive x-ray spectroscopy

ICSD – Inorganic Crystal Structure Database

SEM – Scanning electron microscope

SQUID – Superconducting quantum interference device

GPIB – General purpose interface bus

Chapter 1. Introduction: Background & Motivation

Research into layered crystalline materials has been ongoing for decades, but has not garnered serious interest until recently when the isolation of stable, single-layer graphene sheets was achieved [1]. Once the ability to cleave atomically thin layers of a material was realized in graphene, new directions in materials research became focused on finding single-layer semiconducting materials. Because the evolution of the electronic industry depends heavily on semiconductor material research, having such thin layers of materials offers the possibility for smaller devices or completely new technologies, especially since the limits of Moore's law may be approaching [2]. The layers in these materials are considered quasi two-dimensional, as they are just atoms thick and only weakly bonded together. Although graphene does not have the required bandgap for transistor applications, the discovery of a suitable semiconducting material opens up the possibility to make devices from an atomically thin layer that still maintains the necessary properties of the bulk semiconducting material [1].

Since the discovery of graphene, a wide variety of different 2D materials with interesting properties have either regained attention or been newly discovered, such as black phosphorus, silicene, hexagonal boron nitride (h-BN), transition metal dichalcogenides like MoS_2 , trihalides like RuCl_3 , or metal trichalcogenides of the form CrGeTe_3 [3]–[5]. More 2D materials are expected to be discovered, as many more have been predicted to form by calculations using known crystal structures and density functional theory [6].

Besides semiconductivity, many intriguing properties have already been found to exist in bulk 2D materials: materials with metal-insulator transitions, thermoelectric materials, and magnetic semiconductors [7]. However, characterizing the properties of 2D materials in the few- to mono-layer form is difficult and still ongoing, due to the small size of the flakes, and the lack

of stability in air for many of the materials [7]. Just recently, magnetism was shown to exist in a single layer of ferromagnetic CrGeTe_3 , which was theoretically predicted but not proven until 2017 [5]. While a lot is still unknown about the properties of monolayer 2D materials, the discoveries to date have already made a wide field of applications available.

One of the many uses available for these materials are in van der Waals heterostructures, named after the van der Waals forces that hold layered materials together. With so many different properties available in 2D materials, structures can be designed with the desired properties by stacking single layers of different materials [8]. Magnetic 2D materials have their own interesting niche in applications, apart from the potential seen for semiconducting layered materials. The magnetic types of these layered materials have the potential to be used in spintronics, where the magnetic properties can be controlled using electric fields. By being able to tune the magnetic properties, magnetic switching devices can be made analogous to field effect transistors [7], [9]. Although research into applications for 2D materials has taken off, the technology will require a lot more development before implementation in the open market can occur. This is in part because the field of 2D materials is still rather new, and there is a lot that is yet unknown about the properties and intrinsic behavior of many of these materials.

1.1 Materials of Interest

One recently noticed category of 2D materials still has much to be explored: the family of MXY_3 magnetic semiconductors, with $\text{M} = \text{Cr, Mn, Fe, Co, Ni}$; $\text{X} = \text{P, Si, Ge}$; and $\text{Y} = \text{S, Se, Te}$ [10]. One material outside of this stoichiometry, CrPS_4 , is also included, because it has similar semiconducting, layered, magnetic properties as the other materials, and CrPS_3 has not been found to be a stable compound [11]. Though there are more compounds that form in the MXY_3

structure with a variety of different properties, the research scope of this project is limited to magnetic compounds due to their interesting properties and potential for applications, including spintronics. While the materials studied in this project have potential for applications, they need to be more thoroughly characterized to better understand and predict their performance for applications. In particular, the thermal conductivity of the magnetic MXY_3 materials have been reported for only a few of these materials, and their behavior is not yet fully understood.

Recognizing the potential of these materials, this project aims to investigate their unknown properties by synthesizing a range of materials in the MXY_3 family as well as $CrPS_4$ in single crystal form. After confirming that the crystal quality matches (or exceeds) the quality of samples from the literature reports, we will focus on a study of the thermal conductivity of these single crystal materials. Learning and understanding the properties at a bulk level will provide valuable background for future research into the few-layer form of these 2D materials, where most applications are being explored.

1.2 Materials Background

1.2.1 Crystal Structure

Metal phosphorus chalcogenides were first synthesized by Klingenberg et al. in 1965 [12] and 1973 [13] and Diehl in 1977 [14], with the metal germanium and silicon trichalcogenides discovered later by Carteaux 1995 [15] and Ouvrard 1988 [16]. The MXY_3 materials have an interesting structural architecture, where the transition metal atoms are arranged in a honeycomb pattern, and the P, Si, or Ge form dimers that connect through the center of the transition metal hexagons, shown in Figure 1-1. The chemical formula for these materials is sometimes referenced as $M_2X_2Y_6$, due to this dimer bonding.

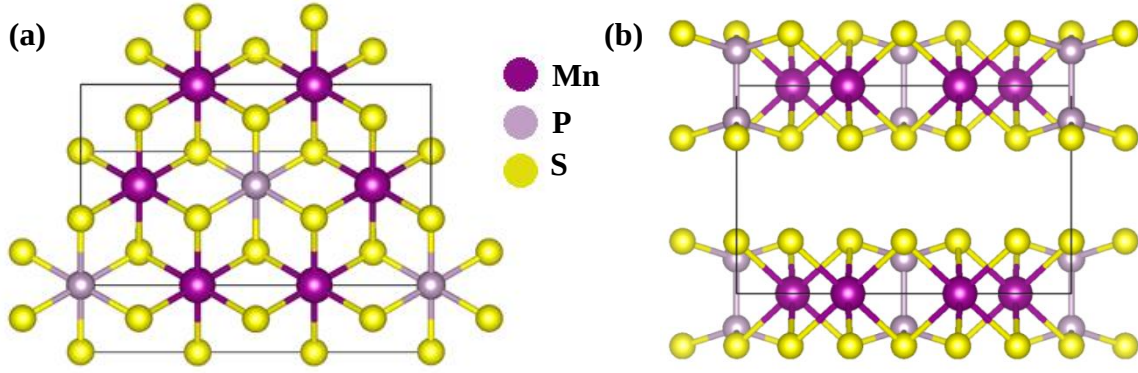


Figure 1-1: Example MnPS₃ crystal structure, along (a) the c-axis of MnPS₃ structure and (b) parallel to the ab-plane showing the van der Waals gap between layers.

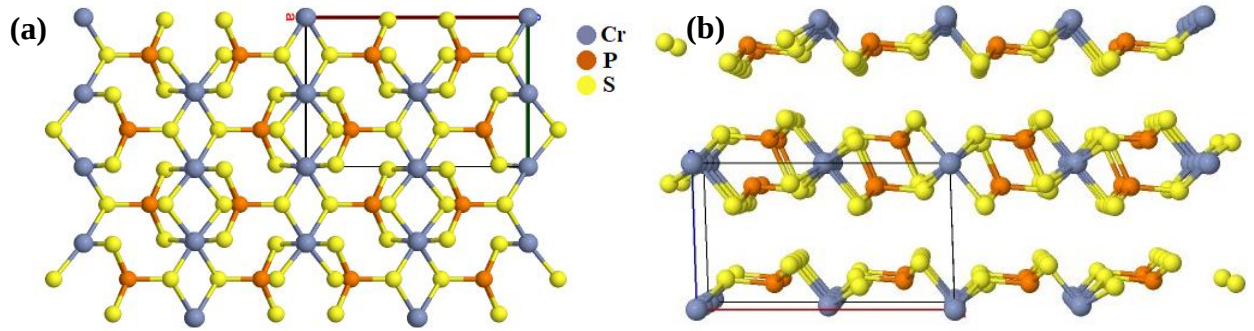


Figure 1-2: CrPS₄ crystal structure, (a) parallel to the ab-plane, showing the rectangular grid of Cr atoms, and (b) perpendicular to the ab-plane.

Table 1-1: Crystal structure and space groups for magnetic semiconducting compounds [17].

Material	Crystal System	Space Group
MnPS ₃	monoclinic	12 (C 2/m)
MnPSe ₃	trigonal	148 ($R\bar{3}$)
FePS ₃	monoclinic	12 (C 2/m)
FePSe ₃	trigonal	148 ($R\bar{3}$)
NiPS ₃	monoclinic	12 (C 2/m)
CrPS ₄	monoclinic	5 (C2)
CrSiTe ₃	trigonal	148 ($R\bar{3}$)
CrGeTe ₃	trigonal	148 ($R\bar{3}$)

The structure of CrPS_4 is a little different from the MXY_3 configuration: the magnetic atoms are arranged in a rectangular grid, while the phosphorus atoms are not aligned above each other or bonded together but instead situated diagonally as shown in Figure 1-2. Sulfur atoms still form the outer layer of the planes, like in the previous structure, with van der Waals forces holding the layers together.

While all the MXY_3 materials have a similar hexagonal structure, there are some small differences in symmetry caused by the different compositions that produces a split into two different space groups and crystal systems, as shown in Table 1-1. Phosphorus-based compounds tend towards the monoclinic structure, while the other compositions form in the trigonal structure. CrPS_4 is in its own space group but is also included in the monoclinic crystal system exhibited by the metal triphosphates.

1.2.2 Magnetic Structure

Although the structures of these materials are similar, there are differences in their magnetic properties. Most of the compounds listed in Table 1-1 are antiferromagnetic, except for the chromium non-phosphorus-based compounds. In addition, the easy-axis orientation of the magnetic moments differs between materials, regardless of the magnetic ground state. Below the magnetic ordering temperature, the materials' magnetic moments are aligned either parallel or perpendicular to the c-axis, as shown in Table 1-2. Among the compounds there are also differences in the organization of the magnetic moments throughout the structure: ferromagnetic, Néel-AFM, stripy-AFM, or zigzag-AFM. A schematic of the different orderings is shown in Figure 1-3, and the individual ordering configuration for each compound is listed in Table 1-2.

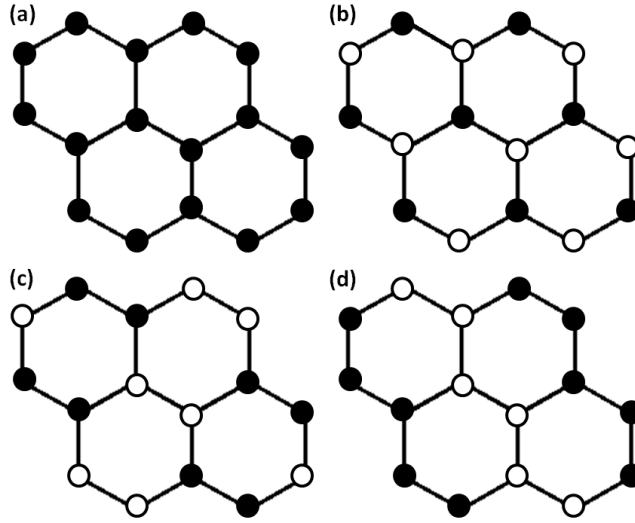


Figure 1-3: Magnetic ordering of transition metals in the ab-plane. Filled and empty circles indicate opposite directions of magnetic moment on transition metal sites: (a) FM, (b) Néel AFM, (c) stripy AFM, (d) zigzag AFM.

Table 1-2: Some magnetic properties of the layered compounds studied in this work.

Material	Magnetic ordering	Moment orientation	Literature ordering temperatures	Transition metal atomic number	References
CrPS ₄	AFM	c-axis	36 K	24	[11], [18]
CrGeTe ₃	FM	c-axis	61-67.3 K	24	[11], [19]
CrSiTe ₃	FM	c-axis	33K	24	[20]
MnPS ₃	Néel AFM	c-axis	78-82 K	25	[21]–[23]
MnPSe ₃	Néel AFM	ab-plane	74 K	25	[21]
FePS ₃	zigzag-AFM (AFM interlayer)	c-axis	111-123 K	26	[22]–[26]
FePSe ₃	zigzag-AFM (FM interlayer)	c-axis	106-123 K	26	[22], [27], [28]
NiPS ₃	zigzag-AFM (FM interlayer)	ab-plane	151-155 K	28	[25], [29]

Also depending on the compound, the magnetic ordering for the honeycomb AFM compounds is either reversed in alternating planes, causing antiferromagnetic interactions between layers, or duplicated between planes, causing ferromagnetic interactions [26]. Having a slightly different structure, CrPS₄ organizes a little differently below the magnetic ordering transition temperature: the in-plane magnetic moments are organized with AFM interactions only, while the interactions are FM in the out-of-plane direction [11]. Although there are many variations in the magnetism of these materials, there is one unifying factor: as the atomic number of the transition metal atom increases, so does the magnetic ordering temperature, regardless of the ordering type [10]. The magnetic ordering, moment orientation and transition temperatures are shown in Table 1-2.

While the magnetic properties of these materials are well known, a complete understanding of the behavior of MXY₃-type materials in possible application settings requires a comprehensive study of other physical properties. With thermal conductivity unexplored at this point, the scope of this work endeavors to greatly expand this area of knowledge. The subsequent chapter describes the details of crystal synthesis and characterization for the materials of interest, followed by the thermal conductivity setup and details, and finally the experimental results and analysis.

Chapter 2. Crystal Growth and Characterization

In the following chapter are the growth details of all the materials studied in this thesis, as well as the results from their characterization to verify appropriate composition and structure.

2.1 Material Synthesis

There are several different crystal growth methods currently in use for synthesizing single crystal magnetic layered materials, including many variations of vapor transport [30], flux growth [31]–[33], and the Bridgman technique [34]. For the present work, vapor transport and flux growth methods were used to grow single crystals of the van der Waals magnets MnPS_3 , MnPSe_3 , FePS_3 , FePSe_3 , NiPS_3 , CrPS_4 , CrSiTe_3 , and CrGeTe_3 . The following sections provide details of these growth techniques, followed by the specifications required for each material's crystal growth.

2.1.1 Vapor Transport Crystal Growth

While there are several different vapor transport techniques in existence, they all grow single crystals through the same general method: a starting material, known as the charge, is transported across a tube or ampoule through a temperature gradient with the help of a volatile gas from either a constituent component of the material or a foreign element, known as the transport agent. As the transported material reaches the opposite end of the tube, it is deposited, nucleating and growing single crystals, as shown in Figure 2.1.

The charge material, shown as $A_{(s,poly)}$, is either the constituent elements in stoichiometric ratio or the desired material compound, usually in powder form to accelerate transport and growth due to higher surface area. Typically, the transport reaction is endothermic, which places the charge at the highest temperature (T_2), while the growth end is lower (T_1). If it were exothermic the temperatures would be reversed. If necessary, a volatile compound is added as a

transport agent, which can be one of many different materials: S, Se, I₂, Cl₂, Br₂, TeCl₄ [35]. When the tube is heated, the transport agent or volatile portions of the material, labeled X_(g), react with the remaining materials to form a vapor which fills the tube. As the vapor expands, it travels across the temperature gradient until it reaches the opposite end, where the change in temperature induces the reverse reaction, depositing the material to nucleate and grow single crystals. Once the volatile gases are released, they diffuse back to the charge material and continue the transport process.

The various vapor transport techniques are separated by their slight differences in transport method. When a transport agent is required, the growth process is categorized as chemical vapor transport (CVT), but reactions that are self-transporting can do so by sublimation, decomposition sublimation, or auto-transport [30]. With this variety of growth methods, many different van der Waals magnets can be grown as single crystals with vapor transport. Because these magnetic materials are composed of more volatile and readily evaporated elements like chalcogens or halogens [26], their crystals are easier to grow using vapor transport. For this reason, the following phosphorus and chalcogen containing materials were grown with vapor transport, specifically CVT for MnPS₃, MnPSe₃, FePS₃, FePSe₃, NiPS₃, and auto-transport for CrPS₄.

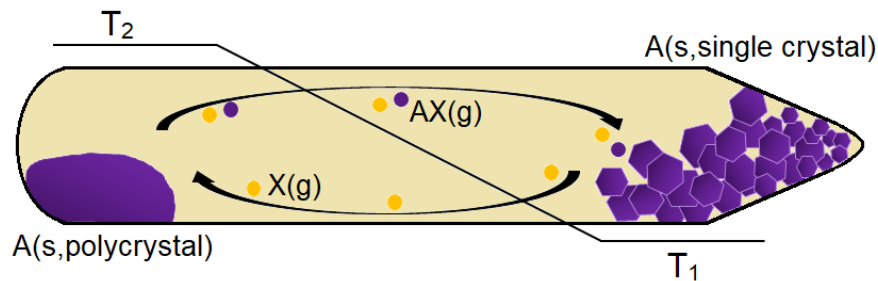


Figure 2-1: Chemical vapor transport process for growing single crystals from a solid ($A_{s,poly}$), using a transport agent (X_g), while under a temperature gradient $T_2 > T_1$. Figure based on [30].

2.1.1.1 Single Crystal Growth of MnPS₃, MnPSe₃, FePS₃, FePSe₃, NiPS₃

For the MPX₃ compounds grown by CVT, the chemical compound first needs to be prepared in powder form. To do this, stoichiometric amounts of the required elements, details shown in Table 2-1, were ground together in an agate mortar under inert atmosphere to avoid oxidation and moisture effects. The mixed powder was then transferred to a pellet press before removing from controlled atmosphere, to minimize air contact with the loose powder. After the mixture was pressed into a pellet, the pellet was placed inside a fused-quartz tube and then connected to a vacuum setup.

The tube was then vacuumed out and flushed with argon three times to remove moisture and air and held at 10⁻² Torr before sealing with a hydrogen-oxygen torch to create a vacuum-sealed ampoule. Wet paper towels were wrapped around the tube end with the pellet, to reduce evaporation of the more volatile elements during tube sealing. The sealed tubes were placed in box furnaces for one week, at 730°C for MnPS₃, MnPSe₃, FePS₃, and FePSe₃, and at 700°C for NiPS₃.

