

**MAGNETIC PROPERTIES OF SELECTED TRANSITION-
METAL-BASED VAN DER WAALS MATERIALS**

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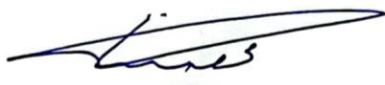
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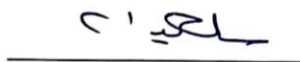
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I would like to dedicate this thesis to
My loving parents, brothers and sisters
My wife and my children

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LIST OF ABBREVIATIONS

vdW	:	Van der Waals
PM	:	Paramagnetism
FM	:	Ferromagnetism
FIM	:	Ferrimagnetism
AFM	:	Antiferromagnetism
TMTs	:	Transition Metal Trichalcogenides
VSM	:	Vibrating Sample Magnetometer
SQUID	:	Superconducting Quantum Interference Device
GCU	:	Gaussian-cgs Units
MF	:	Mean Field Model
2DI	:	2-dimension Ising Model
3DI	:	3-dimension Ising Model
3DH	:	3-dimension Heisenberg Model
CEs	:	Critical Exponents
CI	:	Critical Isotherm
RS	:	Relative Slope

AP	:	Arrott Plot
MAP	:	Modified Arrott Plot
KF	:	Kouvel-Fisher
WSR	:	Widom Scaling Relation
FOMT	:	First Order Magnetic Transition
SOMT	:	Second Order Magnetic Transition
FWHM	:	Full Width at Half Maximum
MCE	:	Magnetocaloric Effect
GMCE	:	Giant Magnetocaloric Effect
MR	:	Magnetic Refrigeration
RCP	:	Relative Cooling Power
AW	:	Atomic Weight
mwt	:	Molecular Weight
LIA	:	Lock-In Amplifier
MC	:	Maxwell Coil
HC	:	Helmholtz Coil

ABSTRACT

Full Name : [Fares Subait Hadi Obad]
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In this study, we synthesized and investigated the magnetic properties of several members of van der Waals transition metal based chalcogenides. The general chemical formula of these materials is MYX_3 , where M is a transition-metal (Cr or V), (Y is Sn or Sb), and X is a chalcogen (S, Se, and Te). The ac-susceptibility measurements revealed that $CrSnS_3$, $CrSbS_3$, and $CrSbSe_3$, exhibit magnetic order transition at $T_c = 119$ K, 115 K and 71 K, respectively. It is also observed that the transition temperature gradually increases with increasing the atomic mass (and the ionic radius) of the chalcogen element.

Two samples; namely $CrSnS_3$ and $CrSbS_3$ exhibit the highest transition temperatures among the known Cr-based chalcogenides, hence were further investigated. We used XRD powder analysis to study the structure of these two compounds and analysed by Fullproof Software. The magnetic properties of these two compounds were studied in detail using the results of ac-susceptibility measurements and isothermal magnetization. Furthermore, we investigated the critical behavior and magnetocaloric effect in $CrSnS_3$ and $CrSbS_3$ compounds. The critical exponents β and γ were determined using a modified Arrott plot and confirmed by the Kouvel-Fisher plot. In contrast, the critical exponent δ

was obtained by a critical isotherms analysis at T_C which is in agreement with the value obtained from the Widom relation. The reliability of the obtained critical exponent (β , γ , and δ) values was confirmed by the universal scaling behavior analysis. An examination of the material's critical behavior revealed that it does not exhibit the behavior of a single universality class, indicating a complex competition of different magnetic interactions. The magnetocaloric effect, including the change in magnetic entropy (ΔS_M), the change in adiabatic temperature (ΔT_{ad}), the specific heat change (ΔC_P), and the relative cooling power (RCP) has been deduced from the isothermal magnetization, $M(H, T)$ data. The examination of the magnetocaloric effect revealed that CrSnS_3 and CrSbS_3 compounds have a moderate value of RCP below 150K, suggesting that they are good candidates for magnetocaloric refrigerator below 150K.

ملخص الرسالة

الاسم الكامل: فارس سبييت هادي عباد

عنوان الرسالة: الخصائص المغناطيسية لمواد فان دير فال ذات بنية تعتمد على المعادن الانتقالية.

التخصص: الفيزياء

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بدأ الاهتمام بدراسة المواد الطبقية (Van der Waals Layered materials) منذ اكتشاف مادة الجرافين حيث أظهرت صفات فيزيائية مميزة قد تؤدي الى تطوير الاجهزة الالكترونية التي تعتمد على اشباه الموصلات. ما شد انتباه الباحثين في الآونة الاخيرة حول المواد الطبقية انه يمكن تحويلها من مواد ثلاثية الابعاد الى مواد رقيقة جدا يمكن اعتبارها ثنائية الابعاد. السبب الرئيسي في ذلك ان الترابط بين الطبقات في هذه المواد ضعيف في حين ان الطبقة الواحدة تكون متماسكة فيما بينها مما سهل في عملية فصل هذه الطبقات عن بعضها. في هذه الرسالة حضرنا اثنا عشر عينة من المواد الطبقية ذات الصيغة الكيميائية العامة MYX_3 . بعد دراسة العينات اتضح لنا ان ثلاث عينات منها تحتوي على تغير مفاجئ في خواصها المغناطيسية عند درجات حرارة مختلفة. اخترنا عيتين فقط من هذه العينات ($CrSbS_3$, $CrSnS_3$) حيث قمنا بالبحث اكثر في خصائصها المغناطيسية عند درجات الحرارة الحرجة باستخدام عدة طرق مثل (Critical isotherms Arrott plot, Kouvel-Fisher)، إضافة إلى خصائص تأثير المغناطيسية الحرارية الخاصة بها. وجد ان العيتين اظهرت درجة حرارة حرجة اكبر من ($CrSbSe_3$) لكنها اقل تاثير في الخصائص المغناطيسية الحرارية. ربما تحتاج بعض التعويضات من عناصر اخرى لكي تتحسن خواصها المغناطيسية.

CHAPTER 1

INTRODUCTION

Ferromagnetism (FM) is a physical phenomenon that is characterised by a magnetic ground state in a magnetic field. Normal magnets have a permanent magnetic moment even in the absence of an external magnetic field below a certain critical temperature (the Curie temperature T_C). Ferromagnetic materials are widely used in technology: from early usage in the compass and electric motors to modern usage in computers and data storage devices. Spintronics is a new emerging field in research that is expected to re-shape the future of all semiconducting technology. It is based on the ability to manipulate the magnetic spins and the charge of the electrons in the new semiconducting devices.

Since the discovery of graphene, 2-dimensional materials are becoming an exciting area of research in basic and applied sciences. These materials are known as van der Waals materials with strong in-plane covalent bonds. The layers are weakly coupled through van der Waals bonding (see Fig. 1)[1]. Various properties, such as electric and magnetic, are directly influenced by these strong in plane and weak part of plane couplings. Recently, ferromagnetism in van der Waals materials have been re-discovered in thin ferromagnets of $\text{Cr}_2\text{Ge}_2\text{Te}_6$, CrI_3 , and VSe_2 [2]. This discovery renewed the hope that magnetic van der Waals materials may lead to a better understanding of 2D intrinsic

ferromagnetism, and that may facilitate their usage in spintronics and other technological applications [3]–[10].

Transition metal trichalcogenides (TMTs) are promising candidates for van der Waals materials. The general chemical formula of TMTs given as MTX_3 where M represents a transition-metal (V, Cr, Fe, Mn), T represents either group IV (Si, Ge, Sn, Ni) or group V (P, Sb, As, Bi) elements and X represent the chalcogens elements (S, Se, Te) [11]–[14]. The structure and magnetic properties of these compounds are presented in the following section and in the literature review chapter 2.

In this thesis, we investigated selected transition metal members of the van der Waals series, in particular the MYX_3 series, where M is Cr or V, Y is Sn or Sb, and X is a chalcogen S, Se, and Te. In order to understand the nature of the magnetic phase transition, we studied the critical behavior of the phase transition. Scaling and universality class behavior analysis provided additional support for the critical behavior of these materials. The modified Arrott plots, Kouvel-Fisher analysis, and critical isotherm analysis provided the base for a detailed critical behavior analysis. As an additional exercise, we investigated the magnetocaloric effect in the MYX_3 series.

Objectives of Thesis

- Prepare polycrystalline samples of the van der Waals Ferromagnetic MYX_3 series.
- Investigate the optimal preparation conditions to obtain single crystals with stable structures of the MYX_3 series.
- Study in detail the critical behavior and obtain the critical exponents (β , γ , and δ) of the phase transition to understand the nature of the magnetic phase transition.
- Study the magnetocaloric effect in the MYX_3 series.

1.1 Van der Waal Materials

A layered material that possesses anisotropic bonds, strong covalent bonds in the electron volt-per-atom range within the plane, and weak van der Waals bonds in the meV/atom range perpendicular to the planar direction is referred to as a van der Waal (vdW) material (see figure 1). Graphite is an excellent illustration of a vdW material that only consists of one component. Strong covalent bonds are formed between atoms that are located within the plane. The interaction between layers is known as the van der Waals interaction, and it is a thousand times weaker than the interaction within layers. Because of this, we are able to peel away individual layers in order to investigate the unusual properties of layered materials. This type of naturally formed vdW surface is, in principle, defect-free and incredibly stable under the conditions of the surrounding environment.

In recent times, a lot of focus has been placed on the isotropic magnetic properties that vdW layered materials. The native structure of the vdW interaction along the c-axis results in a stark contrast between the in-plane spin-spin interaction and the interlayer interaction. Both interactions are characterized by their distinct properties. Not only is the magnetic ordering produced by the exchange interaction between magnetic moments in the same plane, but also the vdW interlayer interaction between layers significantly contributes to the production of ferromagnetic order. [1].

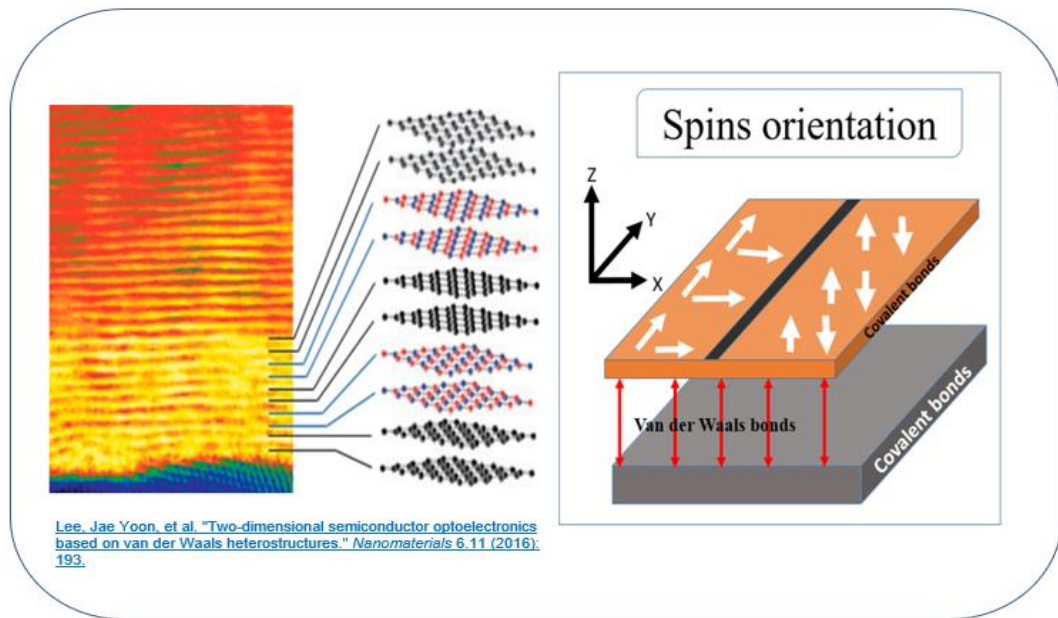


Figure 1: The Layered van der Waals Materials

1.2 Magnetism

The study of magnetism in solids is interesting and rewarding, to say the least. It is a purely quantum phenomenon that cannot be explained by classical physics. Although the origin of various forms of magnetic states and how they are created at a microscopic level is not fully understood, categorizing these magnetic states simplify the magnetic picture. Traditionally, there are five most fundamental forms of magnetic behavior: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism.

It was previously established that the behavior originates from permanent, microscopic magnetic moments possessed by some or all of the ions in the solid; the difference between the behaviors lies in the internal arrangement of these moments along with the existence of some basic exchange interactions. The periodic table provides basic clues about the overall magnetic moments associated with atoms or ions.

During the seventies of last century; a surge of theoretical and experimental activity involving two related magnetic systems: amorphous solids, in which no two atomic sites are identical, and disordered solids, in which different atoms occupy the sites of a regular crystal lattice irregularly. New types of magnetic order have been identified, some of which exist only in the absence of long-range order, while others are exclusive to regular crystal lattices. New types of magnetic order have been identified, some of which exist only in the absence of long-range order, while others are exclusive to regular crystal lattices. Since the original five types of magnetic behavior, the subject has expanded to encompass nearly three times as many, and the terminology has been multiplied proportionally. Mictomagnetism (later known as spin-glass), metamagnetism,

asperomagnetism, speromagnetism, sperimagnetism, spin glass, cluster glass, and a dozen more are just some of the names for magnetism that are currently in use. Theoretical investigation during that period, laid the ground for the recently discovered topological magnetic materials. Obviously, the field gives an outsider a confusing impression [15].

Two ideas underpin the interpretation of magnetic effects in solids. The first is that ions in a solid can be associated with a discrete magnetic moment. An externally applied magnetic field produces induced moments but also spontaneous moments can exist even in the absence of applied magnetic field. The second idea is that these microscopic moments interact with each other through quantum mechanical exchange interaction rather than the ordinary dipole-dipole forces experienced between bar magnets for example. The dipole-dipole forces are far too weak to be significant. The various forms of magnetic order in solids can be attributed to the fact that the so-called exchange forces between magnetic ions are dependent not only on their distance apart but also on their orientation [15].

1.3 Magnetization and Magnetic Susceptibility

The fundamental object in magnetism is the magnetic moment (μ). The magnetic moment of a system measures the strength and the direction of its magnetism. In atoms, the magnetic moment is the summation of the orbital magnetic moment of an electron and the intrinsic magnetic moment due to the spin of an electron. In solid materials, the magnetic moment density in a magnetic material is called magnetization (M). We can express the magnetization according to the volume or mass of solid material.

$$M_v = \frac{\mu}{V} \quad (1.1)$$

$$M_{mass} = \frac{\mu}{m} \quad (1.2)$$

where V and m are the volume or mass of solid material, the response linear of solid material to an external magnetic field (H) is called Magnetic susceptibility (χ).

Magnetic susceptibility, denoted by the symbol (χ), is a physical quantity that is used to describe the properties of a material when it is placed in an external magnetic field. The term "magnetic susceptibility" refers to the ratio of a material's magnetization when it is subject to a magnetic field, to the intensity of the field:

$$M = \chi H \quad (1.3)$$

According to the magnetic susceptibility values, three distinct categories can be assigned to every material [16]

- Diamagnetic materials: $\chi < 0$
- Paramagnetic materials: $0 < \chi \ll 1$
- Ferromagnetic materials: $\chi \gg 1$

The values of magnetic susceptibility are most frequently expressed with reference to the volume susceptibility (χ_v), mass susceptibility (χ_{mass}), and molar susceptibility (χ_{mol}). The equations defining to these terms are provided below:

$$\chi_v = \frac{M_v}{H} \quad (1.4)$$

$$\chi_{mass} = \frac{\chi_v}{\rho} \quad (1.5)$$

$$\chi_{mol} = \chi_{mass} \times \text{molar mass} \quad (1.6)$$

where ρ represents the density of the solid material and the molar mass is in unit g/mol of the solid material [17], [18].

Table 1: Magnetic Units

	Symbol	SI unit	CGS unit	conversion factor
Magnetic moment	μ	Am^2	emu	$1 \text{ Am}^2 = 10^3 \text{ emu}$
Volume Magnetization	$M_v (M)$	A/m	emu/cm ³	$1 \text{ A/m} = 10^{-3} \text{ emu/cm}^3$
Mass Magnetization	$M_{mass} (\sigma)$	Am^2/Kg	emu/g	$1 \text{ Am}^2/\text{Kg} = 1 \text{ emu/g}$
volume susceptibility	χ_v	Dimensionless	Dimensionless	magnetic field.
mass susceptibility	χ_{mass}	m^3/Kg	cm^3/g emu/ Oe.g	$1 \text{ m}^3/\text{Kg} = 10^3/4\pi \text{ emu/Oe.g}$
molar susceptibility	χ_{mol}	m^3/mol	cm^3/mol emu/ mol	

1.3.1 Several Methods are Used for Magnetic Susceptibility Measurements:

a- Older methods are based on the force effects of a magnetic field.

Older methods are based on the force effects of a magnetic field on a magnetized specimen, such as Faraday's and Guoy's methods [16]. French physicist Louis Georges Gouy developed the simplest method for testing transition metal complex magnetic susceptibilities. In 1889, He showed that the force is proportional to the material's volume sensitivity to a homogeneous external magnetic field. Gouy postulated that balance measurements for tubes of material hung in a magnetic field may estimate volume susceptibility using this method. [19]. The Faraday method is one way to measure low-volume V samples' magnetic susceptibility. The sample is placed between the two polar components of a Faraday balance and the magnetic force F exerted by an inhomogeneous field is measured.[20], [21].

b- Inductive methods

Inductive methods are another option. These methods use a change in coil inductance when a magnetically conductive specimen is embedded. An example of these methods is the vibrating sample magnetometer (VSM). Additionally, the correlation between magnetization and induction can be applied:

$$I = \frac{\Phi}{L} \quad (1.7)$$

The amount of current (I) that is induced in a circuit is proportional to the amount of flux (Φ) that is passing through it and the inductance of the circuit (L).

Magnetic properties can be measured using a vibrating-sample magnetometer (VSM), also known as a Foner magnetometer. VSM was developed in 1955 by Simon Foner of MIT Lincoln Laboratory and was first reported in 1959. Assuming the sample is magnetic, placing it in a constant magnetic field will cause its magnetization to align with the field. Most commonly, a piezoelectric material is used for this purpose. The magnetic field produced by the sample's magnetic dipole moment changes over time as it is subjected to oscillating vertical motion. The alternating magnetic field generates an electric current in the VSM's pickup coils. The higher the induced current, the stronger the magnetization of the sample. Therefore, a hysteresis curve is typically recorded, and the sample's magnetic properties are then inferred.

Modern methods measuring magnetization by induction is Superconducting Quantum Interference Device (SQUID magnetometer). The SQUID magnetometer takes advantage of the quantum interference effect, which enables magnetic measurement to be performed with such sensitivity that magnetic quantum units can be detected. Another modern method is magnetic resonance [22].

Magnetic susceptibility (χ) is an exciting quantity to measure for magnetically ordered samples by determining how it varies with temperature and applied magnetic field. Assume a piece of some material is cooled to a low temperature in a zero-field environment, and magnetic susceptibility is measured as temperature decreases. If the magnetic susceptibility increases rapidly as the temperature decreases, there is most likely a phase transition in the temperature region where the moment changes. A feature of magnetic susceptibilities, such as a peak, dip, or change in slope, may provide

additional information about the nature of the magnetic order. However, no single measurement will provide all the information required to characterize a sample fully [23].

1.3.2 Conventional Magnetic Measurements

The experimentalist has a wide variety of options available to them in terms of measurement methods. In this context, "conventional measurements" refers to those measurements that are carried out using commercial equipment and are common throughout the relevant body of academic research. However, there are three primary measurements that are used to gather the vast majority of the magnetic information that is available. These three are ac magnetic susceptibility measurements, static magnetic moment, and neutron scattering. Each method complements the others and offers slightly distinct insights into the magnetic properties of the sample under consideration, whether on a macroscopic or microscopic scale. The data provided by traditional measurement methods are invaluable because they are typically well-understood within the prevailing theoretical framework. This information is typically easy to interpret, allowing for quick and precise comparisons of various substances. When results from standard experiments do not match what can be deduced from current theories, it is a sign that there is some physics going on that we do not fully understand. The static magnetic moment (Magnetization Measurements) and an attempt to understand the dynamic magnetic susceptibility (AC Susceptibility) of systems are made in this work.

1.3.3 Static Magnetic Moment (DC-Magnetic Susceptibility)

The most common technique for determining a material's magnetic properties is to measure its static magnetic moment or magnetization (DC magnetic measurements).