Table 2-1: Source materials for MPX₃ crystals.

Element	Form	Producer	Purity
Manganese	powder	Alfa Aesar	99.95%
Iron	powder	Puratronic	99.998%
Chromium	powder	Alfa Aesar	99.99%
Nickel	powder	Puratronic	99.996%
Phosphorus	pieces	Alfa Aesar	99.999+%
Selenium	powder	Alfa Aesar	99.999%
Sulfur	powder/chunks	Puratronic	99.9995%

After annealing, the reacted compound had expanded into the tube as sparkling polycrystalline powder and small crystals. The tubes were then cut open to retrieve the material, and a sample of each verified for phase purity by powder X-ray diffraction (XRD) on a Bruker D2 Phaser.

For the CVT crystal growth process, 1-2 grams of the annealed powder were placed in the bottom of another 19 mm inner diameter tube along with 10-15 mg/cc of dehydrated iodine crystals. The tube was lined with paper prior to loading the materials in order to keep the tube surface clean, and then carefully removed. After loading, the tube was connected to the vacuum station and sealed at a predetermined length depending on the desired temperature gradient. The required tube length to achieve the desired temperature gradient for the single-zone furnaces was determined previously with a thermocouple, by measuring the temperature gradient from the center to the outer ends of the furnace at different set temperatures. The sealed ampoule was placed in the tube furnace with the charge end in the center of the furnace and the growth end towards the cooler opening. Heating rates were kept at 1°C/hr until reaching growth temperature. Growth details are shown in Table 2-2.

Table 2-2: CVT growth details for MPX₃ compounds.

Material	Tube Length	Temperature Gradient	Growth Time
MnPS ₃	13 cm	700°C - 570°C	< 1 week
MnPSe ₃	13 cm	650°C - 525°C	< 1 week
FePS ₃	10 cm	700°C - 600°C	< 1 week
FePSe ₃	10 cm	670°C - 570°C	1-2 weeks
NiPS ₃	10 cm	700°C - 600°C	1-2 weeks

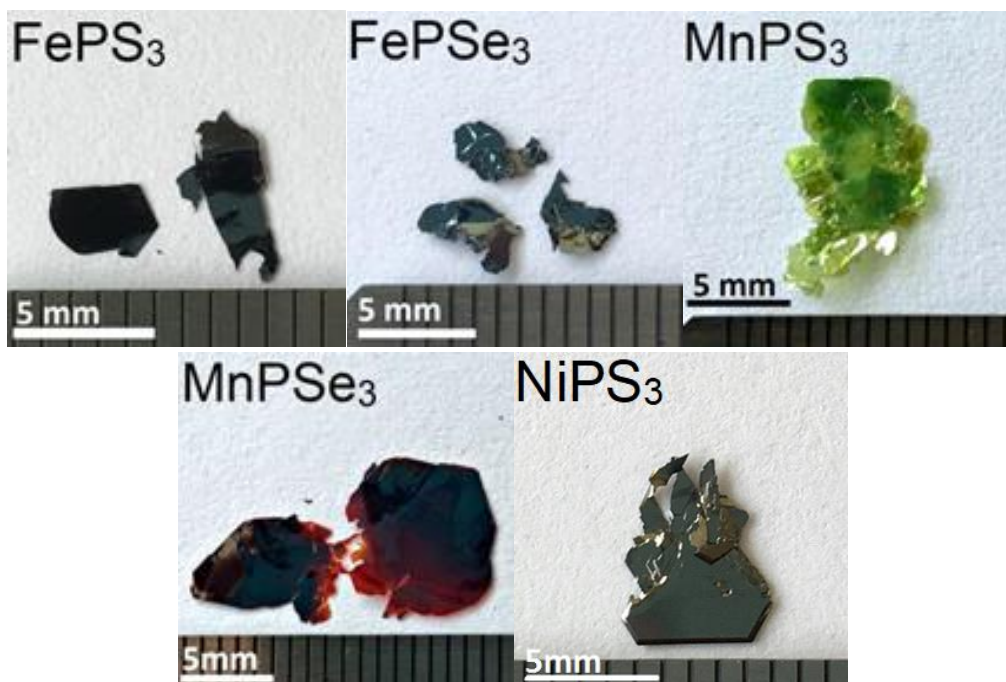


Figure 2-2: Single crystals of MPX_3 materials grown by CVT.

Tubes were reversed in the temperature gradient for the first day if too many tiny crystals nucleated and grew in the initial trials. This allowed any tiny particles on the sides of the tube to transport back to the charge, decreasing the amount of nucleation sites and crystals, but increasing the final crystal size. Images of some single crystals are displayed in Figure 2-2.

2.1.1.2 Single Crystal Growth of $CrPS_4$

The final material synthesized by vapor transport, $CrPS_4$, was grown using auto-transport, based on the method described in reference [11]. Stoichiometric amounts of the elements were weighed out of the source materials are shown in Table 2-3. Five atomic percent additional sulfur was included to ensure appropriate stoichiometry, as free sulfur tends to remain on the tube walls after a growth. The material was placed in a 19 mm inner diameter tube, then vacuum sealed as described earlier. The tube was sealed to a 13 cm length to provide a 700°C to 570°C temperature gradient during growth. After sealing, the tube was placed in a single-zone tube furnace with the

Table 2-3: CrPS₄ crystal growth source materials.

Element	Form	Producer	Purity
Chromium	powder	Alfa Aesar	99.996%
Phosphorus	chunks	Alfa Aesar	99.999+%
Sulfur	chunks	Puratronic	99.9995%

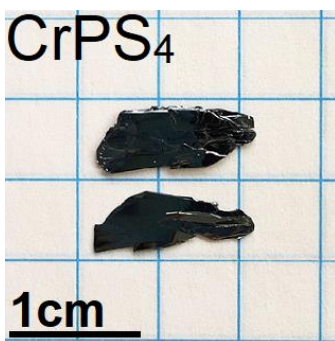


Figure 2-3: Single crystals of CrPS₄ grown by auto-transport.

charge at the hottest part in the center, and the growth end towards the opening. Heating rate was kept at 1°C/hr until reaching hold temperature, and then held there for crystal growth for 1-2 weeks. As in the CVT crystal growths, the tube direction was reversed in the temperature gradient if too many tiny crystals nucleated and grew in the initial growth attempts.

2.1.2 Flux Crystal Growth

Flux crystal growth produces single crystals by first heating the constituent elements or compounds together with a lower melting point material, known as the flux. Usually contained in a crucible or tube, this mixture is held at a high temperature, called the solution temperature, to allow it to become homogeneous. The solution is then cooled at a slow and steady rate until the dissolved material in the flux is forced into an oversaturated state, causing crystals of the compound to begin nucleation and growth on the container walls. Once the crystals have been allowed to grow to the desired size with further cooling, the flux growth is either allowed to cool

quickly to room temperature to halt the growth of other compounds, or the flux is decanted from the crystals while molten.

A variation of flux growth, self-flux, uses elements from the desired compound as the flux material. Additional amounts of one or more of the constituent elements is added into the crucible as the flux material, along with the stoichiometric amounts of the elements for the compound. This method works well for growing large single crystals of both CrSiTe_3 and CrGeTe_3 , using extra Si & Te and Ge & Te as the flux, respectively, and was therefore used to grow single crystals for the measurements carried out in this thesis.

2.1.2.1 Single Crystal Growth of CrSiTe_3 and CrGeTe_3

The materials were synthesized from a 1:2:9 ratio of the elements for CrSiTe_3 , and a 1:3:18 ratio for CrGeTe_3 . Pieces or chunks of the elements shown in Table 2-4 were measured out in the desired ratio and placed in an alumina Canfield crucible set. This crucible set consists of a bottom half where the flux and materials are placed, a strainer disk, and a ‘catch’ crucible. i.e. an inverted crucible that covers the bottom half. The crucible set was placed in a fused-quartz tube with quartz wool as a cushion, and then vacuum sealed in the same manner described for vapor transport growth. After sealing, the vacuum ampoule containing the crucibles was placed upright in a larger crucible to keep the material inside the bottom crucible during heating and growth, and then set in a box furnace. The heating profile followed for the solution and growth process is listed in Table 2-5.

A final step to remove the flux from the grown crystals required removing the ampoule from the furnace with the flux still molten, inverting the tube to allow the flux to flow into the catch crucible, and quickly placing into a centrifuge to spin off the remainder of the flux. Once cooled, the tube and crucible were broken open and the single crystals mechanically separated

Table 2-4: CrSiTe₃ and CrGeTe₃ flux growth source materials.

Element	Form	Producer*	Purity**
Cr	pieces	Alfa Aesar	99.996%
Si	pieces	Alfa Aesar	99.9999%
Ge	pieces	Puratronic	99.9999+%
Te	shot	Alfa Aesar	99.9999%

Table 2-5: CrSiTe₃ and CrGeTe₃ self-flux growth details.

Compound	Heating rate	Dwell Temperature	Cooling Rate	Centrifuge Temperature	References
CrSiTe ₃	200°C/hr	16 hrs @ 1150°C	3°C/hr	Centrifuge @ 700°C	[20]
CrGeTe ₃	200°C/hr	1 hr @ 1000°C	6.11°C/hr	Centrifuge @ 500°C	[36]

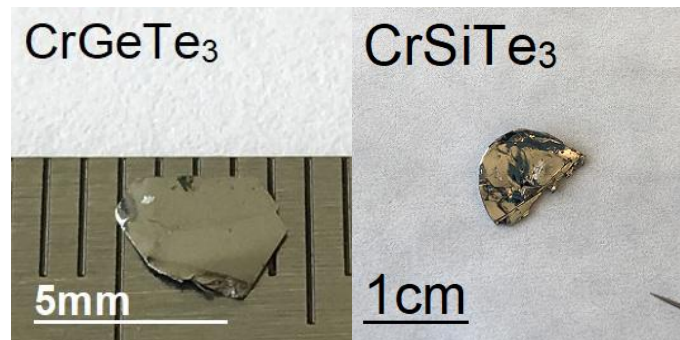


Figure 2-4: Flux grown single crystal samples of CrGeTe₃ and CrSiTe₃.

from the remaining flux. To ensure the correct structure and phase were obtained, some of the crystals were ground to a powder and examined with powder XRD. This is covered later in the characterization section of the chapter. Images of the flux grown crystals for each material are shown in Figure 2-4.

2.2 Characterization

Single crystals grown in the previous sections were verified for the appropriate structure, stoichiometry, and magnetic properties through powder X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), and magnetization measurements, respectively.

2.2.1 Powder X-ray Diffraction

To ensure the desired crystal structure was present in the synthesized single crystals, a few crystals of each compound were ground to a fine powder and characterized using an Empyrean powder diffractometer (Malvern Panalytical). Comparisons between experimental patterns and known patterns accessed from the FIZ Karlsruhe Inorganic Crystal Structure Database (ICSD) database showed good agreement, with no impurity peaks present. The XRD powder patterns are shown in Figures 2-5 to 2-12, with peaks matched to literature sources.

2.2.2 Energy Dispersive X-ray Spectroscopy

Stoichiometry was verified for single crystal samples of each material, through energy dispersive X-ray spectroscopy (EDX) on a Zeiss EVO scanning electron microscope (SEM). Spectroscopy data were taken in a distribution of 8 points across the sample and then averaged to determine an overall composition percentage for each material, as shown in Figure 2-5. The averaged spectroscopy data are shown in Table 2-7. Measured compositions agree well with the appropriate stoichiometry for each material.

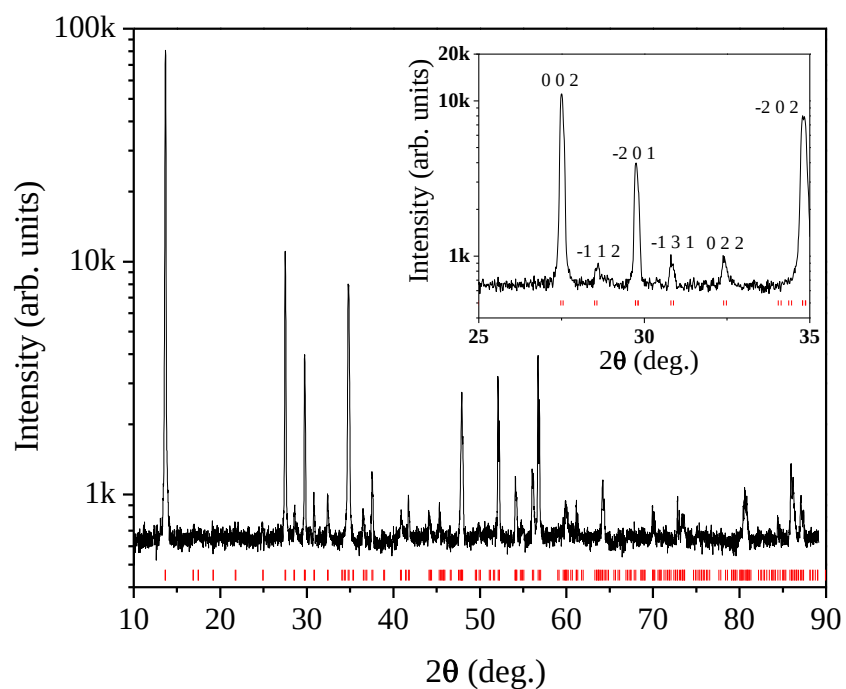


Figure 2-5: Experimental powder XRD pattern for MnPS_3 in black, with red marks indicating peak positions from a known MnPS_3 pattern [37]. Inset shown for better clarity due to density of peaks.

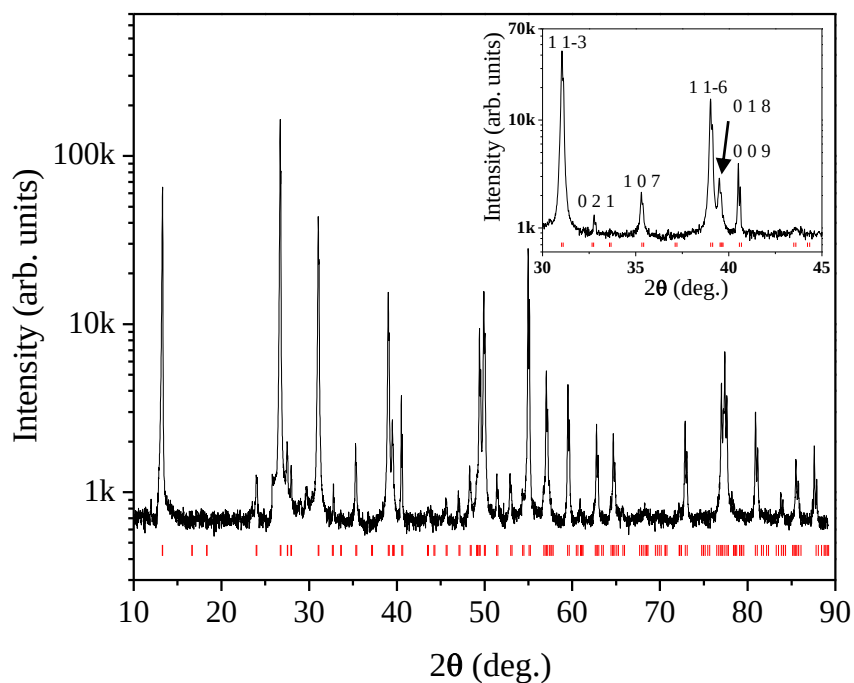


Figure 2-6: Experimental powder XRD pattern for MnPSe_3 in black, with red marks indicating peak positions from a known MnPSe_3 pattern [38]. Inset shown for better clarity due to density of peaks.

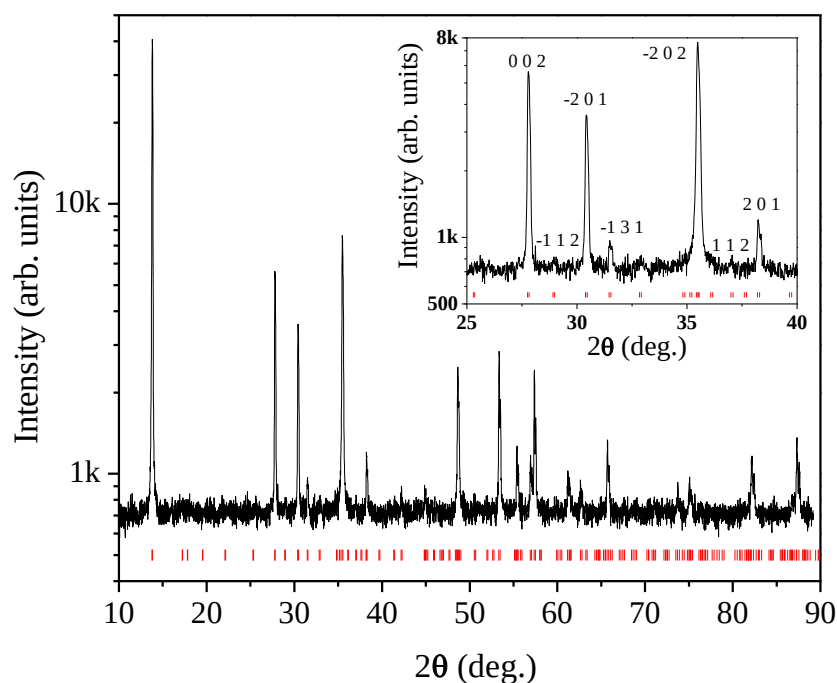


Figure 2-7: Experimental powder XRD pattern for FePS_3 in black, with red marks indicating peak positions from a known FePS_3 pattern [37]. Inset shown for better clarity due to density of peaks.

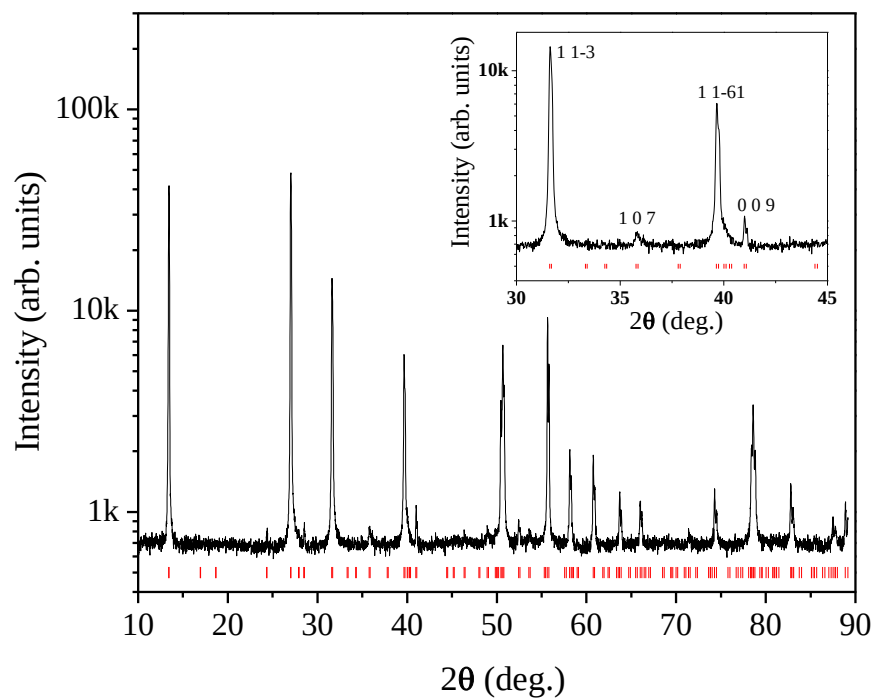


Figure 2-8: Experimental powder XRD pattern for FePSe_3 in black, with red marks indicating peak positions from a known FePSe_3 pattern [38]. Inset shown for better clarity due to density of peaks.

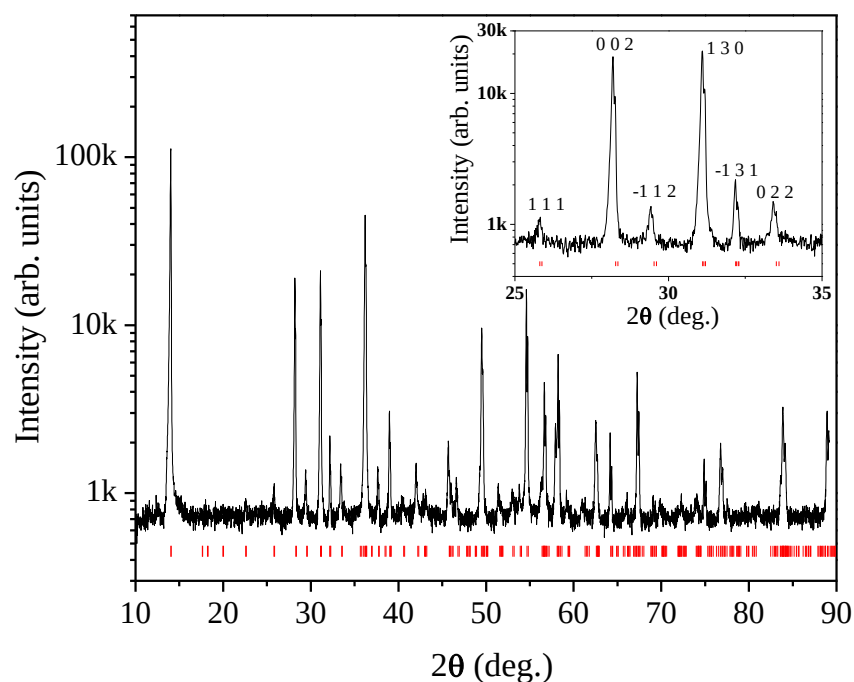


Figure 2-9: Experimental powder XRD pattern for NiPS_3 in black, with red marks indicating peak positions from a known NiPS_3 pattern [29]. Inset shown for better clarity due to density of peaks.

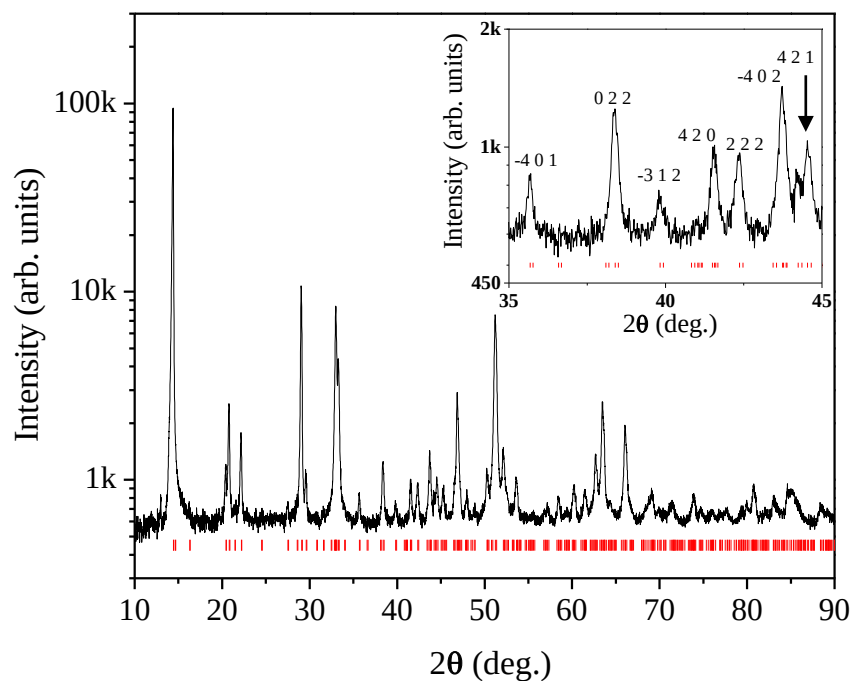


Figure 2-10: Experimental powder XRD pattern for CrPS_4 in black, with red marks indicating peak positions from a known CrPS_4 pattern [14]. Inset shown for better clarity due to density of peaks.

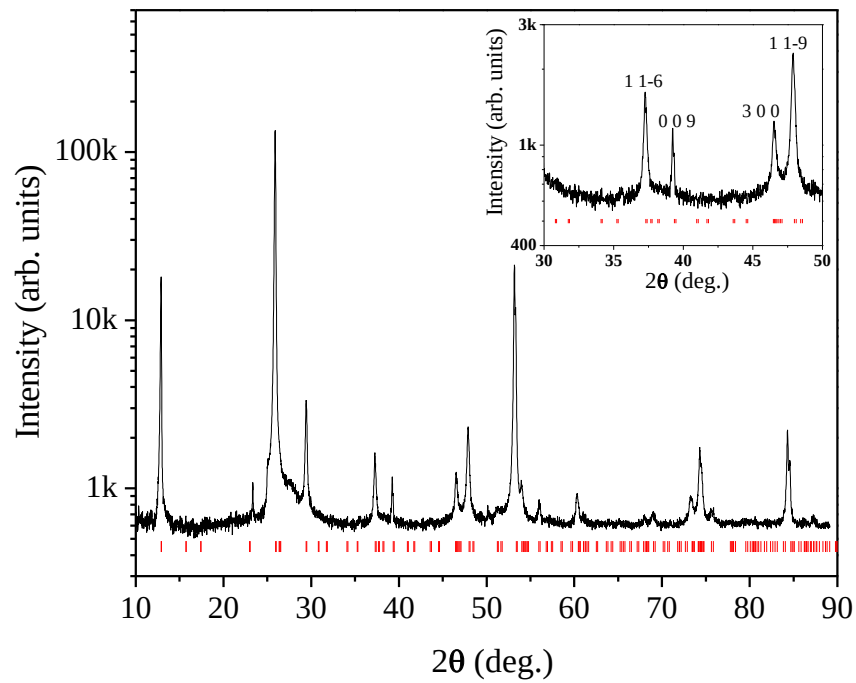


Figure 2-11: Experimental powder XRD pattern for CrSiTe_3 in black, with red marks indicating peak positions from a known CrSiTe_3 pattern [39]. Inset shown for better clarity due to density of peaks.

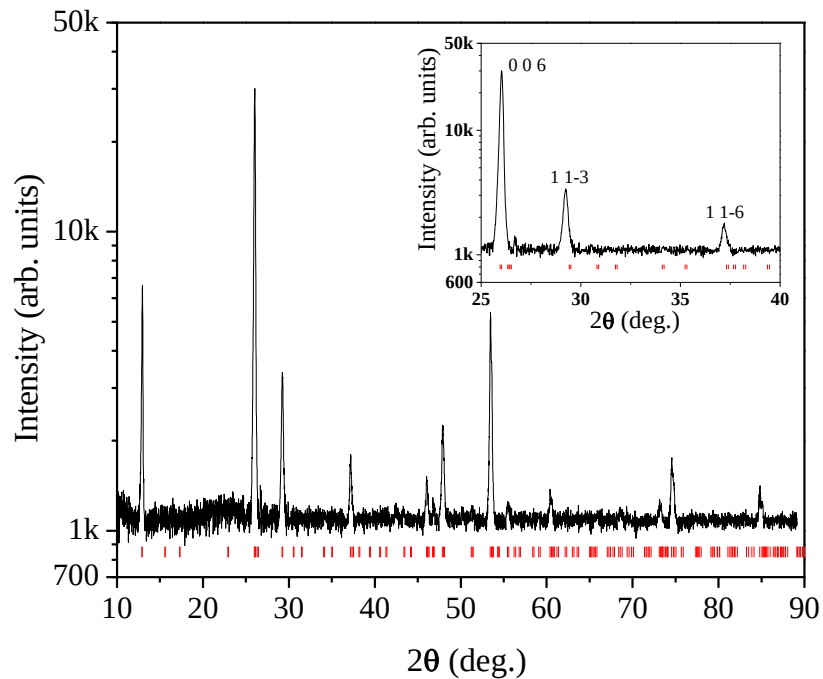


Figure 2-12: Experimental powder XRD pattern for CrGeTe_3 in black, with red marks indicating peak positions from a known CrGeTe_3 pattern [15]. Inset shown for better clarity due to density of peaks.

Table 2-6: Space group and crystal structure for all studied materials.

Material	Crystal System	Space Group
MnPS ₃	monoclinic	12 (C 2/m)
MnPSe ₃	trigonal	148 ($R\bar{3}$)
FePS ₃	monoclinic	12 (C 2/m)
FePSe ₃	trigonal	148 ($R\bar{3}$)
NiPS ₃	monoclinic	12 (C 2/m)
CrPS ₄	monoclinic	5 (C2)
CrSiTe ₃	trigonal	148 ($R\bar{3}$)
CrGeTe ₃	trigonal	148 ($R\bar{3}$)

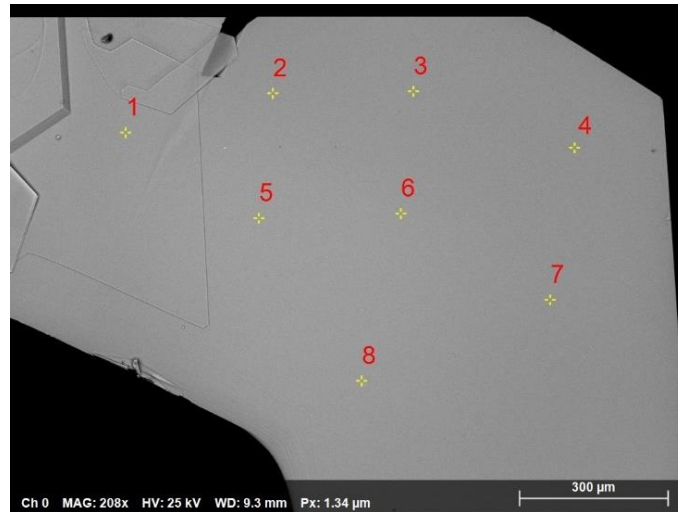


Figure 2-13: Single crystal SEM image of NiPS₃ with EDX analysis points.

Table 2-7: EDX molar ratio results for single crystal samples.

Material	Element 1	Element 2	Element 3
MnPS ₃	1.00(4)	0.99(3)	2.98(9)
MnPSe ₃	1.00(1)	0.96(1)	3.07(1)
FePS ₃	1.00(3)	0.98(2)	2.93(1)
FePSe ₃	1.00(1)	1.01(1)	2.95(1)
NiPS ₃	1.00(3)	0.98(3)	2.98(1)
CrPS ₄	1.00(2)	1.04(1)	4.107(5)
CrGeTe ₃	1.00(3)	0.96(3)	2.97(3)
CrSiTe ₃	1.00(1)	0.82(1)	2.96(1)

2.2.3 Magnetization

Magnetic characterization on single crystals of each material was performed with a SQUID magnetometer (MPMS, Quantum Design), and compared with known results in the literature to verify the magnetic properties. Due to the plate-like structure of the crystals, two moment vs. field measurements were taken for single crystal samples of each material: one measurement with the field parallel to the ab-plane of the crystal, and one with the field perpendicular to the crystal plane, along the c-axis.

The respective moment vs. temperature curves for each direction are shown in Figures 2-13 to 2-21. Table 2-8 contains the magnetic ordering temperatures from the susceptibility measurements, determined by differentiating the susceptibility to find the largest change in slope for each measurement. Magnetic ordering temperatures from the literature are shown in the table for comparison, along with the easy-axis ordering direction for each material. The experimental transition temperatures measured agree well with the temperatures reported in literature.

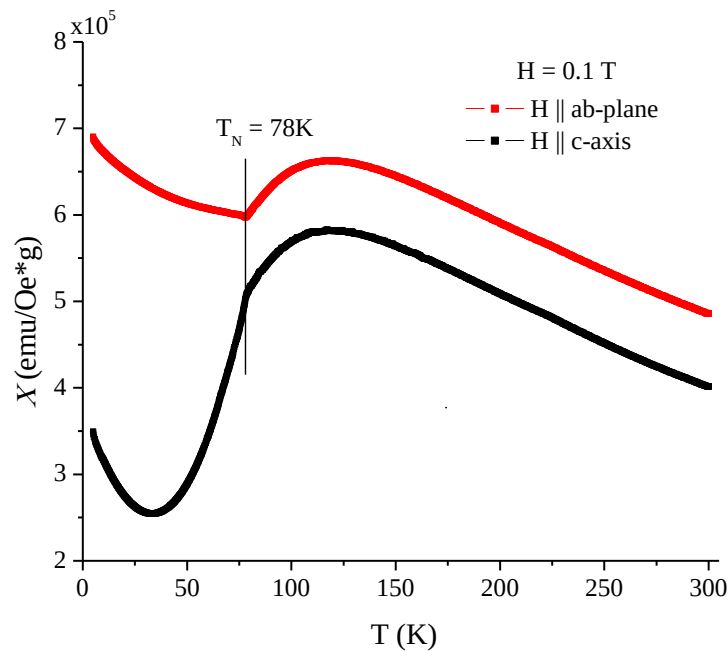


Figure 2-14: Magnetic susceptibility of MnPS₃ vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T. Easy axis || c-axis, Table 2-8.

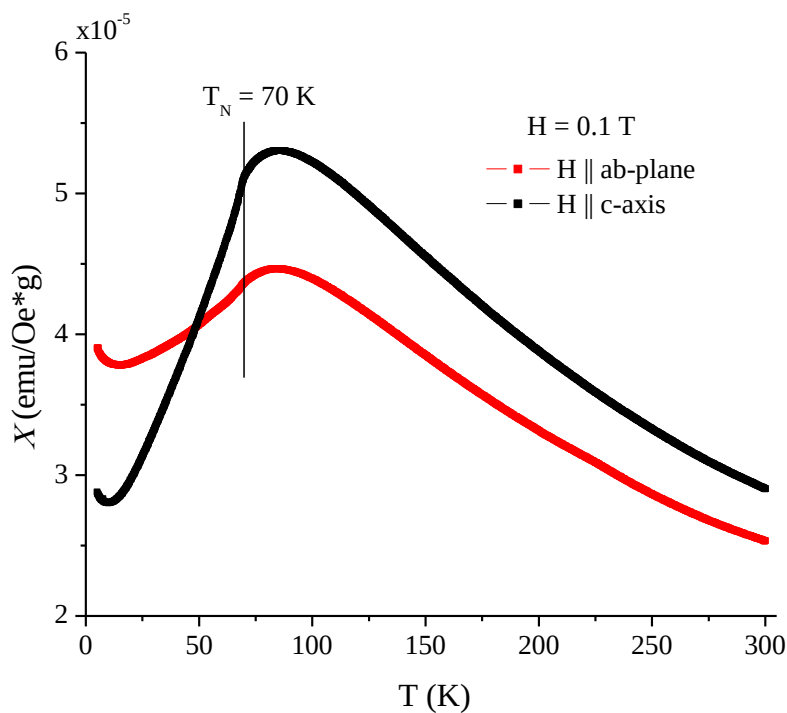


Figure 2-15: Magnetic susceptibility of MnPSe₃ vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T. Easy axis || ab-plane, Table 2-8.