The equilibrium value of magnetization in a sample can be calculated using DC magnetic measurements. By applying a constant magnetic field to the sample and then measuring the resulting magnetic moment, a DC magnetization curve $M(H)$ can be generated [24]. For this purpose, VSM has become a widely employed method. The DC-Magnetic Susceptibility, or static magnetic susceptibility, is typically defined as in Eq (1.3). Static magnetization measurements can be used to determine the paramagnetic moment per magnetic ion (via static susceptibility), saturation moment per ion, material ordering temperature, and anisotropy in a single crystal sample. At temperatures below T_C , the bias field modifies the domain structure of ferromagnetic materials, resulting in the presence of a bulk moment in the sample. For temperatures above T_C in ordered materials or any T in disordered materials, the bias field opposes thermal randomization, resulting in a paramagnetic state with zero moments [23].

1.3.4 AC-Magnetic Susceptibility

A time-varying magnetic field, known as the AC field, is applied to the sample in the process of AC-Magnetic Susceptibility Measurement (also known as the dynamic measurement of magnetic susceptibility). AC measurements provide information about the dynamics of magnetization that can't be obtained from DC measurements. This is due to the fact that the induced sample moment varies with time. Using a conventional AC

susceptometer, the measured signal is derived from an induced voltage in the pickup coils. This enables measurement to be performed without the need for sample motion.

Unlike static moment measurements, data collection does not require the application of an external field. However, the AC field frequency is limited to less than 102 kHz. The alternating field's amplitude can range from 0.1 to 10 Oe. AC susceptibility measurements have been helpful in determining critical indices associated with the first-order or second-order para-to-ferromagnetic phase transition. One significant disadvantage of this technique is the limitation in the applied value of the AC field and frequency [23], [24].

In the limit of low frequencies, where a comparison with dc measurements is possible and the applied ac field $H_{ac} = H_{ao} \cos \omega t$, the time-dependent magnetization can be expressed by:

$$M_{ac} = \frac{dM}{dH} H_{ac} \cos(\omega t) \quad (1.8)$$

where ω is the driving frequency, H_{ac} is the amplitude of the applied field, and the susceptibility χ of the sample is represented by (dM/dH_{ac}) , which is the slope of the $M(H)$ curve.

When the frequency is in the high limit, the magnetic moment of the sample is no longer able to keep up with the driving field and instead begins to fall behind. This effect is picked up by the detecting circuitry, which results in the measurement of two quantities: the magnitude of susceptibility, which is denoted by the symbol (χ) , and the

phase shift caused by the sample lag, which is marked by the symbol (φ) relative to the driving signal.

AC-susceptibility consists of an in-phase component denoted by the symbol (χ'), which is also referred as the real component, and an out-of-phase component, denoted by the symbol(χ''), which is referred to as the imaginary component:

$$\chi = \chi' + i\chi'' \quad (1.9)$$

The magnitude and the phase shift are related to χ' and χ'' by the following relations:

$$\begin{aligned} \chi' &= \chi \cos\varphi & \chi &= \sqrt{\chi'^2 + \chi''^2} \\ \chi'' &= \chi \sin\varphi & \varphi &= \arctan\left(\frac{\chi''}{\chi'}\right) \end{aligned} \quad (1.10)$$

The imaginary component (χ'') indicates dissipative processes occurring in the sample, which have unique causes in each substance. Different measurement procedures provide access to various types of information, and the most common measurements are [24], [25]:

- χ vs. Temperature
- χ vs. AC field amplitude
- χ vs. DC field bias
- χ vs. Driving frequency

- AC-Susceptometer

AC-Susceptometer is often configured with two primary coils that are coiled coaxially over two secondary coils, or pickup coils, that are wound in opposite directions

and electrically coupled in series see (Figure 2). The primary coil, also known as the excitation coil, is supposed to generate an almost uniform alternating magnetic field. Because the pickup coils are wound in opposition to one another, the total magnetic flux induced should ideally be zero in the absence of a sample and external sources. This is because one of the coils generates a current that is of the same magnitude but flow in the opposite direction, which indicates that an equilibrium state has been achieved. The equilibrium state is broken when the sample is placed in the center of one of the pickup coils, and the measured root-mean-square (rms) voltage sensed across the secondary coils is given by:

$$v(t) = -\frac{d\Phi}{dt} \quad (1.11)$$

which is time-dependent because of the ac field and is related to the sample response. This magnetization-dependent induced voltage is defined as follows:

$$v(t) = -Ll \frac{dM}{dt} \quad (1.12)$$

where l is the length of the primary coil and L is the mutual inductance per solenoid primary turn. According to $M = \chi H$ and the applied ac field $H_{ac} = H_{ao} \cos \omega t$ we get: $v_{rms} = 2\pi Ll f H_{rms} \chi$, this is the voltage that was measured at the coil while it was empty. When a sample is placed inside one of the pickup coils, the voltage balance is disturbed, and the amount by which it is affected is related to the amplitude of the sample's ac susceptibility as well as other parameters. Thus

$$v = \left(\frac{1}{\alpha}\right) V f H_a \chi \quad (1.13)$$

where v is the voltage, V is the volume of the sample, α is the calibration constant, and f and H_a are the frequency and magnitude of the applied magnetic field [26].

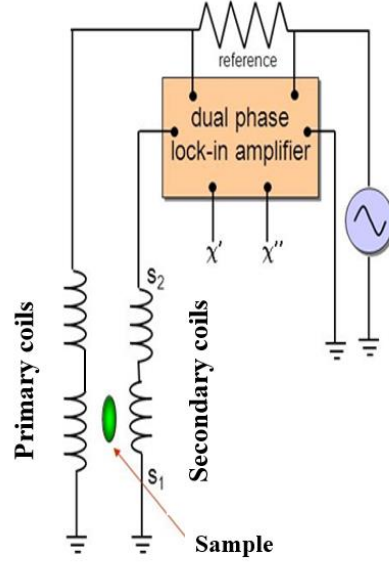


Figure 2: Coil Configuration of The Ac-Susceptometer

1.4 The Curie-Weiss Law

In accordance with the Curie-Weiss law, the following equation can be used to represent the temperature dependence of the molar magnetic susceptibility (χ_{mol}):

$$\chi_{mol} = \frac{C_M}{T-\theta} \quad (1.14)$$

where C_M is a molar Curie constant and θ is a Weiss constant (paramagnetic Curie temperature)[27].

The molar magnetic susceptibility (χ_{mol} or χ_m) is given by:

$$\chi_m = \frac{M}{H N} \quad (1.15)$$

where M is the magnetic moment of the sample, N is the number of moles of the material in the sample, and H is the applied external field [28].

The number of moles of the material in sample N is given by :

$$N = \frac{m}{mwt \text{ of substance}} \quad (1.16)$$

where m is the mass of the substance and mwt is the molecular weight of the substance.

Equation (1.15) can be rewritten as follows:

$$\chi_m = \frac{M \times mwt \text{ of substance}}{H \times m} \quad (1.17)$$

Using Gaussian-cgs units to determine χ_m

Table 2: Gaussian-cgs Units in Magnetism

Quantity	Symbol	Gaussian-cgs units
Magnetic moment	M	emu
The molecular weight of the substance	<i>mwt of substance</i>	g/mol
Applied external magnetic field	<i>H</i>	Oe
Mass	<i>m</i>	gram
Molar magnetic susceptibility	χ_m	emu/mol or emu/mol. Oe

According to equation (1.18) which represents the Curie-Weiss law, a plot of χ_m^{-1} vs. T reveals important information about the magnetic properties of a material. A plot that shows $\theta = 0$ indicates paramagnetism. A plot that shows $\theta > 0$ indicates ferromagnetism, and a plot that shows $\theta < 0$ indicates antiferromagnetism see figure 3.

Experimentally, at high temperatures, the molar Curie constant(C_m) can be found from the linear fit of the plot of χ_m^{-1} vs. T where :

$$C_m = \frac{1}{\text{slope}} \text{ (emu k/mol)} \quad (1.18)$$

The effective magnetic moments (μ_{eff}) were determined by Curie–Weiss fits of the molar magnetic susceptibility in the paramagnetic region as the following:

$$\mu_{eff} = \sqrt{\frac{3 K_B C_m}{N_A}} \quad (1.19)$$

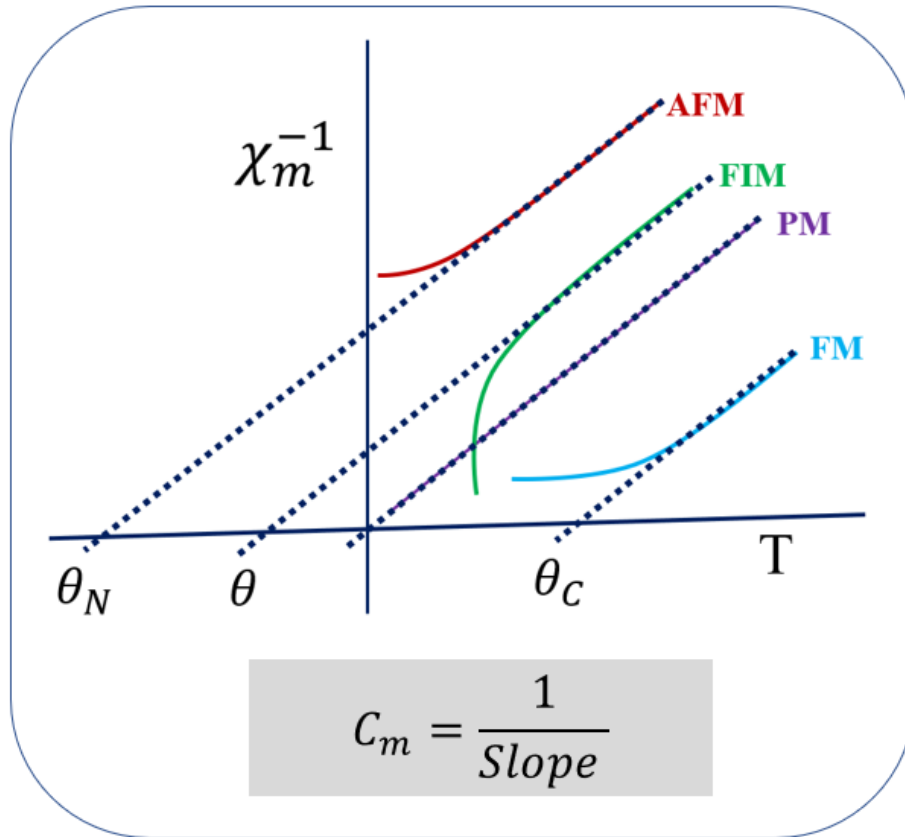


Figure 3: Schematic drawing of The Curie-Weiss Law

The value of effective magnetic moment(μ_{eff}) in the unit of Bohr magneton μ_B can be calculated from the following equation [29], [30]:

$$\mu_{eff} = \sqrt{\frac{3 K_B C_m}{N_A \mu_B^2}} \mu_B \quad (1.20)$$

where in Gaussian-cgs units :

$$K_B = 1.380649 \times 10^{-16} \text{ erg/K} \quad , \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\mu_B = 9.274 \times 10^{-21} \text{ erg/G}$$

$$\sqrt{\frac{3 K_B}{N_A \mu_B^2}} = 2.828$$

Substitute in equation (1.20), we end up with :

$$\mu_{eff} = 2.828 \sqrt{C_m} \mu_B \quad (1.21)$$

1.5 Critical Behavior

There are many theoretical models that describe the magnetic phase transition of materials; each one is characterized by several critical exponents. These exponents describe the order phase transition as it transforms from one phase to the other. The complete analysis of the magnetization as a function of temperature or applied field around the phase transition could help to determine these exponents. This method becomes a useful way to compare the experimental values of the critical exponents with those expected by the theory. For any order phase transition, the critical exponents (β , γ , and δ) are defined generally as the follows:

$$\beta \equiv M \propto (-\tau)^\beta \quad (1.22)$$

$$\gamma \equiv \chi \propto (-\tau)^{-\gamma} \quad (1.23)$$

$$\delta \equiv H \propto (M)^\delta \quad (1.24)$$

$$t \equiv \frac{T-T_c}{T_c} \quad (1.25)$$

where H is the applied magnetic field, M is the magnetization, χ is the susceptibility, t is the reduced temperature, T is temperature, and T_c is the critical temperature (where the phase transition occurs), generally known as Curie temperature for the magnetic phase transition. Table. 3. shows the values of the critical exponents (CEs) for various theoretical models, where:

MF is The Mean-Field Theory,

2DI is The 2-Dimension Ising Model,

3DI is The 3-Dimension Ising Model ,

3DH is The 3-Dimension Heisenberg Model.

Table 3: The Critical Exponent of Models

CE	MF	2DI	3DI	3DH
β	$\frac{1}{2}$	$\frac{1}{8}$	0.33	0.69
γ	1	$\frac{7}{4}$	1.24	1.39
δ	3	15	4.79	3

In order to extract critical exponents from experimental data of magnetization as a function of an applied field, it is often helpful to use the Arrott plot, which is based on the Arrott-Noakes equation of state:

$$H^{\frac{1}{\gamma}} = a \left(T - T_c M^{\frac{1}{\gamma}} + b M^{(\frac{1}{\beta} + \frac{1}{\gamma})} \right) \quad (1.26)$$

when the temperature is close to the critical point, the equation can be further reduced to:

$$b M^{\frac{1}{\beta}} = \left(\frac{H}{M} \right)^{1/\gamma} - a (T - T_c) \quad (1.27)$$

One then plots $M^{\frac{1}{\beta}}$ vs. $\left(\frac{H}{M} \right)^{1/\gamma}$ to get a family of curves. We can fit the curve using the values of the critical exponents for each model; otherwise, we should create a new modified Arrott plot.

Another method, the Kouvel-Fisher method, can be used to determine the critical exponents. The x and y intercepts of the fitting lines should be determined initially in this procedure. These intercepts can be related to M_s and $(\chi_0)^{-1}$ respectively as follows:

$$X(T) = \frac{(\chi_0)^{-1}}{d(\chi_0)^{-1}/dT} \quad (1.28)$$

$$Y(T) = \frac{M_s}{dM_s/dT} \quad (1.29)$$

From the definitions of the critical exponents, $X(T)$ and $Y(T)$ are related to the slopes $1/\beta$ and $1/\gamma$, respectively. We can repeat this method until we get the correct choice of the critical exponents. Then the exponent δ can be calculated from the Widom scaling relation according to the following equation:

$$\delta = 1 + \frac{\gamma}{\beta} \quad (1.30)$$

Furthermore, we can use the data of $M(H)$ at T_c to calculate the exponent δ independently. Using the definition of δ in equation (1.27), the plot of $\ln(M)$ vs. $\ln(H)$ would give a straight line with a slope of $1/\delta$. In addition, we can study the magnetic equation of state in the critical region that can be written as

$$M(H, t) = t^\beta f_\pm \left(\frac{H}{t^{\beta+\gamma}} \right) \quad (1.31)$$

where f_+ for $T > T_c$ and f_- for $T < T_c$ are regular functions, and t is the reduced temperature. This equation indicates that $Mt^{-\beta}$ as a function of $Ht^{-(\beta+\gamma)}$ yields two universal curves: one for temperature $T > T_c$ and the other for temperature $T < T_c$ [31].

1.6 Magnetocaloric Effect

The magnetocaloric effect (MCE) is a magneto-thermodynamic phenomenon that was found for the first time in pure Fe by Emil Warburg in 1881 [32]. Debye [33] and Giauque [34] both independently explained the origins of the MCE. Additionally, they suggested the first practical use of the MCE: the adiabatic demagnetization technique was employed to achieve temperatures lower than liquid helium, which had previously been the lowest experimentally practicable temperature. At the moment, there is a great deal of interest in making use of the MCE as an alternative technology for refrigeration, from room temperature all the way up to the temperatures at which hydrogen and helium liquefaction occur (20-4.2 K). Magnetic refrigeration (MR) offers the possibility of an energy-efficient and environmentally friendly alternative to the current vapor-cycle refrigeration technology [32] [33].

The method of the magnetocaloric effect is based on the following principle:

Suppose that we have a paramagnetic salt whose ions are carrying magnetic moment (spin). We suppose that these spins interact with the lattice and one another in such a weak way that they can be thought of as being relatively free. These properties are realized in some salts of the iron group and of the rare earth. The spins are randomly distributed when there is no magnetic field present. This random state of spin direction results in a relatively high entropy for the crystal. If we now activate a magnetic field H in an isothermal process, the spins will be aligned in the direction that the field is propagating in. The magnetic field will induce a certain degree of orientation, and the entropy will decrease in proportion to that degree of orientation. Now, if the field is

turned off adiabatically, the spins will become randomly oriented again, with no change to the entropy (The entropy remaining constant). Consequently, the temperature drops see figure 4 a and b [34].

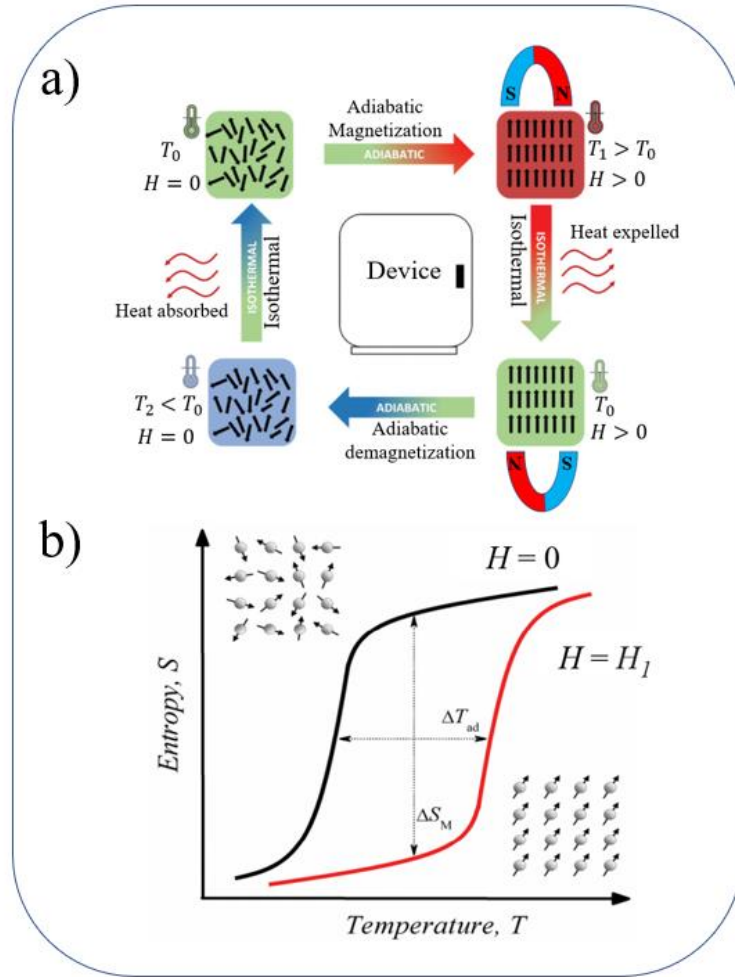


Figure 4: a) Scheme of The Magnetic Refrigeration Cycle of a Magnetocaloric./b) Schematic of The Total Entropy in Zero-Field ($H = 0$) and in Magnetic Field $H = H_1 (> 0)$

The term "magnetocaloric effect" (MCE) can refer to either the change in magnetic entropy, denoted by the symbol (ΔS_M), or the change in adiabatic temperature, denoted by the symbol (ΔT_{ad}). Both ΔS_M and ΔT_{ad} have been deduced from the isothermal magnetization, $M(H, T)$ data [35]–[37].

Thermodynamic theory predicts that as the magnetic field changes, there will be a corresponding change in the isothermal magnetic entropy, as shown by the expression [38]–[40]:

$$\Delta S_M(H, T) = \int_0^{H_{max}} \left(\frac{\partial S(H, T)}{\partial H} \right)_T dH \quad (1.32)$$

From Maxwell's thermodynamic relationship:

$$\left(\frac{\partial M(H, T)}{\partial T} \right)_H = \left(\frac{\partial S(H, T)}{\partial H} \right)_T \quad (1.33)$$

Eq. (1.32) can be rewritten as follows:

$$\Delta S_M(H, T) = \int_0^{H_{max}} \left(\frac{\partial M(H, T)}{\partial T} \right)_H dH \quad (1.34)$$

where M , S , T , and H are the magnetization of the material, the magnetic entropy, the temperature of the system, and the applied magnetic field, respectively.