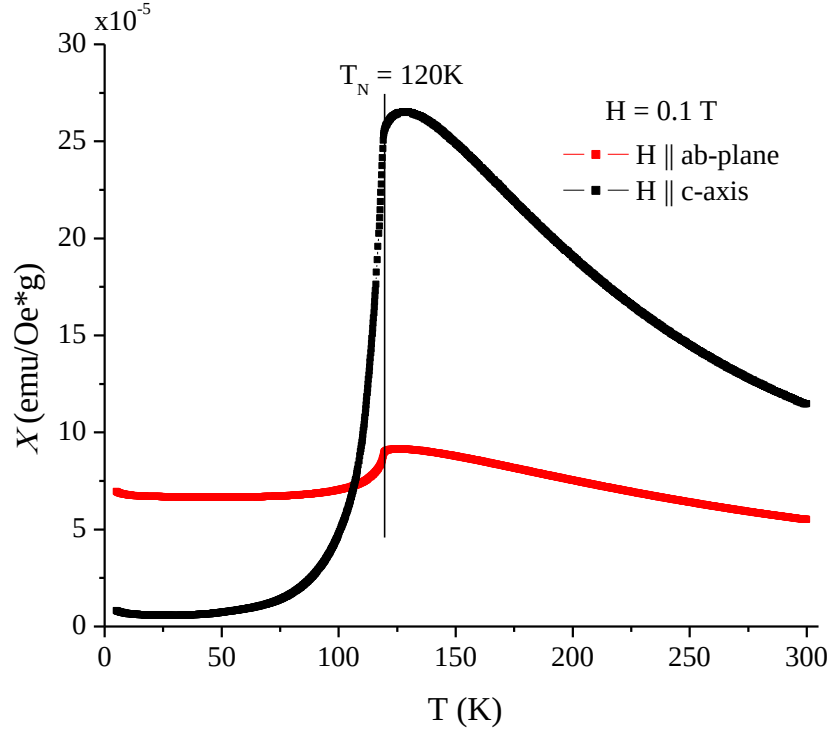


Figure 2-16: Magnetic susceptibility of FePS_3 vs. temperature, measured parallel to both the ab -plane and c -axis. Applied field was 0.1 T. Easy axis $\parallel c$ -axis, Table 2-8.

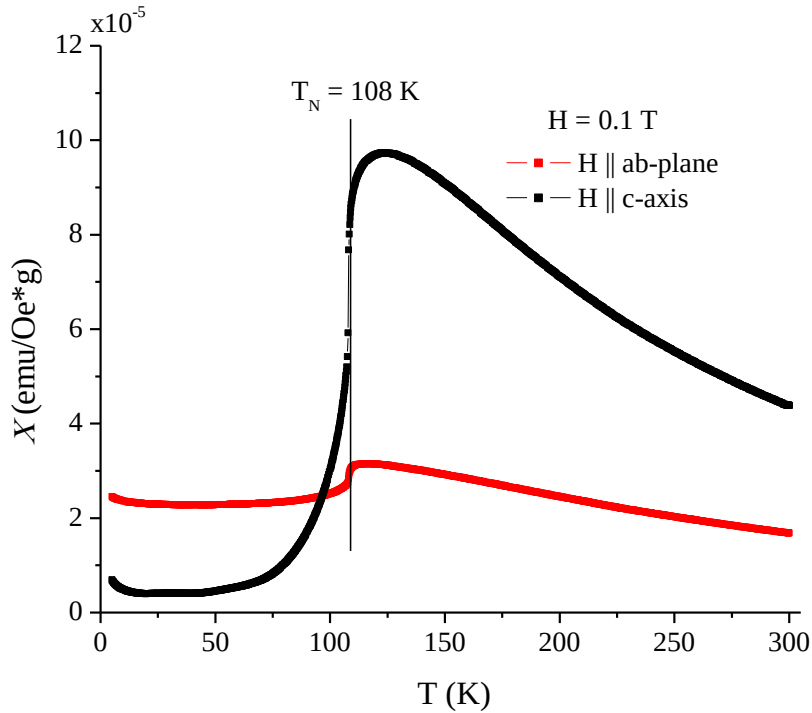


Figure 2-17: Magnetic susceptibility of FePSe_3 vs. temperature, measured parallel to both the ab -plane and c -axis. Applied field was 0.1 T. Easy axis $\parallel c$ -axis, Table 2-8.

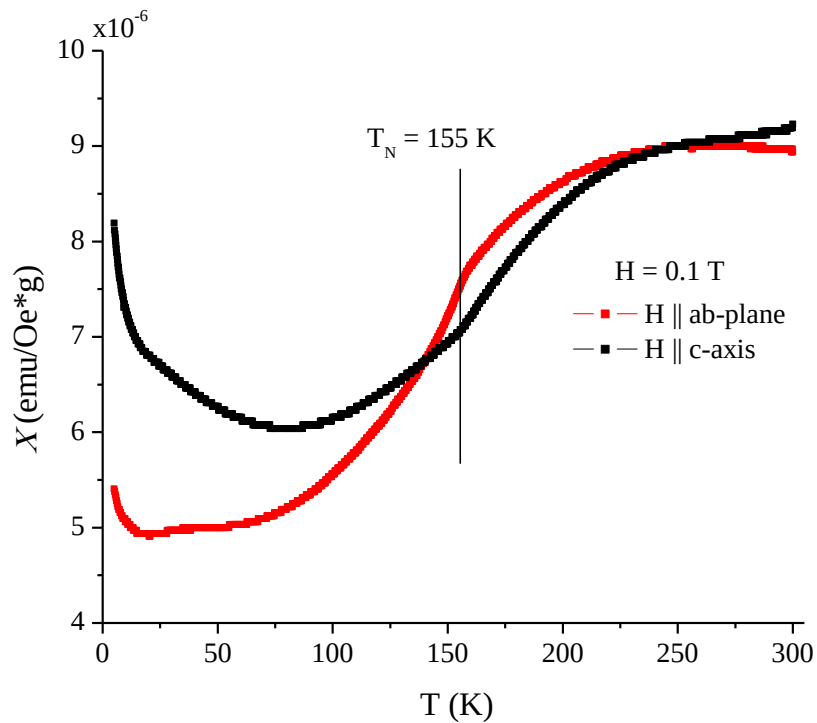


Figure 2-18: Magnetic susceptibility of NiPS_3 vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T. Easy axis $\parallel$ c-axis, Table 2-8.

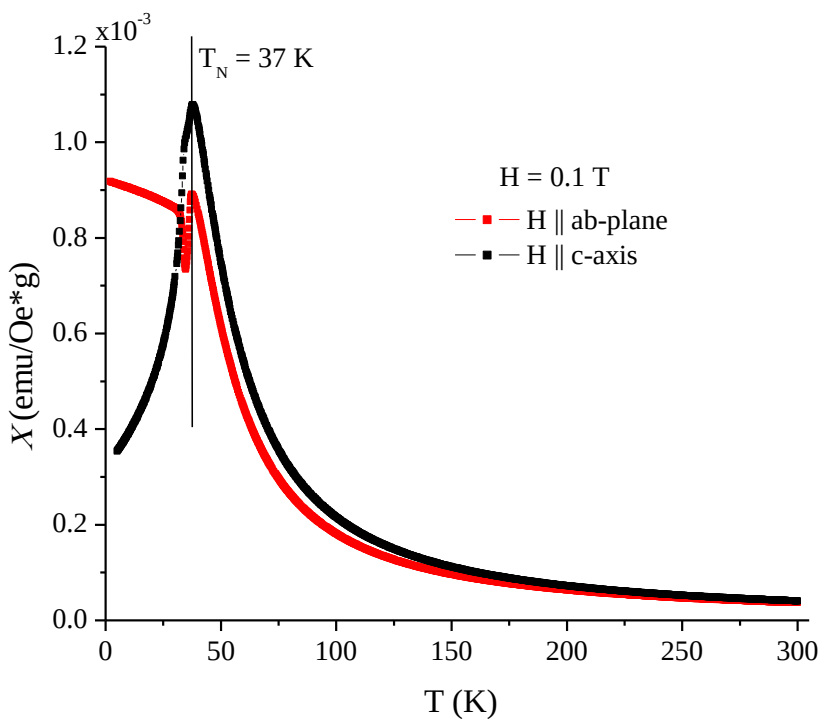


Figure 2-19: Magnetic susceptibility of CrPS_4 vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T.

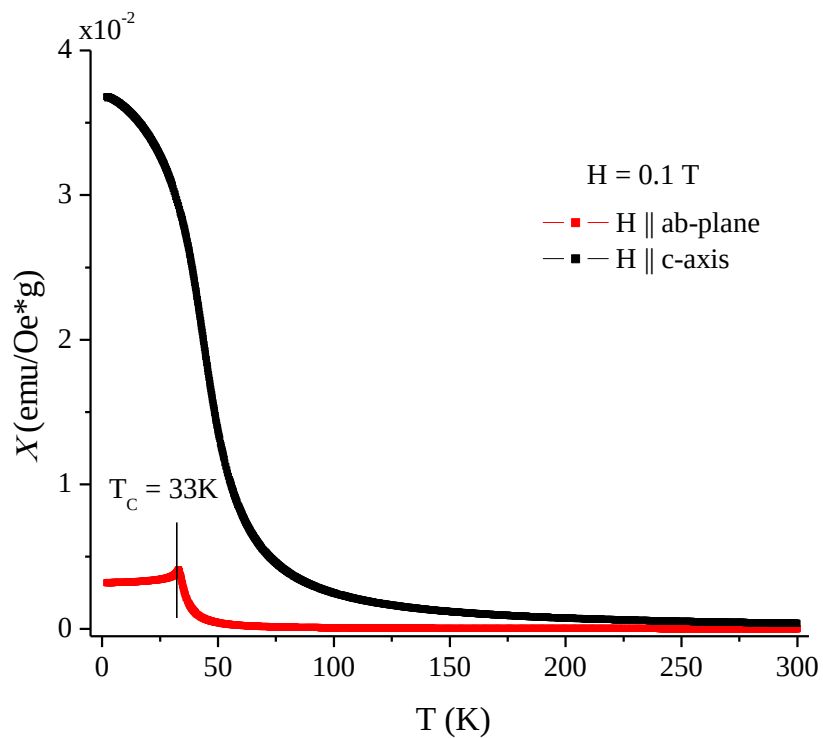


Figure 2-20: Magnetic susceptibility of CrSiTe_3 vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T.

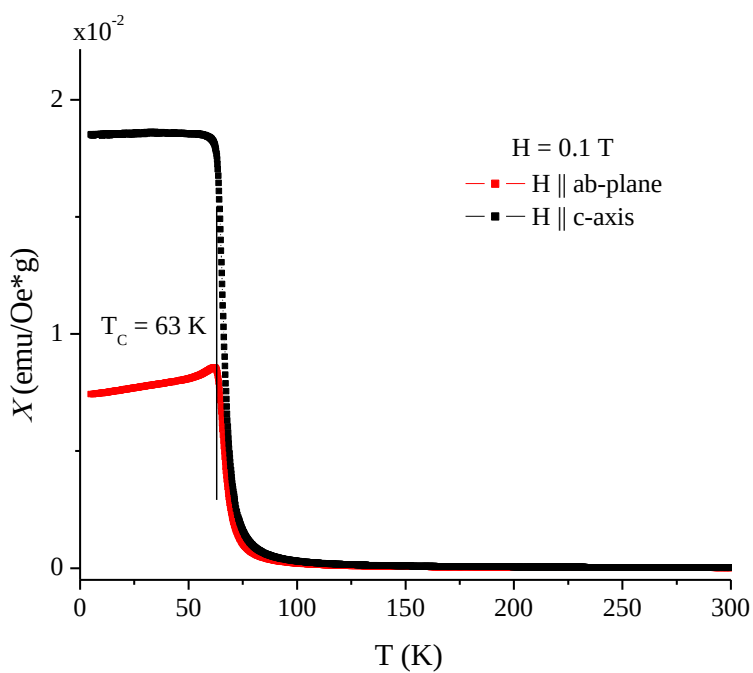


Figure 2-21: Magnetic susceptibility of CrGeTe_3 vs. temperature, measured parallel to both the ab-plane and c-axis. Applied field was 0.1 T.

Table 2-8: Magnetic ordering, easy-axis orientation and ordering transition temperatures of experimental vs. literature values.

Material	Magnetic ordering	Moment orientation	Experimental	Literature	References
MnPS ₃	Néel AFM	c-axis	T _N = 78 K	78-82 K	[21]–[23]
MnPSe ₃	Néel AFM	ab-plane	T _N = 70 K	74 K	[21]
FePS ₃	zigzag-AFM (AFM interlayer)	c-axis	T _N = 120 K	111-123 K	[22]–[26]
FePSe ₃	zigzag-AFM (FM interlayer)	c-axis	T _N = 108 K	106-123 K	[22], [27], [28]
NiPS ₃	zigzag-AFM (FM interlayer)	ab-plane	T _N = 155 K	151-155 K	[25], [29]
CrPS ₄	AFM	c-axis	T _N = 37 K	36 K	[11], [18]
CrGeTe ₃	FM	c-axis	T _C = 63 K	61-67.3 K	[15], [19]
CrSiTe ₃	FM	c-axis	T _C = 33 K	33K	[20]

Chapter 3. Thermal Conductivity Measurements

The layered magnetic materials in this project were synthesized in order to further explore and analyze their basic properties and behavior, which have not yet been fully characterized. As part of this work, we have focused on obtaining thermal conductivity data for these layered materials. While some data exists for materials such as CrGeTe_3 at high temperature or CrSiTe_3 below room temperature [20], [40], the remaining materials have no reported thermal conductivity behavior in the literature as yet. To further the known scope of these materials' characterization, thermal conductivity was measured vs. temperature for single crystals of each material. The following chapter describes the experimental setup and methods used to perform these measurements.

3.1 Thermal Conductivity Measurement Methods

Various thermal conductivity measurement techniques exist for bulk materials, including multiple steady-state methods. Steady-state refers to the heat flow through the sample during the measurement, which is kept at a constant value. Four different methods use this form of heat transfer to measure thermal conductivity: the absolute technique, comparative technique, radial heat flow method, and parallel conductance method [41], [42]. All of these methods have one basic idea in common: heat flows through a sample while the temperature difference is measured across two points on the sample. Thermal conductivity can be calculated using the heat flow and the temperature difference, along with the cross-sectional area of the sample.

As shown in Figure 3-1, the different methods can be chosen for various sample geometries and properties. The absolute technique is the simplest, with a rectangular sample

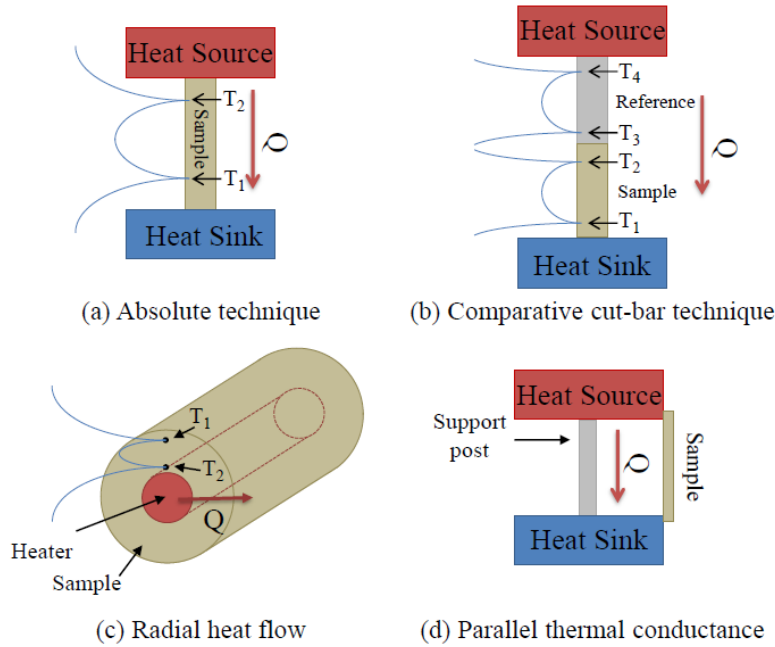


Figure 3-1: Diagram of various steady-state thermal conductivity measurement methods: (a) absolute technique measurement by total power from heater (b) comparative technique measurement by comparing heat flow with a reference (c) radial heat flow method for lower heat loss of higher-temperature measurements, measures by heat flow from inside sample (d) parallel thermal conductance measurement by subtracting holder conductance to give sample values.

sandwiched between a heat source and sink. Heat flows from the source to the sink while differential thermocouples (or multiple thermocouples) are spaced along the sample to measure the temperature difference. The temperature differential and the power output of the heater are used to directly calculate the thermal conductivity [43].

With the comparative technique, a material of known and similar thermal conductivity is put in series with the unknown sample. Thermocouples are attached along both the known and unknown sample, and heat flows through as in the previous method. However, instead of using the absolute power of the heater to calculate thermal conductivity, the temperature differential across the known and unknown sample are compared to determine the unknown's thermal conductivity, while assuming a constant heat flow through both materials [44].

The radial heat flow method is more often used at high temperatures, as it limits the loss of heat due to radiation from the sample surface and the heat source. Heat is applied from an inner cylinder, while the temperature change is measured radially outward from the heater and across the unknown material [45].

The fourth steady-state method shown in the figure is for small or needle-like samples that are too delicate to support the weight of a heater or thermocouples, requiring a different approach. Parallel thermal conductance technique uses a support to connect the heat source and sink, and then thermal conductivity is measured from the support. Next, the sample is attached across the heat source and sink, and thermal conductance measured again. The previous measurement is subtracted out to find the thermal conductivity of the sample [46].

For the thermal conductivity measurements in this work, the comparative technique was considered at first, but after difficulties with matching the thermal conductivity of the reference sample with the unknown samples, this method was discarded. Instead, the absolute technique was chosen since no reference material is required. At the same time, the various lengths and widths of the single crystal samples work well with this technique compared with the other available methods. In the following sections are details of the measurement setup and the equipment used or built to determine the temperature-dependence of the thermal conductivity for these crystalline materials.

3.2 Thermal Conductivity Measurement Setup

3.2.1 Temperature & Measurement Control

Temperature-control for the test setup was achieved using a closed-cycle cryostat (Advanced Research Systems), consisting of a temperature-controlled arm, or cold finger, with a small stage for sample testing on the end. A stainless-steel tube was fitted over this cold finger

and maintained at the same temperature for heat radiation shielding. A second stainless-steel vacuum shield covers both the cold-finger and the tube and provides additional radiation and temperature shielding.

The sample stage was modified to add multiple electronic connection posts required for the thermal conductivity measurements, shown in Figure 3-2. Wires were also run from the connection posts at the sample stage back down the cold finger to a connection port in the cryostat casing, to allow measurement and control of the sample stage from outside the vacuum shield. From outside the cryostat, the connection port is connected to a break-out box with individual banana plug sockets for each post on the sample stage. These are for use with current supply and voltage measurement, needed for the thermal conductivity measurements.

For temperature reading and control, a Cernox thermometer (LakeShore Cryotronics) was secured to the end of the cold finger near the sample stage and connected with a LakeShore 355 Temperature Controller.

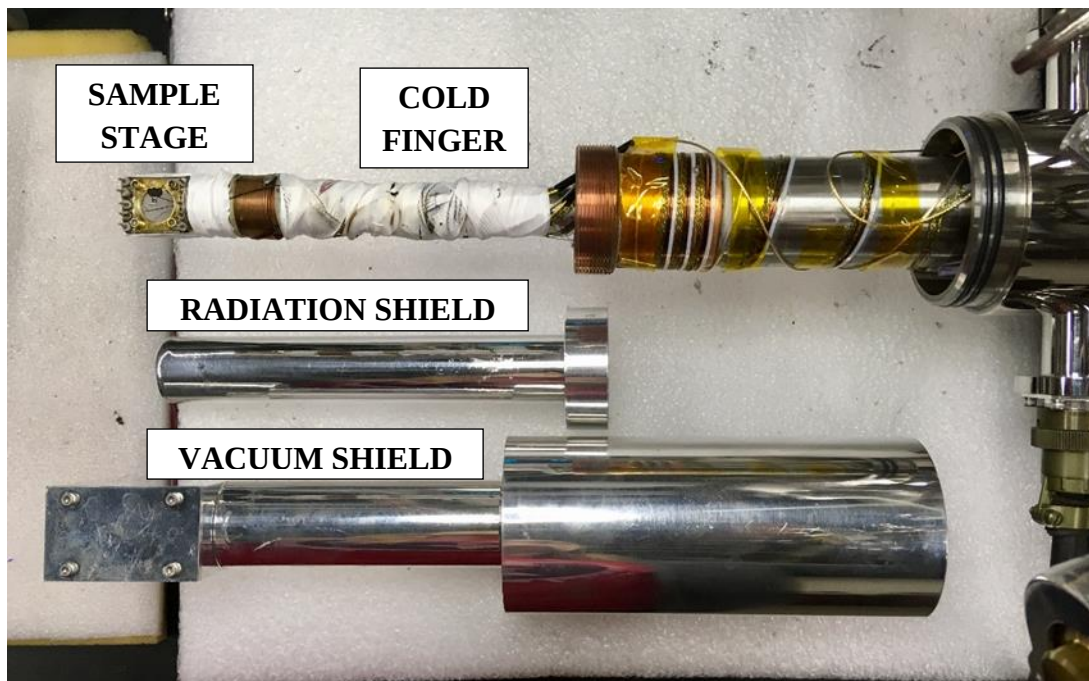


Figure 3-2: Sample stage, cold finger, radiation shield, and vacuum shield.

The voltage of the differential thermocouple was measured using a Keithley Model 2182a nanovoltmeter, through the breakout-box connections. Current was sourced to the heater chip through the breakout box with a Keithley Model 2450 SourceMeter. All three pieces of equipment were connected by GPIB (General Purpose Interface Bus) cables to a computer, where measurements were controlled using a LabVIEW program (National Instruments).

3.2.2 Sample Preparation

Following the requirements of the absolute technique for thermal conductivity, flat crystals of uniform thickness were chosen from the materials prepared earlier, described in Chapter 2. For each measurement, a crystal was cut into a rectangular shape and the dimensions recorded. Then the sample was attached by one end to a gold-coated copper heat sink (Quantum Design) with Loctite Stycast 2850FT (Henkel), and the Stycast allowed to set overnight. A 100 Ω RuO_{2-x} resistance heater chip (Vishay Thick Film Resistor 0.5 Watt) was then glued perpendicular to the free end of the sample with super glue, as shown in Figure 3-3. Once the heater was securely glued in place, gold wires 1" in length and 0.001" diameter were attached to the heater chip for later connection to the current source in the test setup.

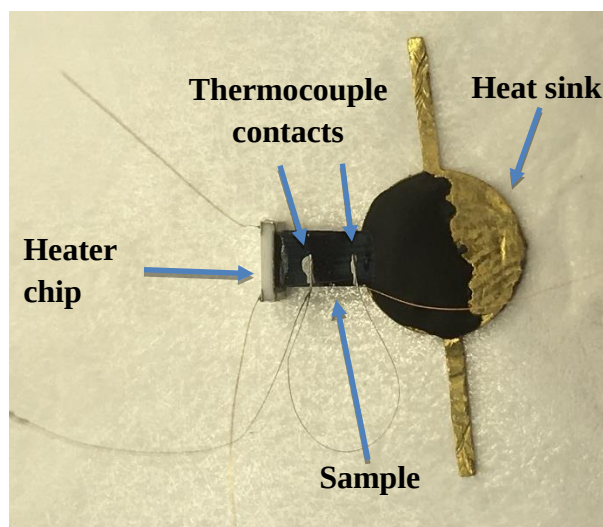


Figure 3-3: Sample prepared for installation in cryostat.

3.2.3 Thermocouple Construction

For measuring heat flow through the samples, a differential T-type thermocouple was made for each new sample measurement. T-type was chosen because of its linear voltage-output behavior for low temperatures, which is better for measurement accuracy [47]. Each end of a ~0.75” long, 0.001” diameter Constantan wire (Omega Engineering, SPCC-001-50) was twisted together with the end of a ~1” long, 0.001” diameter copper wire (Omega Engineering, SPCP-001-50), and then soldered or coated with conductive silver paint (SPI Supplies) to form two thermocouple junctions in series. After verifying that a good electrical connection was established across the thermocouples, the thermocouple junctions were each attached to the sample with silver paint about 1-2 mm apart, depending on the dimensions of the sample, with the Constantan wire forming a loop between the two junctions. This completed the initial step of sample setup, as shown in Figure 3-3, making it ready for transfer to the measurement and temperature control system.

3.2.4 Final Setup Preparation

For our thermal conductivity measurements, the prepared sample setup was placed on the sample stage with the gold heat sink securely screwed down to one side of the stage, leaving the sample and heater chip suspended in space. Silver paint was used to connect the two copper wires of the differential thermocouple to posts on the sample stage, and the same was done with the gold wires leading from the heater chip for current sourcing. After allowing the silver paint to fully dry, resistance was measured across the differential thermocouple and heater chip to determine good electrical connection, $<55\ \Omega$ and $<116\ \Omega$, respectively. The complete setup is shown in Figure 3-4.



Figure 3-4: Prepared sample installed on sample stage.

With the contacts and sample preparation complete, the radiation and vacuum shield were placed over the setup and then pumped down to 10^{-7} Torr with a HiCube Pfeiffer turbo vacuum pump to minimize effects of radiation and convection currents, which would reduce the accuracy of the thermal conductivity measurement. The cooling compressor was then switched on and the setup was allowed to cool down for two hours to stabilize to its lowest operating temperature of $\sim 6\text{K}$.

Once the temperature stabilizes, but before starting the measurement, the baseline voltage of the differential thermocouple needs to be recorded each time. While this value would ideally be zero for a temperature-stabilized setup, the recorded voltages are typically within -0.0010 to -0.0015 mV. These thermal voltages remain present due to connections between differing metals throughout the test setup, from the thermocouple connections out to the nanovoltmeters [48].

Resistance across the thermocouple and heater chip were also recorded at low temperature, before measurement, to ensure the connections were still secure, with typical values of $\sim 25\text{-}50$ Ohm for the thermocouple and ~ 123 Ohm for the heater chip. Lower resistance is expected for the thermocouple wire due to the reduced resistance of metal with decreasing

temperature, while higher resistance is expected of the RuO_{2-x} resistance heater due to the disorder-induced localization at low temperature.

3.3 Running the Measurements

To begin the measurements, a temperature gradient was applied across the sample by supplying a constant current to the heater chip. After waiting two minutes for the temperature gradient to initiate, the sample was slowly heated from 6K to 300K at a heating rate of 1K/minute while voltage differential measurements were recorded every 2 seconds across the differential thermocouple. Three samples were measured of each material, to ensure repeatability of the measurement and accuracy of the values recorded.

Because the sample dimensions were different for each new sample measurement, the amount of heat initially required to produce a sufficient temperature gradient was unknown. Therefore, measurements were repeated for each sample with 3-4 different heating source currents, typically between 5-12 mA. These current levels were chosen to be high enough, so a positive voltage value was sustained across the thermocouple during the whole measurement temperature range. The positive voltage indicated enough heat was being produced by the heater chip to maintain a high-to-low temperature gradient across the sample from heater chip to heat sink.

However, heat flow was also kept as low as possible for two reasons: temperature dependent material properties and heat shunting. As heat flow increases, so does the total average temperature of the sample. This can result in smearing or shifting of temperature-dependent features in the data, such as magnetic transitions. Excessive applied heat can also cause some heat flow to be re-directed through the connecting wires if the heat cannot flow fast enough through the sample, increasing the error of the measurement. After taking into account

both the high and low requirements for heat flow, differential voltage vs. temperature curves were recorded for each sample, and then calculations were required to transfer the voltages into thermal conductivity data.

3.4 Calculations & Corrections

As mentioned previously, thermal conductivity is calculated by measuring the flow of heat through a sample. This requires knowing the cross-sectional area, A , where heat is flowing through sample, the temperature difference between two points on the sample in the direction of heat flow, ΔT , and the amount of heat applied, Q . Area is calculated from the dimensions of the sample, the temperature differential is measured by the differential voltage in the previous section, and the heat flow determined from the resistance of the heater and the supplied current. The following sections contain the details of calculations for each of these variables, as well as the corrections and errors for the final thermal conductivity vs. temperature curves.

3.4.1 Determining Temperature Differential across the Sample

Once the differential voltage was measured vs. temperature, the zero (or baseline) voltage that was recorded before the measurement began was added or subtracted as necessary to counteract thermal voltages in the setup. With this corrected data, the process to calculate thermal conductivity could begin.

First, the thermoelectric voltage of the differential thermocouple had to be calculated for the range of temperatures recorded during the measurement, using a standard polynomial for T-type thermocouples from NIST [49]. At each measured temperature value, the derivative of the calculated voltages was taken with temperature, in order to find the ratio of voltage produced per Kelvin of temperature change across the thermocouple. Because the thermocouple was

differential, this value gives the Seebeck coefficient of the constantan in the thermocouple as it changes with temperature:

$$S = \frac{\Delta V}{\Delta T}$$

$$\Delta T = V_{diff} * S$$

The respective Seebeck coefficient S for each measurement temperature was then multiplied by the voltage differential V_{diff} measured by the differential thermocouple, giving the temperature difference ΔT across the sample for each data point [42].

3.4.2 Heater Resistance Correction

Before thermal conductivity could be calculated from the temperature differential, heat flow through the sample had to be determined with $P=I^2R$, where P is the heater power in Joules, I is current in Amps, and R is resistance of the heater in Ohms. However, due to the large temperature range of the measurements, a heater with constant resistance across the entire range could not be obtained. The RuO₂ heater chosen for these measurements has a stable resistance of 100 Ohms from 300K to ~180K, but begins to increase below that range, which means the power produced by the heater would not be constant for the whole measurement. To increase the accuracy of the thermal conductivity measurement, the resistance of the heater was independently measured from 300K to 5K and fit with a 6th-order polynomial for an R² value of 99.78, and standard error of deviation of 0.003 Ohm. This polynomial equation was used to calculate the change in resistance with temperature for each measurement, from low temperature to 180K. Above that, a value of 100 Ohm resistance was assumed.

3.4.3 Correction for Thermal Voltage Variations

A significant amount of noise occurred in some of the measurements at lower temperatures, which hampers comparing measurements on different samples of the same material. This noise is assumed to be due to thermal voltage variations with changing temperature in the wire connections throughout the setup, since connections between dissimilar metals was unavoidable. Data smoothing was attempted, but the variations in the differential voltage data were too drastic for this method to have much of an effect. Due to this problem, the differential voltage curves from low temperature to 50K were instead fit to 4th-order polynomials with an R^2 value of 99% or better. For data that contained too much noise to analyze, this polynomial was used to replace the voltage data for that temperature range before calculating thermal conductivity. Error of the fit was also calculated with the standard estimate of the error, using the following equation:

$$\sigma_{estimate} = \sqrt{\sum \frac{(Y_{actual} - Y_{estimate})^2}{n}}$$

where $Y_{actual} - Y_{estimate}$ is the difference between the experimental values and the fitting line calculation, and n is the number of data points [50]. This error estimate represents the average distance between the fitting curve and the experimental data, which varied from sample to sample, from 9% up to 26%.

3.4.4 Radiation Loss Corrections

At higher temperature measurements, usually above 200K, radiation effects began to appear that artificially caused the thermal conductivity to be skewed upwards with increasing temperature. This occurs because the sample starts to radiate a significant amount of heat to the radiation shield at higher temperatures, even though the sample chamber is under vacuum. While

the shield also radiates heat back to the sample, the energy being released from the sample gradually becomes much larger than the heat radiated back. The difference in heat transfer can be calculated over the range of temperatures measured for the material with the Stefan-Boltzman equation:

$$P_{rad} = \sigma_T * (A/2) * \varepsilon * [T_{hot}^4 - T_{cold}^4]$$

Where P_{rad} is the heat energy lost from the sample, σ_T is the Boltzman constant, A is the total surface area of the sample, ε is emissivity of the sample, while T_{hot} is the temperature of the hot end of the sample and T_{cold} is the temperature of the system [42]. Emissivity was assumed to be ~ 0.1 , similar to that of a polished metal surface, since the single crystals have a metallic appearance [51]. This calculated energy loss is due to the temperature difference between the sample and the surroundings and was subtracted from the total heat flow to correct for the radiation loss.

However, the radiation loss calculated and subtracted here made very little effect on the radiation tail seen in the data. Further radiation loss must be attributed to other sources. Wire connections could be a small contribution, though this is minimal due to the very small diameter (0.001”) wires used for all connections. Another source could be radiation from the heater itself, though this can be difficult to estimate. Because the radiation tail cannot be corrected for properly, reliable thermal conductivity data can only be reported up to 200 K. Fortunately, there do not appear to be any interesting features above that point for any of the materials, especially since all of the magnetic transitions are well below 200 K, rendering the data beyond 200 K less significant.

3.4.5 Final Calculations for Thermal Conductivity

Having dealt with the necessary corrections and adjustments to the raw data, thermal conductivity was finally determined. With the temperature differential across the sample and the actual heat flow through the sample known, the thermal conductivity versus temperature was calculated using the following equation:

$$\kappa = \frac{(Q * l)}{(A * \Delta T)}$$

where κ is thermal conductivity in W/m*K, Q is the calculated heat flow through the sample in Joules, l is the distance between thermocouples placed on the sample surface in meters, A is the cross-sectional area of the sample in square meters, and ΔT is the temperature difference measured between the thermocouple connection points on the sample surface in Kelvin.

Inaccuracy in measurement of sample dimensions can be one of the largest sources of error for these measurements, especially due to the small nature of the samples. This error was determined to be +/- 0.03mm for width and length, +/-0.005mm for thickness, and +/- 0.1mm for thermocouple spacing on the sample surface and was included in the calculations and graphing for the thermal conductivity data. The thermal conductivity data was plotted vs. temperature for each sample and is presented and discussed in Chapter 4.

Chapter 4. Results and Discussion

4.1 Thermal Conductivity: General Behavior

In general terms, thermal conductivity is the transfer of heat through a material by the movement of electrons or phonons [42]. However, the materials studied here are semiconductors, which mean their thermal transfer is mostly governed by phonon behavior, and the electronic part can be ignored as insignificant. Phonon thermal conductivity, also known as lattice thermal conductivity, can be estimated with the Debye approximation:

$$\kappa = \frac{1}{3} C v l$$

Where κ is the thermal conductivity, C is the total heat capacity, v is the phonon velocity through the material, and l is the mean free path. The total heat capacity reduces towards room temperature due to phonon-phonon Umklapp scattering and is responsible for the $1/T$ behavior seen in Figure 4-1.

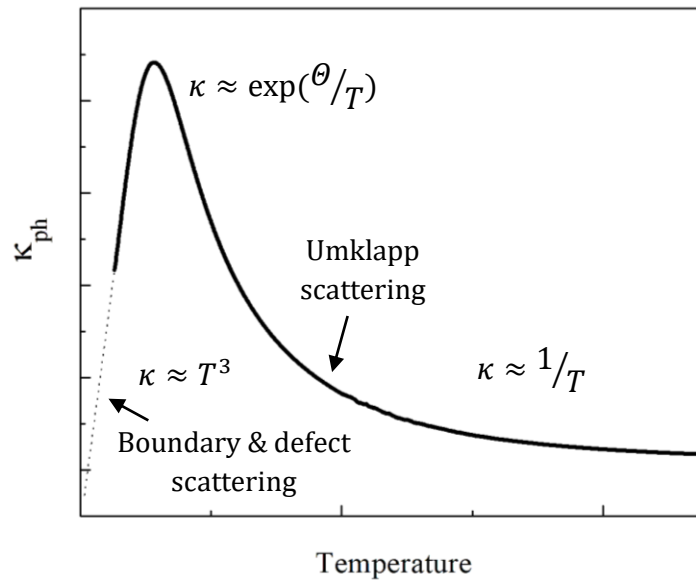


Figure 4-1: Phonon thermal conductivity as governed by the Debye approximation [42].