Using data gathered from isothermal magnetization measurements, a numerical evaluation of the change in magnetic entropy was computed based on the formula (1.34). Despite the fact that magnetization was measured at small discrete field and temperature intervals, an approximation of ΔS_M can be derived from equation (1.34) using the following formula:

$$\Delta S_M(T, H) = \sum_i \frac{M_{i+1}(T_{i+1}, H) - M_i(T_i, H)}{T_{i+1} - T_i} \Delta H \quad (1.35)$$

where M_i and M_{i+1} are the magnetization values measured at temperatures T_i and T_{i+1} in a field H , respectively.

At a randomly selected temperature T , the adiabatic temperature change (ΔT_{ad}) can be approximated as:

$$\Delta T_{ad}(T, \Delta H) = - \int_{H_1}^{H_2} \frac{T}{C_P(H, T)} \left(\frac{\partial M(H, T)}{\partial T} \right)_H dH \quad (1.36)$$

From Maxwell's thermodynamic relationship equation (1.36) can be further reduced to [41]:

$$\Delta T_{ad} = - \frac{T}{C_P(H, T)} \Delta S_M \quad (1.37)$$

Equation (1.36) shows that a material's magnetocaloric effect (MCE) is significant when $(\partial M / \partial T)_H$ is large and $C_P(H, T)$ is small at the same time. This condition holds true for paramagnetic materials that are close to absolute zero Kelvin, where the magnetic susceptibility diverges, and the heat capacity nearly vanishes. However, near room temperature, the heat capacity is often quite high and follows the Dulong-Petit rule $C \sim 3NR$, where R is the molar gas constant, and N is the number of atoms [42].

Another important measure is the relative cooling power (RCP) which is defined as “the amount of heat transferred between two temperatures.” RCP depends on the magnitude of the change in the magnetic entropy between the two temperatures, T_1 and T_2 , and can be calculated according to the formula in Eq 1.38 [43]

$$RCP = \int_{T_1}^{T_2} |\Delta S_M| dT \quad (1.38)$$

According to the Curie-Weiss law for ferromagnetic, large $|\Delta S_M(T, H)|$ is expected at Curie point T_C [44]. The influence of short-range order and spin fluctuations well above the T_C in an order-disorder magnetic phase transition frequently reduces the maximum possible $\left(\frac{\partial M(H, T)}{\partial T}\right)_H$, effectively decreasing the maximum MCE.

Theoretically, a first-order phase transformation should take place at a constant temperature, therefore $\left(\frac{\partial M(H, T)}{\partial T}\right)_H$ may be infinitely large, leading to a massive, giant magnetocaloric effect (GMCF). However, the extraordinary hysteresis that manifests in some materials during a first-order phase transition may reduce the cooling process's actual efficiency. On the other hand, the second-order magnetic phase transition materials typically have a smaller value of ΔS_M than first-order materials, but their magnetization shows excellent reversibility for temperature/magnetic field cycling, which is extremely desirable for the application of magnetic refrigeration technology [38], [39],[45].

1.6.1 Specific Heat Change (ΔC_P)

The fast and accurate determination of magnetic field–temperature (H, T) phase diagrams in condensed matter physics are essential for optimal modeling and prediction. Thermal parameters like specific heat and entropy help us understand microscopic systems. Over the past decade, many thermodynamic investigations in very high magnetic fields have investigated specific heat (C_p) and magnetocaloric effect (MCE). The heat capacity (C) of a material can be considered a fundamental thermodynamic variable. It is defined as the amount of energy or heat, denoted by (δq), that is necessary to raise the temperature of a material by a certain amount (δT) [46], [47] where:

$$C = - \frac{\delta q}{\delta T} \quad (1.39)$$

Using the definition of entropy (S):

$$T dS = \delta q \quad (1.40)$$

The specific heat can be expressed as :

$$C_P = T \left(\frac{\partial S(H,T)}{\partial T} \right)_H \quad (1.41)$$

The following expression can be used to compute the specific heat change (ΔC_P) from the magnetic contribution to the entropy change (ΔS_M) produced in the material:

$$\Delta C_P = T \left(\frac{\partial \Delta S_M}{\partial T} \right)_H \quad (1.42)$$

CHAPTER 2

LITERATURE REVIEW

2.1 The Structure and Magnetic Properties

The unique physical and chemical features of layered phases are what make them such attractive compounds. These characteristics are rarely seen in three-dimensional materials. The sequence of layered compounds known as transition metal dichalcogenides is both significant and well-known. Covalent bonding occurs mostly in the structural slabs of these compounds. In these, infinite sheets of strongly bonded slabs composed of two anionic planes enclosing a cationic plane. Because the van der Waals forces that link the structural slabs together are relatively weak, this type of appealing physical features (layered phases) can be found [48].

Several new host material families have recently been reported, such as layered lanthanide oxychlorides, transition-metal thiophosphates, and novel transition-metal oxysulfides. Of these new host systems, the MTX_3 phases have very unusual structural features as well as interesting physical properties including spontaneous magnetization, low-dimensional magnetic behavior, and transition-metal site rearrangement upon intercalation. MTX_3 compounds are van der Waals materials where M represents a transition-metal (V, Cr, Fe, Mn), T represents either group IV (Si, Ge, Sn, Pb) or group V (P, Sb, As, Bi) elements and X represent the chalcogens elements (S, Se, Te). They are likely to have interesting magnetic properties related to 1D, 2D and 3D magnetism,

which is determined by the structural type of the compound and by the M cations. In MTX_3 compounds, Group IV compounds differ significantly from group V compounds in that group IV elements replace the group V phosphorus (P) atom inside the $(P_2X_6)^{4-}$ a skeleton with $(A_2X_6)^{6-}$ bipyramid ions, and group IV atoms have one fewer electron than group V atoms. As a result, group IV compounds are more negatively charged and have larger nominal metal cation valences (3^+) as opposed to (2^+) in group V compounds. This alteration is responsible for significant adjustments in the resulting magnetic and electrical properties. It may cause increased in-plane negativity and stronger 2-dimensional behavior, such as stronger anisotropy effects. For example, group V compounds like MPX_3 and MPS_3 were studied by B L Chittari et-al.[49] and R. Brec et-al.[48], respectively. Group IV compounds like MAX_3 were studied by B L Chittari et al.[50].

Less research has been done on MTX_3 compounds with $M=Cr$ than other transition metal chalcogenides. There are various structure types of the compound $CrTX_3$, which belongs to a subgroup of the MTX_3 group of ternary chalcogenides. Most structures are formed by CrX_6 polyhedra (either octahedra or trigonal antiprisms) stacked in various ways, which can lead to the formation of 1D, 2D, or 3D infinite networks of CrX_6 octahedra responsible for the dimensionality and type of magnetic interactions. These findings suggest that the symmetry and type of $CrTX_3$ structure formed are highly sensitive to the M cation. Recently, it was demonstrated that nonmagnetic Sb could partially replace Cr, resulting in the formation of a new spinel compound with spin glass magnetic behavior [51].

The structure type of CrSbX_3 ($\text{X}=\text{Se}, \text{S}$) is closely related to those of GaCrSe_3 and CeCrSe_3 . V. V. Volkov et al. studied the compounds CrTX_3 in which $\text{T}=\text{Sb}$ and $\text{X}=\text{Se}$ or S . They used high-resolution electron microscopy (HREM) along the $[010]$ direction to directly generate the CrSbX_3 structural model. It consists of edge-sharing CrX_6 octahedra forming double rutile chains along the b -axis and separated by columns of Sb atoms, which are roughly positioned in the pentagonal tunnels of X atoms. The structural model was refined by the full profile XRD powder Rietveld method. The compound CrSbS_3 is orthorhombic with lattice parameters ($a = 8.68\text{\AA}$, $b = 3.62\text{\AA}$, $c = 12.88\text{\AA}$). It is isostructural to CrSbSe_3 . Both compounds seem to have properties consistent with 1D ferromagnetism below the Curie temperature. As mentioned, 1D ferromagnetic properties for both compounds (CrSbSe_3 , CrSbS_3) can be expected from magneto-structural considerations. Due to the absence of a direct metal bond Cr—Cr , the only connection between the paramagnetic Cr atoms should be the superexchange interaction via the ligand bridges Cr—Se—Cr . Under these conditions, only quasi-1D ferromagnetic superexchange coupling is expected to occur in both compounds. This means the magnetic moment is formed only by 3d electrons, and the magnetic properties will be governed only by spin exchange interactions. It was discovered that CrSbS_3 sulfide exhibited magnetic behavior. The compound exhibits its typical paramagnetic behavior above T_C . Their magnetization below T_C is field-dependent; it tends to saturate only at low temperatures. The small hysteresis loop that results from this lack of complete FM ordering is suggestive of the low-dimensional nature of their magnetism [51].

A wide range of van der Waals materials is found in Transition Metal Trichalcogenides (TMTs). Recently, B Chittari et-al. used the density functional theory to

investigate TMTs compound with the MAX_3 formula where ($\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$; $\text{A} = \text{Si}, \text{Ge}, \text{Sn}$, and $\text{X} = \text{S}, \text{Se}, \text{Te}$). They found that the structure is almost truncated as in the bulk form, and the atomic structure for the unit cell has two possible choices, a rectangular cell represented with red lines and a smaller triangular cell represented by black dashed lines arranged in a honeycomb (see Fig. 5.). Also, they found that the magnetic phase is typical for these van der Waals materials and the configuration of the magnetic phase has two possible choices which include semiconducting ferromagnetic (FM) phases or semiconducting antiferromagnetic (AFM) phases depend on the combination between the transition metal/chalcogen elements [50].