Average phonon velocity can be assumed in place of v , and is approximately equal to the sound velocity in solid materials. The mean free path of the phonon is the distance a phonon can travel before it collides with something: either grain boundaries, other phonons, or even sample boundaries. This length increases with decreasing temperature for semiconductors, as there is less thermal energy in the material, which in turn helps reduce the number of phonon collisions. Eventually, the mean free path reaches a maximum as limiting processes start to take effect, such as boundary and defect scattering. The overall Debye shape seen here is typical for crystalline materials, and can be used to predict their general behavior [42].

4.2 Literature: CrSiTe₃ Thermal Conductivity

In the literature, thermal conductivity data of only two MXY₃ materials has been measured so far, CrSiTe₃ and CrGeTe₃, and both are ferromagnetic semiconductors. Since these are layered materials, single-crystal thermal conductivity measurements perpendicular to the layers can be very difficult, as the layers tend to exfoliate and separate easily. Due to this, the only thermal conductivity data available for CrSiTe₃ was measured across the ab-plane on a single crystal by Casto et al. [20].

There are a few features of interest in the behavior for CrSiTe₃; the in-plane thermal conductivity, κ_{ab} , acts with a glassy phonon behavior in the paramagnetic region above the T_c of 33K, rapidly increases below the T_c until peaking around 8 K, and there is a shoulder in the data curve at 24 K seemingly unrelated to the T_c .

For crystalline materials, the lattice thermal conductivity should typically follow $1/T$ dependence with increasing temperature, after peaking at some temperature below 100 K. The behavior of CrSiTe₃ shows a significant discrepancy from the typical lattice thermal conductivity. Instead of decreasing with heating, the κ_{ab} increases to about 3 W/m*K at room

temperature, exhibiting phonon glass behavior. Since the thermal conductivity increases rapidly at T_c , the phonon glass behavior is most likely due to magnetic fluctuations causing phonon scattering, that are lessened upon reaching the magnetic ordering temperature. The same phonon glass effects have been seen in other materials with strong spin-orbit-lattice coupling, so this might be the cause for the behavior of CrSiTe_3 as well.

Even in the ferromagnetic ordering range below T_c , κ_{ab} behavior does not return to the expected lattice thermal conductivity, since it peaks at only 5.5 W/m*K around 8 K. The Debye fit to the κ_{ab} data is also affected by the abnormally low thermal conductivity over the T_c , since the fit towards higher temperatures is much lower than the data. Low overall thermal conductivity and the shoulder in the data at 24 K are both indications that temperature dependent magnetic fluctuations are inhibiting normal phonon thermal conductivity; more proof that strong spin-lattice coupling is a big influence on the thermal conductivity behavior for CrSiTe_3 . The phonon scattering length appears to be inversely proportional to the magnetic correlation length, though this needs further research to be proven. If true, this would also be a factor in determining the thermal conductivity behavior below the T_c , since the thermal conductivity carriers are almost entirely phonon dependent in semiconducting CrSiTe_3 .

4.3 Literature: CrGeTe_3 Thermal Conductivity

Magnetic effects on the thermal conductivity are not available for ferromagnetic CrGeTe_3 , also known as $\text{Cr}_2\text{Ge}_2\text{Te}_6$, as the only experimental data available is from 300 K to 825 K which is well above the magnetic ordering T_c of 61 K [52]. The restriction of measurement to this temperature range is due to $\text{Cr}_2\text{Ge}_2\text{Te}_6$ having potential as a mid-temperature thermoelectric material. These samples were not single crystal, like those in the CrSiTe_3 paper, but instead pressed and flash-sintered powders of the compound. Pressing the samples induces some

differences in the thermal conductivity data, which is indicated by the A and P labels, along and perpendicular to the pressing direction. Thermal conductivity can be decreased even further with a Cr site deficiency of 3% than the low value seen for $\text{Cr}_2\text{Ge}_2\text{Te}_6$, as can be seen when comparing $\text{Cr}_2\text{Ge}_2\text{Te}_6$ with $\text{Cr}_{1.94}\text{Ge}_2\text{Te}_6$.

Though the effects of magnetism on thermal conductivity for CrSiTe_3 cannot be directly compared with CrGeTe_3 , the values near room temperature are fairly close, $\sim 3 \text{ W/m}\cdot\text{K}$ for CrSiTe_3 and $\sim 2.3 \text{ W/m}\cdot\text{K}$ for CrGeTe_3 , indicating the possibility of similar thermal conductivity mechanisms between the two materials.

While the ferromagnetic range is unavailable for CrGeTe_3 , the above-room-temperature behavior of lattice (κ_L) vs. electronic (κ_e) thermal conductivity was examined by calculating κ_e , where $\kappa_e = L\sigma T$, L is the Lorentz number $1.5 \times 10^{-8} \text{ V}^2/\text{K}^2$, σ is electrical conductivity, and T is temperature. Subtracting κ_e from the total thermal conductivity, κ_T , leaves lattice thermal conductivity. This does not produce a substantial difference between κ_T and κ_L below 700 K, indicating most thermal conductivity is from κ_L below 700 K. In addition, since the thermal conductivity linearly decreases from room temperature to 700 K, this shows the main mechanism affecting the κ_L is phonon-phonon umklapp scattering.

In the case of CrGeTe_3 , the reduction in overall thermal conductivity when compared with the expected value for a crystalline material was explained with help from theoretical calculations. There are two possible contributions, one being: phonons are scattered by the interfaces between the layers of material, while the weak van der Waals bonds between the layers act as a buffer to further dampen phonon transport. Another possibility might be the differing chemical bonds in CrGeTe_3 . Strong intralayer bonds and weak interlayer van der Waals

bonds could cause unique lattice dynamics such as large lattice anharmonicities and low sound velocities in the material, which would induce low lattice thermal conductivity [52].

Both CrSiTe_3 and CrGeTe_3 appear to derive most of their thermal conductivity through phonon transport, but why the thermal conductivity is so low is still up for debate. While there are some theories for the behavior of thermal conductivity in these two MXY_3 materials, being able to compare data in overlapping temperature ranges would help with further understanding of how they function. In addition, since the only two compounds measured in the MXY_3 class are ferromagnetic, there may be new behaviors seen in the yet-unmeasured antiferromagnetic materials. So, the remaining MXY_3 compounds, including CrPS_4 , still need to be measured for two reasons: more data is needed to understand how thermal conductivity works in these materials, and the thermal conductivity values of the unmeasured compounds are needed to determine their potential for applications.

4.4 Thermal conductivity: Experimental Data – Analysis and Discussion

In the following section are the results of the temperature dependence of thermal conductivity measurements for CrSiTe_3 , CrGeTe_3 , MnPS_3 , MnPSe_3 , FePS_3 , FePSe_3 , NiPS_3 , and CrPS_4 . The magnetic ordering temperatures listed in the figures are taken from the experimental magnetic susceptibility measured in Chapter 2. Because CrSiTe_3 and CrGeTe_3 are the only materials with literature data, the discussion will begin with their results. Data is plotted with thermal conductivity on both the linear and log scale for ease of comparison between materials and literature data.

4.4.1 Thermal conductivity: CrSiTe₃

The behavior, shown in Figure 4-2, follows that seen previously in literature, though the values for this measurement are higher. This could be attributed to the lower accuracy associated with this measurement – reaching within 10-20% of the actual value is typical. The glassy behavior is again apparent with the increase in thermal conductivity from T_c towards room temperature, though the room temperature value measured in this case is probably closer to 5-6 W/m*K compared with the literature ~ 3 W/m*K. As seen before, magnetic ordering also clearly coincides with the onset of the phonon peak. The shoulder at ~ 24 K is not as visible, but some change in curvature appears to be occurring around that temperature. The inset shows a magnified view of the differential of thermal conductivity with temperature, which was used to more easily determine the transition temperature seen in the thermal conductivity due to the magnetic ordering. There are two different temperatures shown in the inset, 29.4 K and 32.2 K, marking the beginning and the end of a transition. As the two temperatures are within just a couple degrees of each other near the magnetic ordering temperature, they indicate just a short duration of time is needed for the ordering to fully take place before having a positive effect on the thermal conductivity. As mentioned before, phonon-magnon scattering has most likely been reduced once the magnetic ordering occurs, which greatly increases the mean free path of the heat-carrying phonons [53].

4.4.2 Thermal conductivity: CrGeTe₃

While no low-temperature data exists in the literature for CrGeTe₃, some comparison can be made between this material and CrSiTe₃, which is also a FM with the same structure type. Like CrSiTe₃, CrGeTe₃ also shows the onset of the phonon peak occurring with the magnetic ordering temperature, shown in Figure 4-3, with a drastic increase in thermal conductivity at T_c .

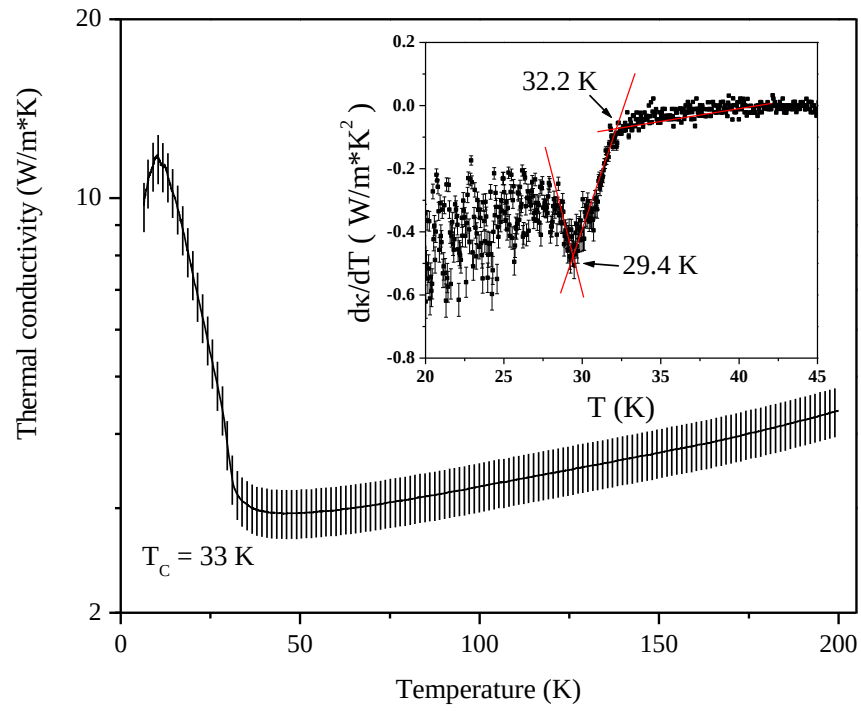
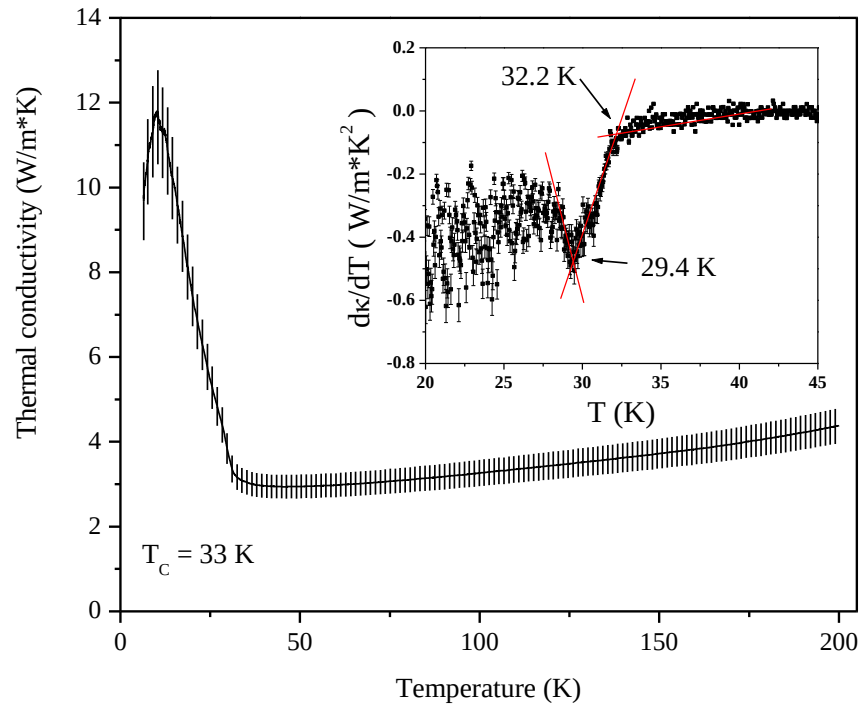


Figure 4-2: Linear and log thermal conductivity dependence on temperature for CrSiTe_3 .

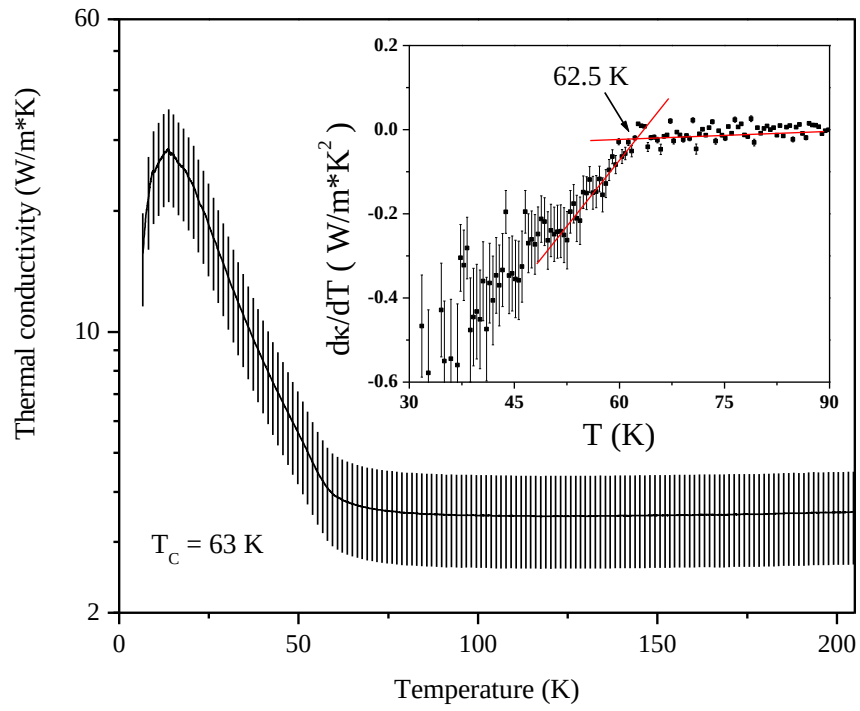
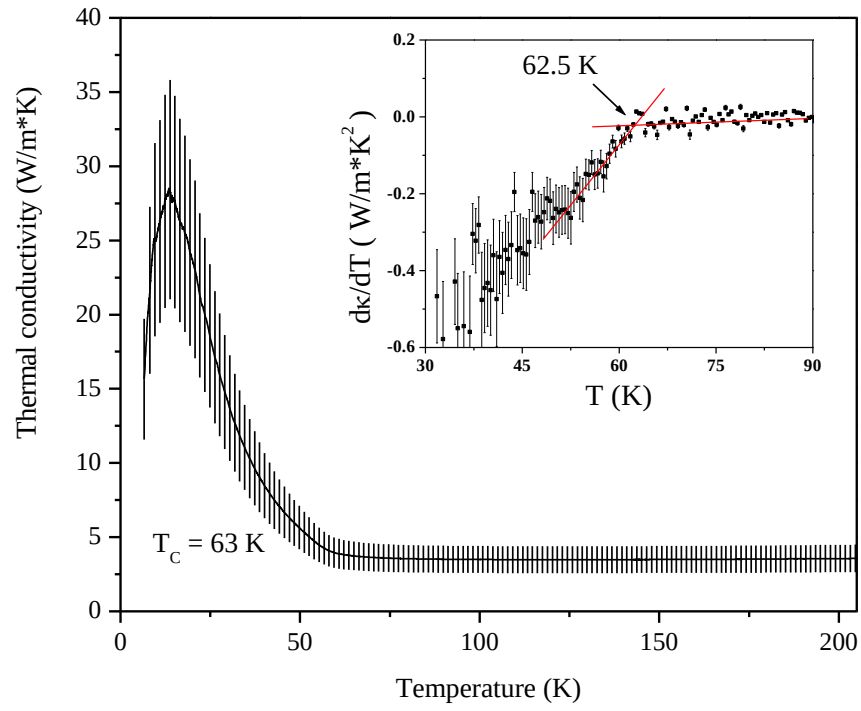


Figure 4-3: Linear and log thermal conductivity dependence on temperature for CrGeTe_3 .

The ordering temperature measured through magnetic susceptibility was measured to be 63K, which agrees well with both literature [5] and the transition temperature of 62.5 K shown in the thermal conductivity inset. Phonon-glass behavior above T_c is not obvious here, since the thermal conductivity appears almost flat. A slight increase might be occurring, but not as much as seen in the CrSiTe_3 data. However, the thermal conductivity is not decreasing with $1/T$ which would be expected for typical Debye behavior, so the material might be exhibiting some glass-like behavior. Extrapolating out to room temperature, the thermal conductivity appears to be ~ 3.5 W/m*K, which is again higher than the previously reported values of 1.0-2.3 W/m*K [52], and 1.4-1.8 W/m*K [54] for spark plasma sintered samples. However, since there are more obstacles to phonon transport through a powdered polycrystalline material vs. a continuous single crystal plane, it follows that a compressed powder would most likely have a lower value than the in-plane value for a single crystal. Stacking faults in the layers of the material is another possible cause for low thermal conductivity suggested for these materials [54]. Interruptions in the layer planes would certainly decrease the mean free path of heat-carrying phonons.

4.4.3 Thermal conductivity: MnPS_3 and MnPSe_3

Since their behavior is very similar, the MnPS_3 and MnPSe_3 antiferromagnetic compounds can be discussed together, shown in Figure 4-4 and 4-5, respectively. Both materials follow the basic Debye behavior, with a prominent phonon peak at low temperatures, while the thermal conductivity slope decreases greatly and then trails off with the characteristic $1/T$ behavior. For MnPS_3 , the magnetic ordering temperature does not seem to have as much effect as seen in the two ferromagnetic layered materials. At the experimentally measured T_N of 78 K, there does seem to be some increase in the thermal conductivity, but the phonon peak has already begun by that point. Looking at the inset, while less sharp than what was seen in the

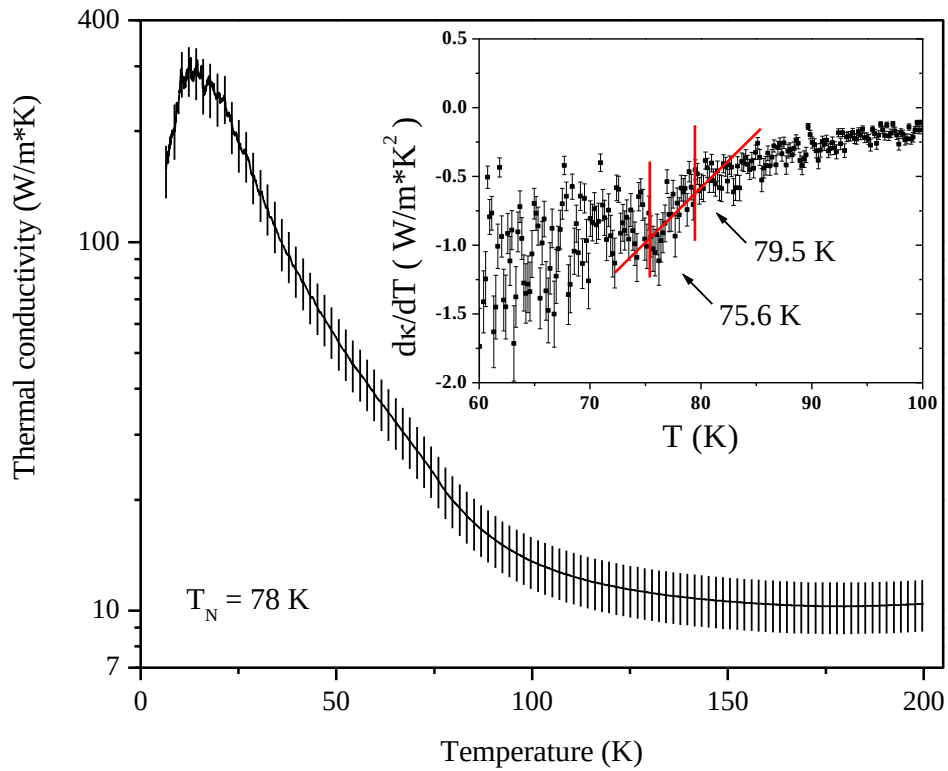
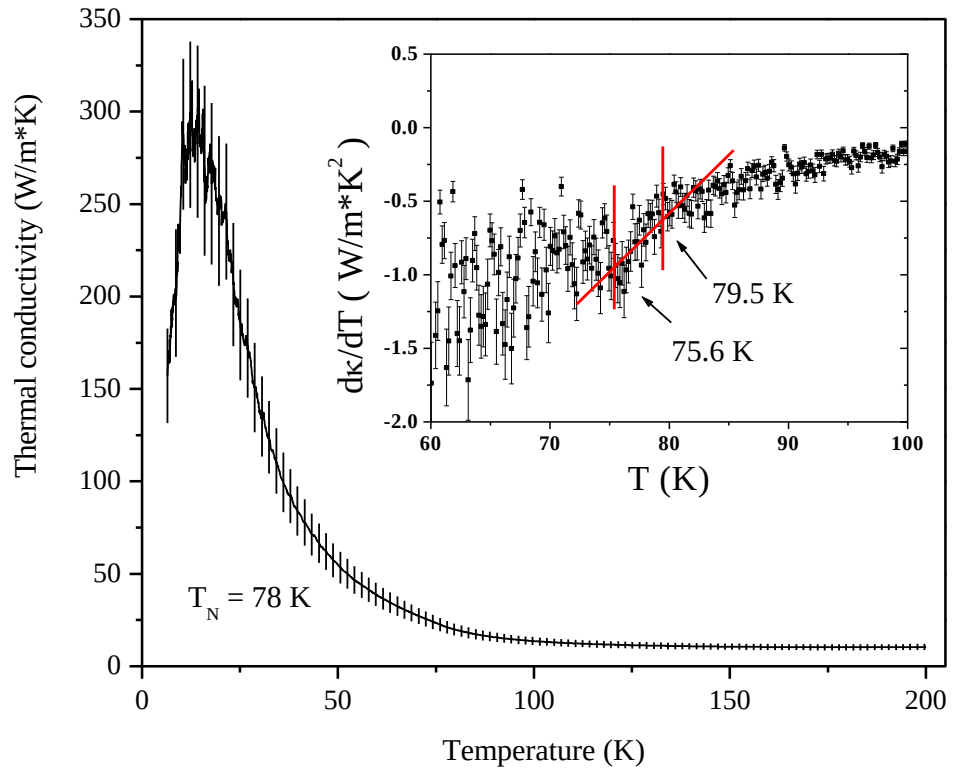


Figure 4-4: Linear and log thermal conductivity dependence on temperature for MnPS_3 .

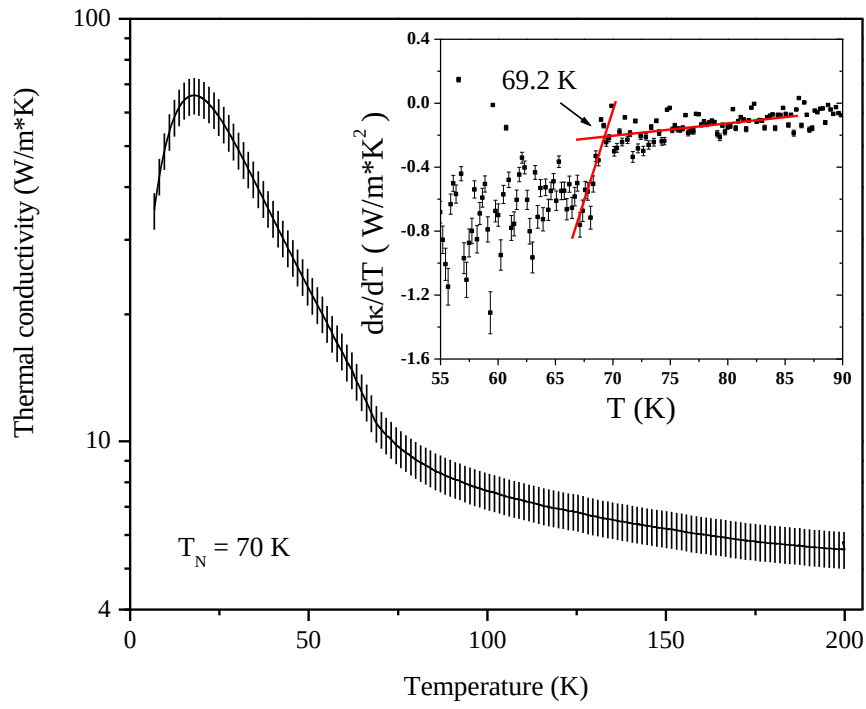
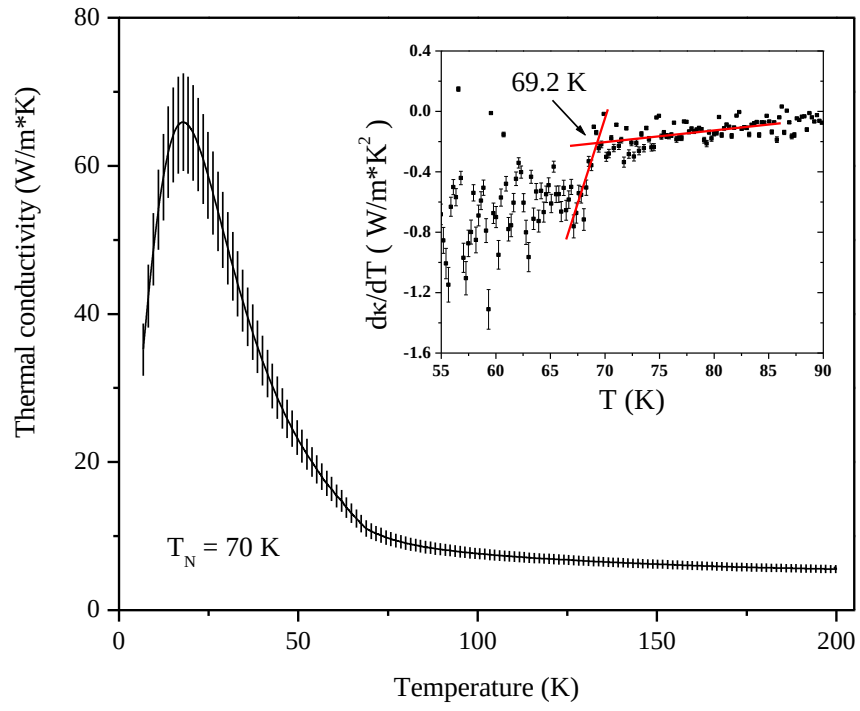


Figure 4-5: Linear and log thermal conductivity dependence on temperature for MnPSe_3 .

ferromagnetic materials, the effect of the magnetic ordering appears to have a larger transition range, 75.6 K to 79.5 K. The magnetic transition itself is not so gradual, so the reason for this is not quite understood. MnPS_3 has a sharper and less gradual transition, shown in the inset, perhaps only 1 degree over the change in slope. This might be why the thermal conductivity exhibits a sharper change in slope at the magnetic ordering temperature, of $T_N = 70$ K. However, the slope is already gradually increasing in the cooling direction before the onset of the magnetic ordering in the typical Debye behavior. One cause for the sharpness of the transitions between MnPS_3 and MnPSe_3 might be the change in crystal structure due to different compositions, from monoclinic to trigonal. Substituting selenium for sulfur changes the bonding distances as well as the structure orientation, which probably has some effect on the strength of the magnetic-phonon interactions in the material. Regardless of the effect of magnetic ordering, both materials decrease in thermal conductivity towards room temperature, indicating no glassy behavior is present in these materials. Extrapolating from 200 K to 300 K, the room temperature thermal conductivity values appear to be higher than in the ferromagnetic materials, with $\sim 10\text{-}12$ W/m*K for MnPS_3 , and $\sim 4\text{-}5$ W/m*K for MnPSe_3 .

4.4.4 Thermal conductivity: FePS_3 & FePSe_3

FePS_3 and FePSe_3 are also antiferromagnetic materials with similar behavior to each other, so these compounds will be discussed together as was done with the Mn-based materials, in Figure 4-6 and 4-7, respectively. These two Fe-based compounds appear to share characteristics more closely related with CrSiTe_3 and CrGeTe_3 than with MnPS_3 and MnPSe_3 . Both FePS_3 and FePSe_3 show a sharp onset of the phonon peak coinciding with the magnetic ordering temperature, in addition to glassy behavior in the paramagnetic region above the ordering temperature. However, the magnetic ordering transition effects on the thermal

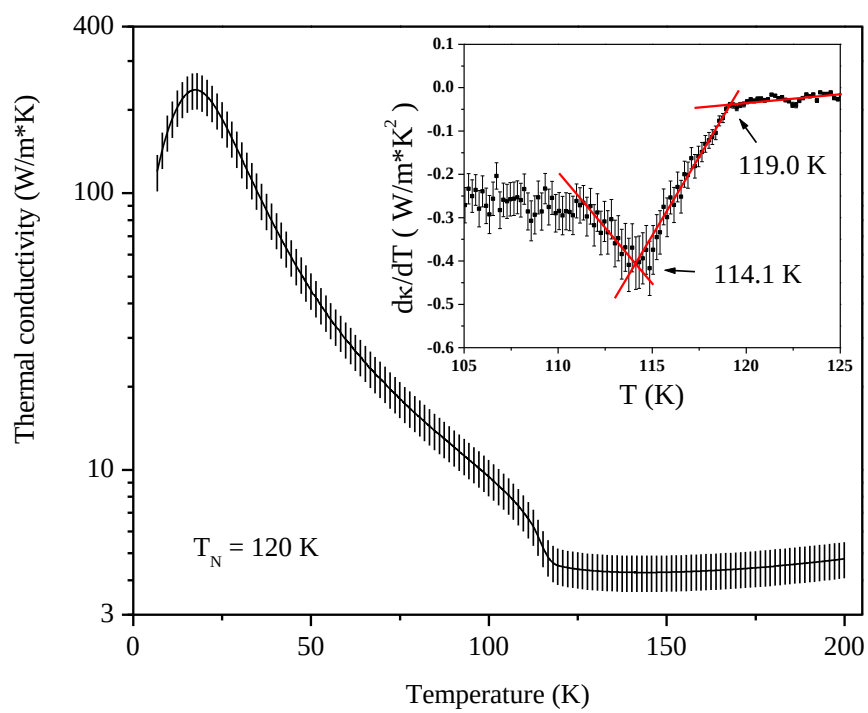
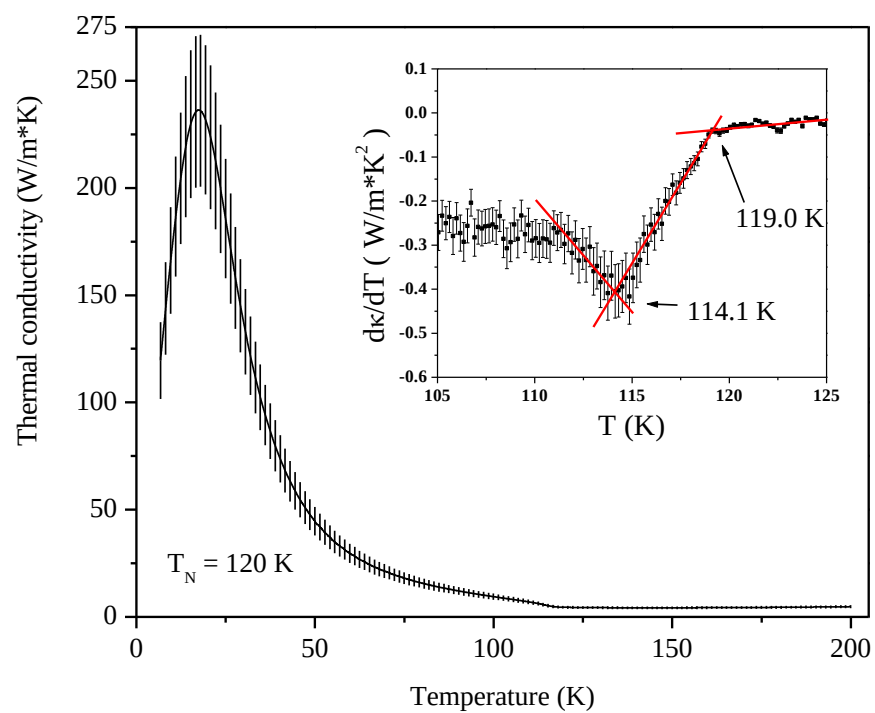


Figure 4-6: Linear and log thermal conductivity dependence on temperature for FePS_3 .