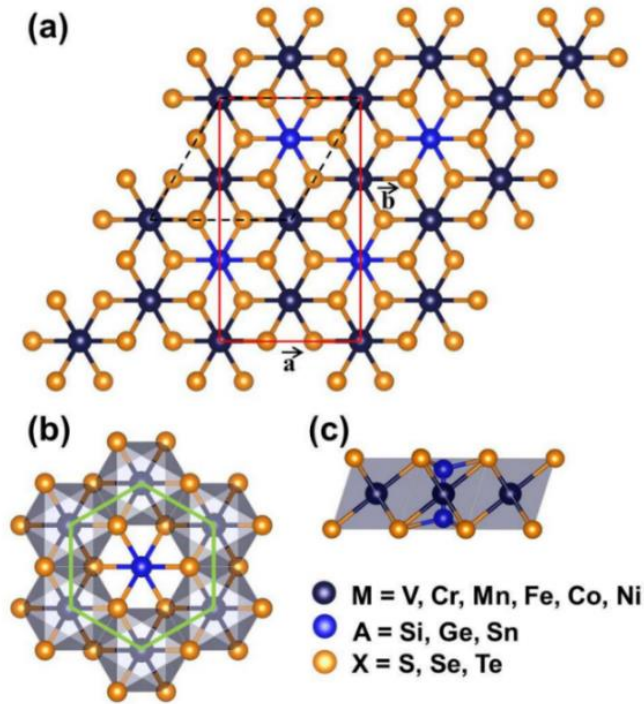


Figure 5: Schematic Representation of the Atomic Structure of MAX_3 Compounds

B L Chittari et-al. surveyed the magnetic properties and electronic structure of MPX_3 ($M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn$, and $X = S, Se, Te$). They found that the structure of bulk crystals consists of individual layers stacked in an ABC sequence that are held together by van der Waals forces. The magnetic properties were similar to the result of B Chittari et al [52]. L Webster et-al. and W Zhang et al. studied the CrX_3 ($X = Cl, Br$, and I). The structure was similar to the previous groups. The magnetic phase was ferromagnetic for $X=I$ or Br with a critical temperature of 68 and 32.5 K, respectively, and antiferromagnetic for $X=Cl$ with $T_c = 14K$ [53], [54]. The crystal structure and the magnetic properties of bulk $CrXTe_3$ ($X = Si, Ge$) were studied by neutron powder diffraction, X-ray diffraction, magnetization, and susceptibility measurements. The sample was prepared by heating a stoichiometric mixture of the elements in an evacuated sealed quartz tube, followed by cooling for ten hours. The hexagonal cell parameters of the single crystal are: $a = b = 6.7578(6)\text{\AA}$, $c = 20.665(3)\text{\AA}$ for $X=Si$ and $a = b = 6.8275(4)\text{\AA}$, $c = 20.5619(9)\text{\AA}$ for $X=Ge$. The phase structure was a ferromagnetic semiconductor with a critical temperature T_c of 33K and 61K for $X= Si, Ge$, respectively [55]–[79]. More investigation of this van der Waals crystal $CrXTe_3$ ($X = Si, Ge$) was done by Xingxing Li et al. based on first-principles calculations incorporating classical Heisenberg model Monte Carlo simulations. They found that the van der Waals gap (layers spacing) was ($d_0 \approx 3.3\text{\AA}$) (see Fig. 6.), and the phase structure is well preserved even after cutting the bulk form into nanosheets with a critical temperature T_c at 35.7K and 57.2K for $X= Si$ and Ge , respectively [80]–[88]. The same series of bulk $CrXTe_3$ was studied by H L. Zhuang et-al. But they used $X= Sn$ instead of ($X = Si, Ge$) based on hybrid density functional methods of single-layer $CrSnTe_3$ structure. They found that the

magnetic phase was semiconducting ferromagnetic with $T_c = 170\text{K}$ [89]. Another series of Cr, the layered van der Waals crystal of CrXSe_3 ($X = \text{Sn, Ge, Si}$), was investigated by Zihan et al. as a monolayer. They found that the phase transition is a ferromagnetic transition with magnetic moments of $6.0\mu_B$ per unit cell. Additionally, they are semiconducting with energy band gaps of 0.76, 0.87, and 1.1 eV for X being Sn, Ge, and Si, respectively[90]. The spin glass phase was exhibited in CrSnSe_3 below 30K[91]. Depending on Magnetic susceptibility measurements, an antiferromagnetic ordering of $\text{Cr}_2\text{Sn}_3\text{Se}_7$ was shown at 12 K, which could be related to a spin glass transition [92]. Based on density functional theory, the magnetic and electronic properties of 2D ferromagnetic semiconductors of CrGeS_3 have been explored by W.Wan et-al. [93]. However, many other combinations have been predicted from theory but still need to be explored experimentally.

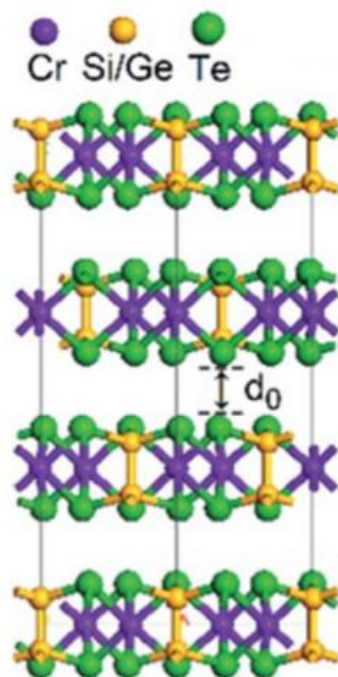


Figure 6: Crystal Structure of Bulk CrXTe_3 ($\text{X} = \text{Si, Ge}$)

2.2 The Critical Behavior

The critical behavior of bulk CrI_3 was studied by Y Liu et-al. around the paramagnetic to the ferromagnetic phase transition. They found that the critical temperature is $T_c = 60\text{K}$. They use the Kouvel-Fisher (KF) method to calculate the Critical exponents β and γ , whereas for δ they used a critical isotherm analysis at T_c [94]. The critical behavior of CrXTe_3 ($T_c = 31$ and 67.9K for $\text{X}=\text{Si}$ and Ge respectively) was investigated around the paramagnetic-ferromagnetic phase transition. The Critical exponents were obtained using various techniques such as the Kouvel-Fisher plot, modified Arrott plot, and critical isotherm analysis [95], [96]. M. Kh. Hamad et-al. investigated the critical behavior of $\text{CrTe}_{1-x}\text{Sb}_x$ samples using the Kouvel-Fisher plot and modified Arrott plot (MAP) [97].

Yu Liu et al. reported critical behavior in a quasi-one-dimensional ferromagnetic CrSbSe_3 single crystal. The critical behavior analysis around $T_c \sim 70\text{ K}$ gives that the critical exponents $\beta = 0.26(1)$, $\gamma = 1.32(2)$, and $\delta = 6.17(9)$ for $\text{H} \parallel \text{a}$, while $\beta = 0.28(2)$, $\gamma = 1.02(1)$, and $\delta = 4.14(16)$ for $\text{H} \parallel \text{b}$. From the calculated critical exponents, we can infer that the anisotropic magnetic coupling in CrSbSe_3 is highly sensitive to the direction of the applied magnetic field. Furthermore, there are several papers that studied the critical behavior around the phase transition [98]–[126].

2.3 The Magnetocaloric Effect

The magnetocaloric effect was originally discovered in 1880 by E. Warburg in pure Fe. However, the observed adiabatic temperature change ΔT_{ad} upon demagnetization is very small and occurs at temperature much higher than room temperature. This limits the practical using Fe and other **3d** transition metals. The magnetocaloric effects typically show a peak-like behavior near the Curie temperature of the magnetic material. Rocker & Kohlhaas [127] have studied the magnetocaloric effect in Co in ten different magnetic fields up to 2.32 T. Potter has studied it in Fe in three magnetic fields up to 0.8 T [128], and Hashimoto et al. [129] detected it in Ni at 1.78 T. The maximum ΔT_{ad} values measured are 3.25 K at 2.32 T for Co, 2.0 K at 0.8 T for Fe, and 1.32 K at 1.78 T for Ni. For a given magnetic field, the relative cooling power [RCP(T)] values are 182 K² for Co at 2.32 T, 286 K² for Fe at 3.0 T, and 63 K² for Ni at 3.0 T. All these RCP(T) values are much smaller than the Gd RCP(T) value. Gadolinium (Gd) is the prototype of magnetocaloric material, and considered very efficient room-temperature magnetic refrigerant [130]. It has the largest measured value of ΔS_M in the group of rare earth and their alloy, which was ~ 13.7 J /Kg K at T_C (~ 293 K) under a magnetic field of $H = 8$ T [44].

Rare earth based magnetocaloric materials are very expensive and plagued with oxidation problems. Alternative materials such as transition metal-based alloys and intermetallic compounds have been investigated for their possible use in magnetocaloric effect (ΔT_{ad}). Hirschler and Rocker, for example, have directly evaluated the magnetocaloric effect of the solid solution alloy of Si in Fe, $\text{Fe}_{0.9357}\text{Si}_{0.0643}$ [127]. The magnetocaloric effect exhibits a roughly typical caret-shaped peak at 3T, with a

maximum of ($\Delta T_{ad} = 5$ K measured at 1013 K, which is a little lower than that of pure Fe ($\Delta T_{ad} = 5.2$ K at 1042 K). Between 983 and 1043 K, $\text{Fe}_{0.9357}\text{Si}_{0.0643}$ has a relatively high cooling power $\text{RCP}(T) = \sim 300 \text{ K}^2$. However, these temperatures are very high compared to room temperature. Znamenskii and Fakidov investigated another solid solution alloy which was $\text{Mn}_{0.225}\text{Cu}_{0.775}$ [33]. In magnetic fields ranging from 0.13 to 1.38 T, the MCE in this alloy has been directly measured between 77 and ~ 130 K. The MCE is positive for ΔH greater than 0.42 T down to 77 K, but for smaller magnetic fields, the MCE turns negative at the experiment's lowest temperature, indicating the occurrence of antiferromagnetic interactions in $\text{Mn}_{0.225}\text{Cu}_{0.775}$. With the exception of the negative sign, the MCE in $\text{Mn}_{0.225}\text{Cu}_{0.775}$ exhibits typical caret behavior, peaking at 95 K ($\Delta T_{max} = 0.145$ K for $\Delta H = 1.38$ T) and has a shallow relative cooling power $\text{RCP}(T) = \sim 3.6 \text{ K}^2$ between 83 and 108 K.