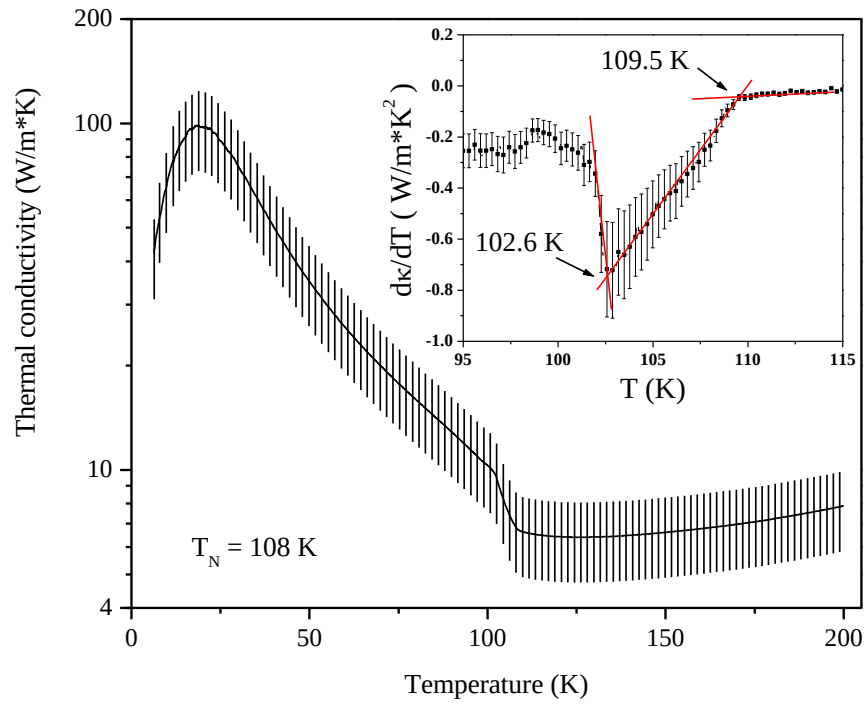
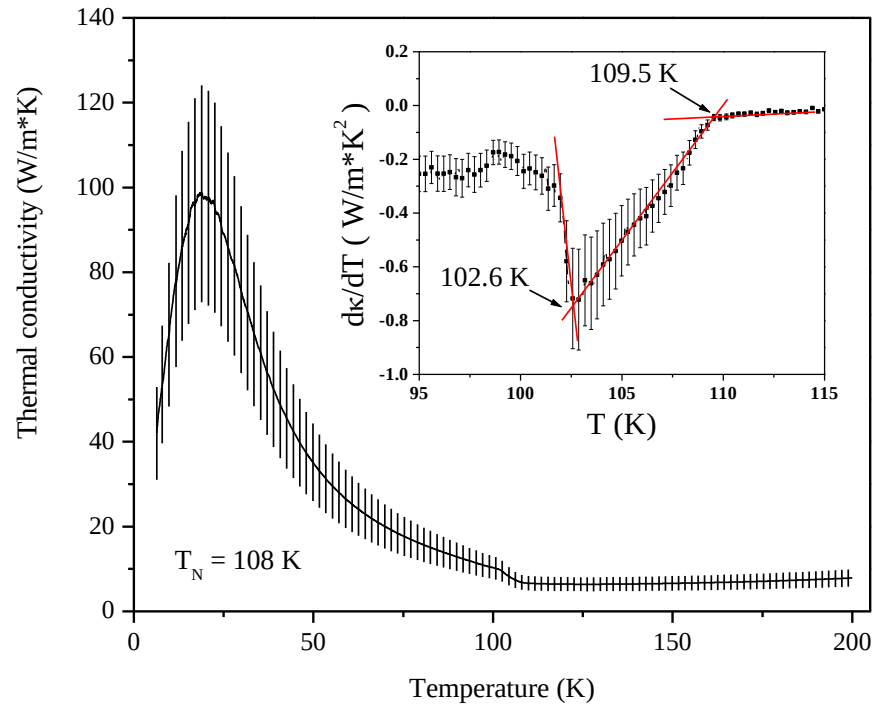


Figure 4-7: Linear and log thermal conductivity dependence on temperature for FePSe_3 .

conductivity have a larger temperature window than seen in the ferromagnetic materials. For FePS_3 , the experimentally measured T_N is 120 K, while the transition seen in the thermal conductivity occurs from 119 K to 114.1 K. In FePSe_3 , the magnetic ordering temperature is 108 K, while the thermal conductivity transition spans from 102.6 K to 109.5 K. The reason for the wide transitions in both materials is unknown, as the magnetic ordering transition measured with magnetic susceptibility is much smaller, spanning only a couple of degrees. However, as seen in the manganese materials, the selenium-based compound also seems to have a sharper transition in the thermal conductivity when compared to the sulfur variant, with the accompanying same structure change of monoclinic for the sulfur compound and trigonal for the selenium compound. At higher temperatures above the T_N , both materials show the glassy behavior seen in CrSiTe_3 and CrGeTe_3 , with the thermal conductivity increasing from the ordering temperature onwards. Extrapolating to room temperature, FePS_3 would appear to approach $\sim 6 \text{ W/m}\cdot\text{K}$, while FePSe_3 is around $10 \text{ W/m}\cdot\text{K}$.

4.4.5 Thermal conductivity: NiPS_3

The third variant of the MPS_3 structure, NiPS_3 has the same monoclinic structure as the other sulfur-based compounds: MnPS_3 and FePS_3 . However, while magnetic ordering of FePS_3 had a strong effect on the thermal conductivity, and a slightly less significant effect on MnPS_3 , the magnetic transition is almost imperceptible in NiPS_3 , seen in Figure 4-8. Around the experimental Néel temperature of 155 K, there seems to be a very slight change in the thermal conductivity slope, which is not visible in the differential data in the inset. Besides this small deviation, the thermal conductivity shows very typical Debye behavior for a crystalline solid, with a phonon peak below 100 K which gradually slopes into $1/T$ behavior as the temperature

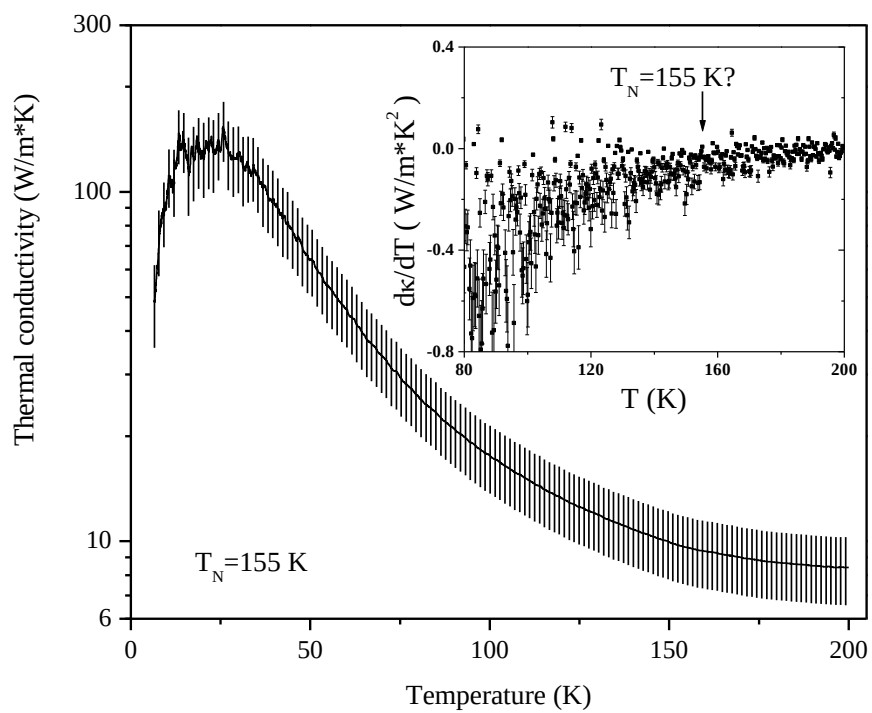
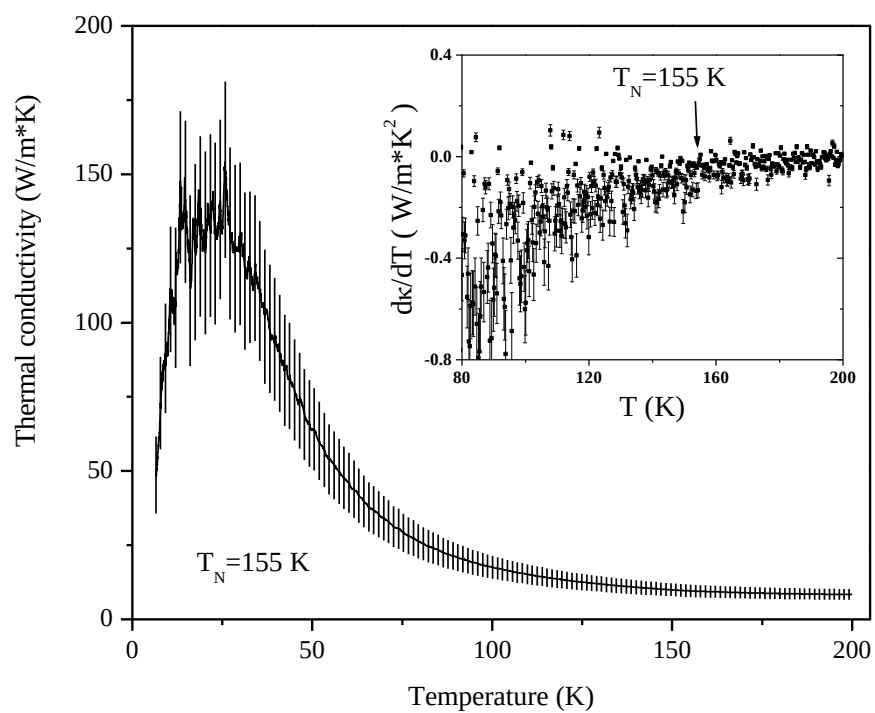


Figure 4-8: Linear and log thermal conductivity dependence on temperature for NiPS_3 .

increases. No glassy behavior is seen in this compound, like what was present in the Mn based materials.

4.4.6 Thermal conductivity: CrPS₄

The final material studied in this series, CrPS₄, has a slightly different crystal structure and composition than the rest. While monoclinic like the other sulfur-based compounds, this material is in a different space group, and contains a fourth sulfur atom. Though this material is semiconducting, layered, and antiferromagnetic like many of the other compounds, the magnetic Cr atoms are arranged in a rectangular grid instead of the honeycomb pattern seen in the other compounds studied here. Despite these differences, the thermal conductivity behavior is much like the other compounds, shown in Figure 4-9. Probably the closest comparison is seen with MnPSe₃: thermal conductivity again follows the Debye behavior, but still a significant increase is seen with the magnetic ordering temperature. The measured T_N of 37 K agrees with both literature [11] and the slope transition seen in the thermal conductivity data. Magnetic ordering occurs much higher up the phonon peak with CrPS₄ when compared to the other materials; this may contribute to the sharper peak shape. There also seems to be only one sharp transition instead of a range, shown in the inset. No glassy behavior is seen in this material, as the thermal conductivity drops towards room temperature with the typical $1/T$ Debye behavior.

4.4.7 Thermal Conductivity: Overall Behavior

Looking at the thermal conductivity results for all the materials, there appear to be some trends across their behavior. Four materials tend to follow the Debye behavior: MnPS₃, MnPSe₃, NiPS₃, and CrPS₄. Although there are still some magnetic ordering effects in the thermal conductivity, the general shape for their curves follows the typical phonon peak at lower

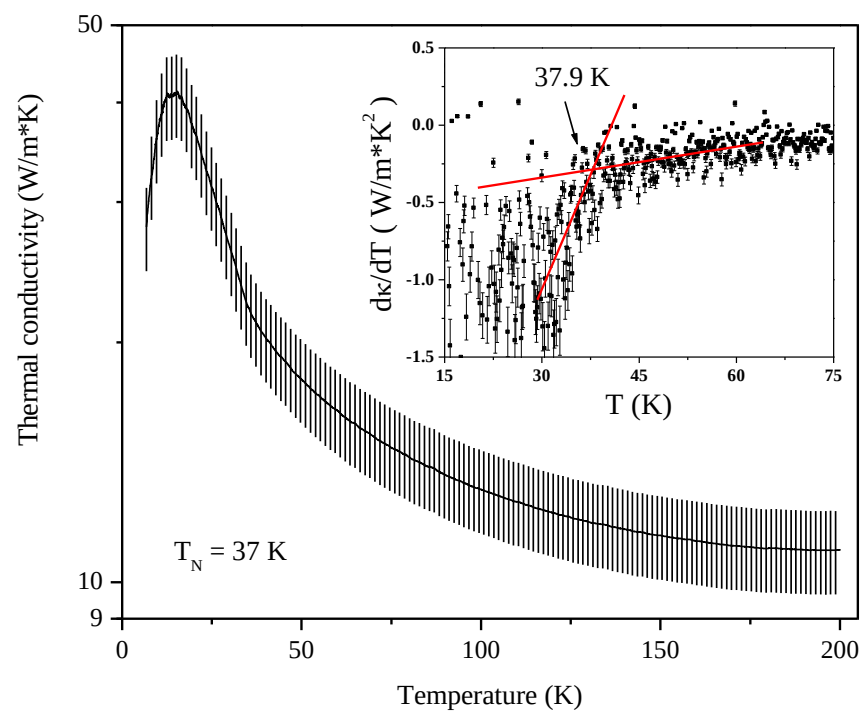
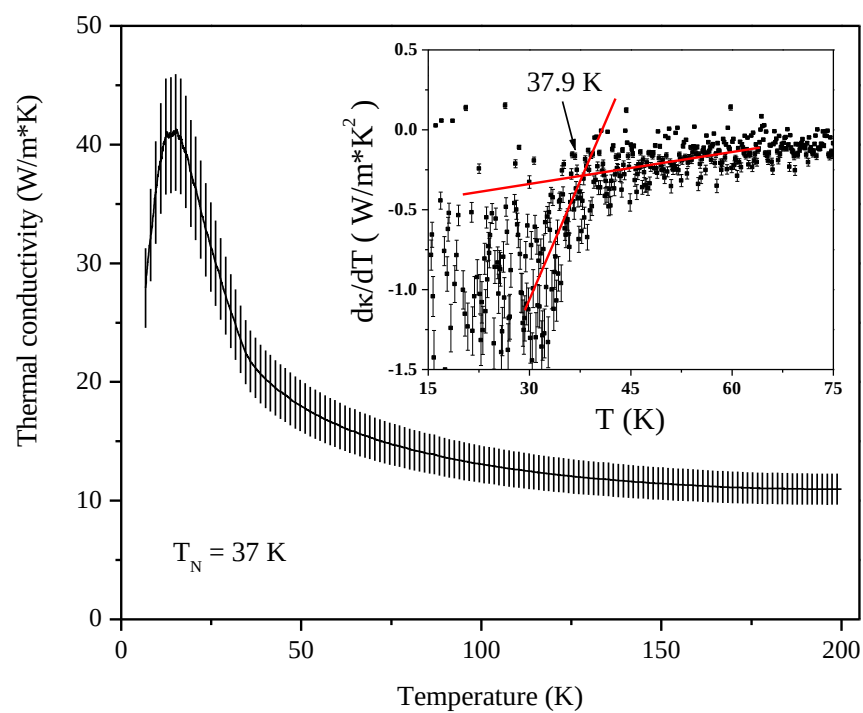


Figure 4-9: Linear and log thermal conductivity dependence on temperature for CrPS₄.

temperatures, with a decrease in the thermal conductivity by $1/T$ towards room temperature. The remaining four materials, CrGeTe_3 , FePS_3 , FePSe_3 , and CrSiTe_3 , all follow the glassy temperature dependence above the magnetic ordering transition, staying constant or increasing slowly towards room temperature.

Though the magnitude of effect varies from material to material, the magnetic ordering marked an increase in the thermal conductivity in all materials. However, there did seem to be a defining difference in behavior between the Debye and glassy materials. With the glassy behavior, the magnetic transition definitively marked the onset of the phonon peak. For the Debye materials, the thermal conductivity showed a small increase or change in slope at the transition temperature, but the magnetic ordering did not initiate the phonon peak.

Overall, the room temperature thermal conductivity was low for every material regardless of behavior, in the range of 3-12 $\text{W/m}^*\text{K}$ for all materials. This is comparable with other layered materials: 2 $\text{W/m}^*\text{K}$ for Bi_2Te_3 or BN with a value of 20 $\text{W/m}^*\text{K}$ [4]. As mentioned before, some possible reasons for the low values could be attributed to magnetic fluctuations appearing above the magnetic ordering temperature, which might additionally be responsible for the glass behavior in some materials [53]. Another cause for lowered thermal conductivity may be phonon scattering from the interfaces between layers, where the van der Waals bonding acts as a buffer or damper to the phonons when they impact the layer surface. An additional theory suggests large differences in bonding type: van der Waals bonding in the interlayer vs. strong bonding intralayer causing large lattice anharmonicities and reducing the velocity of traveling phonons [52]. The final theorized possibility: stacking faults could be another cause, as they would shorten the mean free path of phonons [54].

Chapter 5. Summary & Conclusions

A wide range of magnetic layered materials, CrSiTe_3 , CrGeTe_3 , FePS_3 , FePSe_3 , MnPS_3 , MnPSe_3 , NiPS_3 , and CrPS_4 , were successfully synthesized in single crystal form, their known properties characterized to verify quality, and then the thermal conductivity dependence on temperature measured. The first material, CrSiTe_3 , was shown to follow the behavior previously reported in literature, although the experimentally measured thermal conductivity values were a little higher than the reported values. Glass-like thermal conductivity behavior after a dramatic change at the magnetic ordering was also seen in the next three materials: CrGeTe_3 , FePS_3 , and FePSe_3 , but no unifying cause for this common behavior has yet been determined. Typical Debye behavior governs the remaining four materials: MnPS_3 , MnPSe_3 , NiPS_3 , and CrPS_4 , with more easily understood magnetic ordering effects. As magnetic transition occurs in these materials, the material becomes more ordered, reducing effects on phonon scattering and therefore increasing the thermal conductivity.

More study and investigation into the thermal conductivity of these materials is still needed to fully understand their behavior, but some interesting trends have been discovered. While the origins behind the thermal conductivity are not yet explained, the existence of the data will help advance future studies into these materials. By measuring one property across an entire class of materials, behavioral trends can be more easily analyzed and understood and perhaps applied to future layered materials. At the same time, important intrinsic material properties are being provided, which will be useful for future applications of these materials.

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Vita

Amanda Haglund was born in Homewood, Alabama, to the parents of Laura Pfister and Steven Haglund. She is the second oldest of eight children, Erin, Allen, Tom, Andrew, Sarah, Nicholas, and Jeremiah. After a combination of public school and homeschooling while moving around the country, she finished her high school education via homeschooling with a GED in Birmingham, Alabama. Next, she attended a year of pre-engineering courses at Jefferson State Community College in Birmingham, then transferred to the University of Alabama at Birmingham to complete her Bachelor's in Materials Science and Engineering with a minor in Chemistry. While at the university, she had many opportunities to experience research as an undergraduate, which encouraged her to pursue a graduate degree. After acceptance into graduate school at The University of Tennessee, Knoxville with a graduate research fellowship through the Bredesen Center for Interdisciplinary Education and Research, she graduated with her Masters of Science in 2015 followed by Doctor of Philosophy in 2019 in Materials Science and Engineering.