The magnetocaloric properties of several 3D-based intermetallic compounds, with relatively large magnetocaloric effect. Some of the promising compounds are: $\text{Ni}_2(\text{Mn}_{1-x}\text{Nb}_x)\text{Sn}$, $\text{Mn}(\text{As}_{1-x}\text{P}_x)$, $\text{Mn}_{3-y-x}\text{Cr}_y\text{AlC}_{1+x}$, $\text{Ni}_2(\text{Mn}_{1-x}\text{V}_x)\text{Sn}$, Cr_3Te_4 , $(\text{Hf}_{0.83}\text{Ta}_{0.17})\text{Fe}_{2+x}$, and FeRh have been studied. Using direct magnetocaloric effect measurement, Kuhrt et al. investigated $\text{Mn}(\text{As}_{1-x}\text{P}_x)$ in magnetic fields up to 7T [131]. When the magnetic field is reduced to low levels (below 3 T), the MCE for both $x = 0.09$ and 0.08 exhibits a double-peak behavior consistent with an antiferromagnetic ground state and magnetic field-induced metamagnetism, but when the magnetic field is increased to high levels (below 7 T), the MCE behavior changes to a conventional pattern. For $\text{Mn}(\text{As}_{0.92}\text{P}_{0.08})$ and $\text{Mn}(\text{As}_{0.91}\text{P}_{0.09})$, the MCE maximum occurs at 225 K and 233 K and in 7T, with ΔT_{ad}

peaking at about 1.3 K respectively. The relative cooling power $RCP(T)$ for both alloys at $H = 7$ T is around 70 K^2 , which is quite a low value

Herbst et al. used the indirect MCE (magnetization measurements) to investigate three $(\text{Hf}_{0.83}\text{Ta}_{0.17})\text{Fe}_2\text{C}_x$ alloys, where $x = 0.09, 0$, and -0.09 , at low magnetic fields (0.9 T) [132]. Near room temperature, antiferromagnetic ordering was observed in all three materials. Their MCE values were also down ($-5.6, -16$, and $-11 \text{ mJ/cm}^3 \text{ K}$, respectively), showing behavior that is quite close to the norm. Relatively low values of $RCP(S)$ ($\sim 178, \sim 247$, and $\sim 254 \text{ mJ/cm}^3$) were obtained for $x = 0.09, 0$, and -0.09 , respectively. It was noted by Herbst et al. that the sharpness of the magnetic phase transition at $x = -0.02$ suggests the possibility of the enormous magnetocaloric effect with $-\Delta S_M$ surpassing $220 \text{ mJ/cm}^3 \text{ K}$, but no quantitative MCE data were provided.

FeRh is the first reported intermetallic substance with an enormous magnetocaloric effect at or near room temperature [133], [134]. Unusual features of the MCE behavior in this material include its sign (being negative for a positive ΔH), its irreversibility, and its great sensitivity to processing history. Between 296 and 316 Kelvin, the FeRh MCE exhibits an inverted skyscraper behavior, with a significant relative cooling power, $RCP(T)$ of -166 K^2 between those temperatures.

At 316 K and 2 T magnetic field, the conventional MCE (measured directly) of Cr_3Te_4 approaches $\Delta T_{ad} = 1.1 \text{ K}$. The relative cooling power of Cr_3Te_4 , which is equal to 41 K^2 at this temperature, is quite low.

Recently, since their discovery by Morelli et al., the magnetocaloric characteristics of the lanthanum-manganese perovskite complexes $(\text{La}_{1-x}\text{M}_x)\text{MnO}_3$, where $M = \text{Li, Ba, Na}$,

Ca, K, Y, and Sr, have been the subject of extensive research [135]. The magnetocaloric effect at temperatures between 250 and 350 K for some of these phases is reasonable but not outstanding magnetocaloric effect values (about one-third of Gd metal at best). Others have since been discovered with a field change from 0 to 1 T, the ΔS_M values in several of these phases are comparable to gadolinium's value [33].

Maximum magnetocaloric effect were found in the lanthanum manganites ($\text{La}_{1-x}\text{Ca}_x$) MnO_3 phases for $0.20 \leq x \leq 0.33$, with ΔS_M values from -18.2 to -21.8 $\text{mJ/cm}^3 \text{ K}$.

It should be noted that Morelli et al. [135] measured the magnetocaloric effect for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and found (as estimated from the 1 and 2 T field changes) a much smaller ΔS_M value, $\sim -4.8 \text{ mJ/cm}^3 \text{ K}$, with $\delta T_{\text{FWHM}} = 62 \text{ K}$, which is a much wider breadth of the peak compared with what Guo et al. [44] measured, $\delta T_{\text{FWHM}} = 11 \text{ K}$ and $\Delta S_M = -32.7 \text{ mJ/cm}^3 \text{ K}$ for a field change of 1.5 T. It was noted that $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ with compositions close to $x = 0.33$ had been proposed as promising candidates for use as magnetic refrigerants.

In general, the MCE in transition metal-based alloys is lower than that in lanthanide-based alloys for the same temperature range, according to the limited amount of experimental data that is currently available. Due to this, they are unlikely candidates for use as magnetic refrigerant materials below 300 K, but they could be valuable materials for magnetic refrigerators/heat pumps that reject heat well above room temperature. But if new 3d-based alloys are discovered with enormous MCEs that are reversible and of a magnitude comparable to that seen in FeRh, they would be a potential supply of materials for highly efficient magnetic refrigerants.

The critical behavior and Anisotropic magnetocaloric effect in a quasi-one-dimensional ferromagnetic CrSbSe_3 single crystal are reported by Yu Liu et al.[136]. The scaling investigation of the magnetic entropy change ΔS_M has confirmed that the PM-FM transition is second-order in nature and occurs close to $T_c = 70$ K. The relative cooling power RCP is 163.1 J kg^{-1} for the easy a axis and 142.1 J kg^{-1} for the hard b axis at T_c with a magnetic field change of 50 kOe. $-\Delta S_M^{\max}$ is $2.16 \text{ J kg}^{-1} \text{ K}^{-1}$ for the easy a axis and $2.03 \text{ J kg}^{-1} \text{ K}^{-1}$ for the hard b axis representing the maximum magnetic entropy change. The critical temperature and Anisotropic magnetocaloric effect in Chromium-Based Compounds are summarized in the following figure[137]–[143]:

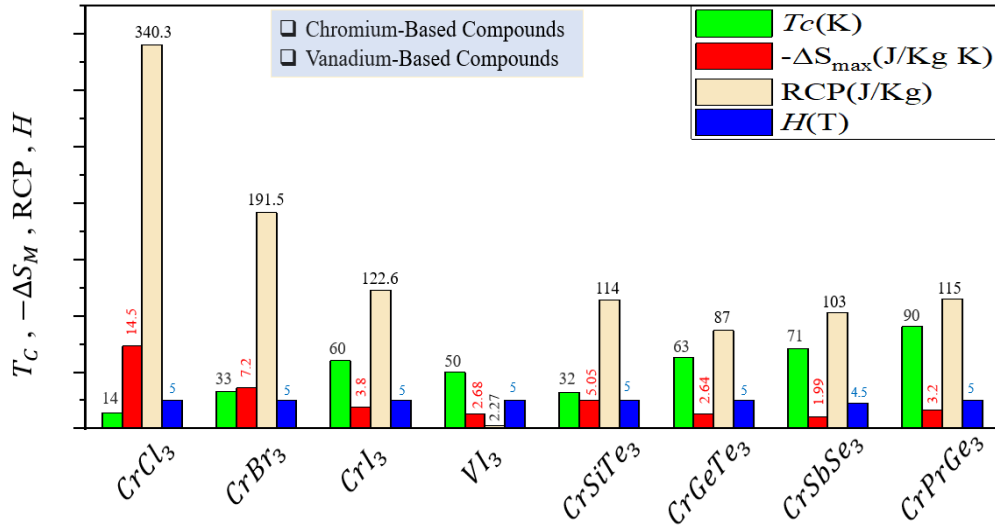


Figure 7: The Critical Temperature and Anisotropic Magnetocaloric Effect in Chromium-Based Compounds

In 1997, two significant developments made commercial and industrial production of magnetic refrigerators more realistic. The first is that a prototype system for magnetic refrigeration at nearly room temperature was developed by Zimm et al. at Ames Laboratory. The second is that $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ exhibited a giant MCE, as observed by Pecharsky and Gschneider. For comparison, the magnetocaloric effect of $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ is about twice as large as that of Gd [$-\Delta S_M^{\max} = \sim 19 \text{ J/Kg K}$ at T_C ($\sim 276 \text{ K}$) under a magnetic field of $H = 5 \text{ T}$]. The ΔT_{ad} value of $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ is larger than the corresponding ΔT_{ad} values for Gd by $\geq 30\%$ [$\Delta T_{ad} = 15.5 \text{ K}$ at T_C ($\sim 276 \text{ K}$) under a magnetic field of $H = 5 \text{ T}$][144].

Several materials with giant/large MCE have been realized in the last three decades, including MnAs-based compounds manganites $(\text{RE}, \text{M})\text{MnO}_3$, ($\text{RE} = \text{lanthanide}$, $\text{M} = \text{Ca}$, Sr , and Ba) $(\text{RE}, \text{M})\text{MnO}_3$, RECo_2 ($\text{RE} = \text{Er}$, Ho , and Dy) alloys, MnTX ($\text{T} = \text{Co}$, Ni , and Fe , $\text{X} = \text{Si}$, Ge) based compounds, $\text{La}(\text{Fe}, \text{Si})_{13}$ and related compounds, Ni-Mn-X ($\text{X} = \text{Ga}$, In , and Sn) based Heusler alloys and a few intermetallic compounds based on rare earth elements [40].

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 Sample Preparation

The polycrystalline and several single crystalline layered van der Waals materials have been prepared. The general formula is MYX_3 series where M is transition-metal (Cr or V), (Y is Sn or Sb), and X is a chalcogen (S, Se, or Te). Stoichiometric ratios of high purity elements (~99.99%) have been used. The powder of these elements of each sample was mixed, ground, and then vacuum-sealed in quartz tube under a partial pressure of argon. Annealing was performed on these tubes according to different temperature procedures to obtain high-quality samples.

The following tables provide an illustration of the stoichiometric ratios of these elements for each sample where we prepared 12 samples (compounds).

Table 4: Concentration of Each Constituent for 2 Grams of Polycrystalline CrSnX₃.

Element	Wt- (g/mol)	CrSnS ₃	CrSnSe ₃	CrSnTe ₃	MP°C	BP°C
Cr	51.996	0.38968	0.2552	0.1879	1907	2672
Sn	118.69	0.8895	0.5824	0.4289	231.93	2602
S	32.06	0.7208			112.8	444.7
Se	78.96		1.1624		217	684.8
Te	127.6			1.3832	449.6	987.8
CrSnS ₃	266.876					
CrSnSe ₃	407.566					
CrSnTe ₃	553.486					
		2 g	2 g	2 g		

Table 5: Concentration of Each Constituent for 2 Grams of Polycrystalline CrSbX₃.

Element	wt-g/mol	CrSbS ₃	CrSbSe ₃	CrSbTe ₃	MP°C	BP°C
Cr	51.996	0.3853	0.2533	0.1868	1875	2665
Sb	121.75	0.9021	0.5930	0.4375	630	1380
S	32.06	0.7126			119	444.6
Se	78.96		1.1538		217	685
Te	127.6			1.3756	449.5	989.8
CrSbS ₃	269.926					
CrSbSe ₃	410.626					
CrSbTe ₃	556.546					
		2 g	2 g	2 g		

Table 6: Concentration of Each Constituent for 2 Grams of Polycrystalline VSnX₃.

Element	wt-g/mol	VSnS ₃	VSnSe ₃	VSnTe ₃	MP°C	BP°C
V	50.9414	0.3833	0.2506	0.1844	1900	3260
Sn	118.69	0.8930	0.5839	0.4297	231.9	2270
S	32.06	0.7237			119	444.6
Se	78.96		1.1654		217	685
Te	127.6			1.3859	449.5	989.8
VSnS ₃	265.8114					
VSnSe ₃	406.5114					
VSnTe ₃	552.4314					
		2 g	2 g	2 g		

Table 7: Concentration of Each Constituent for 2 Grams of Polycrystalline VSbX₃.

Element	wt-g/mol	VSbS ₃	VSbSe ₃	VSbTe ₃	MP°C	BP°C
V	50.9414	0.37893	0.2488	0.1834	1900	3260
Sb	121.75	0.9057	0.5945	0.4384	630	1380
S	32.06	0.7154			119	444.6
Se	78.96		1.1567		217	685
Te	127.6			1.3782	449.5	989.8
VSbS ₃	268.8714					
VSbSe ₃	409.5714					
VSbTe ₃	555.4914					
		2 g	2 g	2 g		

3.2 Experimental Techniques:

3.2.1 X-ray Diffraction

All samples have been analyzed by X-ray diffraction (XRD) using a Bruker XRD D2-Phaser fitted with Cu K α ($\lambda=1.54056$ Å) beam. FULLPROOF has been used to analyze the XRD-patterns (10-80° range) using the Rietveld refinements. Bragg's law is the foundation of X-ray structural analysis which is given by:

$$2d_{hkl}\sin\theta_{hkl} = n\lambda \quad (3.1)$$

where hkl are the Miller indices, d is the inter-planes spacing, n is an integer, θ is the Bragg angle, and λ is the X-ray wavelength [145].

3.2.2 Vibrating Sample Magnetometer (VSM)

The magnetization isotherms have been measured using our 9-Tesla vibrating sample magnetometer (VSM) (Fig.8). To generate a signal; the sample is set to vibrate between two oppositely wound coils placed in a uniform magnetic field produced by a superconducting magnet. An electrical signal will be induced in the astatic pair of pick-up coils that connect to the lock-in Amplifier to record the signal.

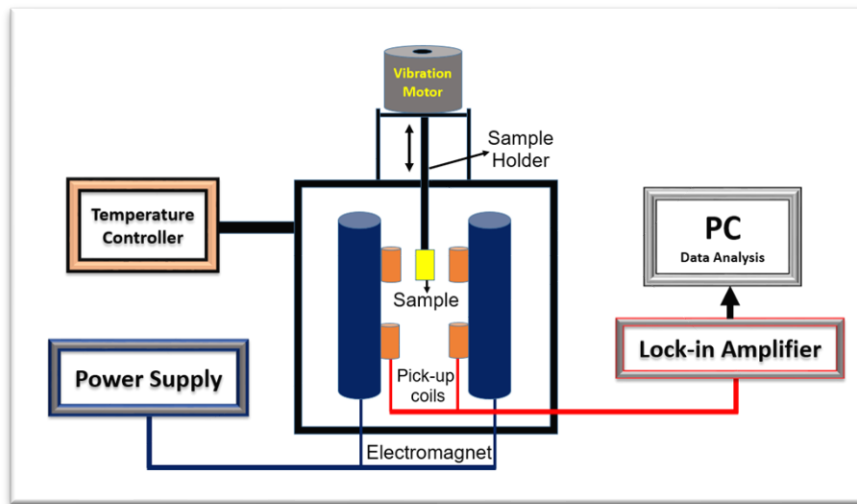


Figure 8: Experimental Set-up of Vibrating Sample Magnetometer.

3.2.3 Ac-Susceptibility Measurement

The ac-susceptometer system we designed and built is rather straightforward, requiring only a few central elements to function and create an ideal experimental setting. This section provides a basic overview of the system (Fig. 9.):

- **Cryostat**

The cryostat used is Janis Model SHI-4T. It hosts the sets of ac-coils, temperature sensors and local heaters installed on the cold finger of the closed cycle refrigerator (model RDK-408D2). The operating temperature range is 4-325 kelvin. The setup consists of four primary components: Compressor (model CSA-71), temperature controller (model 336), turbo-molecular Pump and (model XDD 1) closed-cycle refrigeration.

- **Lock-in Amplifier(*LIA*)**

The DSP Lock-In Amplifier (*LIA*) is from Stanford Research Systems (SR830). It provides an ac-current to the primary susceptometer coils and measure the secondary output after appropriate amplification and filtering. Due to its ability to differentiate between the real and imaginary components of the susceptibility, this instrument is beneficial in measuring AC susceptibility.

- **Temperature Controller**

We use a LakeShore Model 336 Temperature Controller to adjust the cryostat's temperature.

- **Computer**

The collection of data and its subsequent storage are both done by the computer.

- **The design of the sets of coils:**

The susceptometer has two coils, each one comprises a primary coil wound around a secondary coil. Two non-magnetic low temperature plastic tubes were used as a base on which the wires were wound see Fig. 10. The Parameters of coils are shown in table 8. To calculate the magnetic field generated by the primary coils, we used the finite coils approximation formula [146]–[148] given by:

$$B = \left(\frac{L}{\sqrt{d^2 + L^2}} \right) \mu_0 n I \quad (3.2)$$

where d is the average diameter of the primary coil, I is the current, μ_0 is the vacuum magnetic permeability, $n = N/L$ is the number of turns per unit length (L is the total length of the coil, and N is the number of turns in the primary coil). The field current ratio is then calculated as:

$$\frac{B}{I} \approx 0.043 \frac{T}{A} \approx 0.43 \text{ Oe/mA} \quad (3.3)$$

Table 8: Coil Parameters

	Secondary Coil		Primary Coil	
	Coil 1	Coil 2	Coil 1	Coil 2
Wire Diameter	0.152 mm	0.152 mm	0.152 mm	0.152 mm
Number of turns	~ 250 turns	~ 250 turns	~320 turns	~320 turns
Number of layers	8 layers	8 layers	12 layers	12 layers
Resistivity	15.3 Ω		20.3 Ω	

For a typical measurement, we use 5mA, which produce $B \sim 2.2$ Oe.

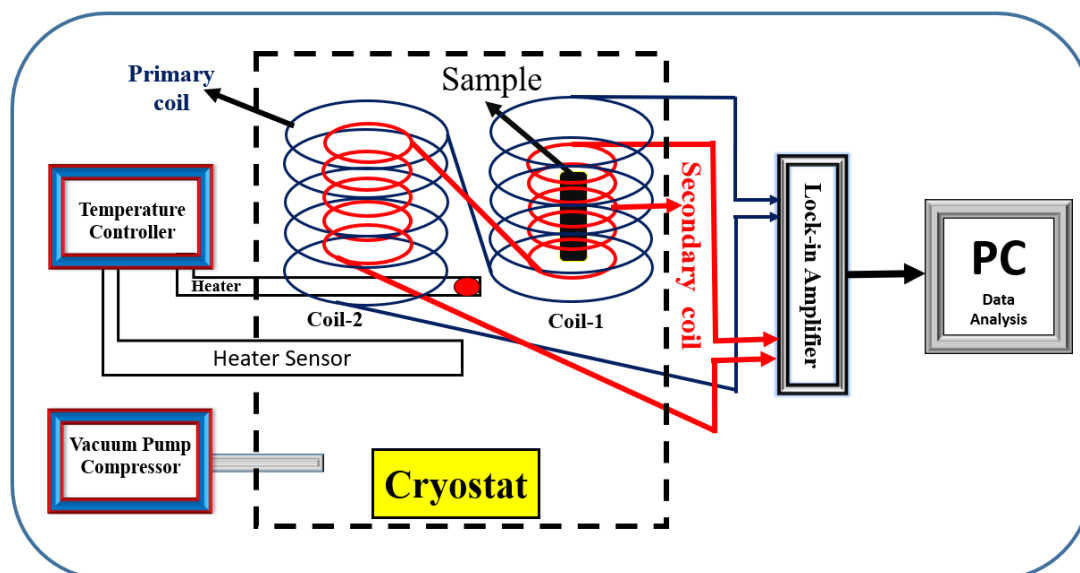


Figure 9: System Set-up for the AC susceptibility Measurements



Figure 10: Real Picture of Coils

- **Maxwell Coil**

An additional uniform-magnetic field was needed in our measurements. We designed a modified set of Maxwell coils to produce a highly uniform magnetic field at the sample position. The coils configuration consists of three separate coils (Fig. 11): two Helmholtz coils and a third short cylinder in between. The Helmholtz coils are two similar coils such that the distance between them equal the radius of a single coil. A third coil is placed between the Helmholtz coils to strengthen the produced applied magnetic field and enhance the uniformity of the field at the sample position. This arrangement of coils is commonly known as Maxwell's coil.

The original design of Maxwell coils (1873), the three coils are concentric to a virtual sphere of radius R . The middle coil has radius R , the outer two coils have radius $(4/7)^{0.5}R$, the spacing between the coils $= (3/7)^{0.5}R$. In our design, we replaced the central coil with a short cylinder that has the same radius as the Helmholtz coils.

In the original design of Maxwell coil, the radius of the third coil is given as R . In the following section we present the mathematical analysis for the strength and uniformity of the field produced by the three sets of coils. In Table 9, the coils' parameters are displayed.

Table 9: Maxwell Coil Parameters

	Coil 1		Coil 2		Coil 3
Diameter of wire	0.71 mm	0.56 mm	0.71 mm	0.56 mm	0.56 mm
Layers	15	7	14	10	
Turns	457	273	412	318	
Total Layers	22		24		24
Total Turns	730		730		1642
R (Ohm)	23.6		20.9		50.7

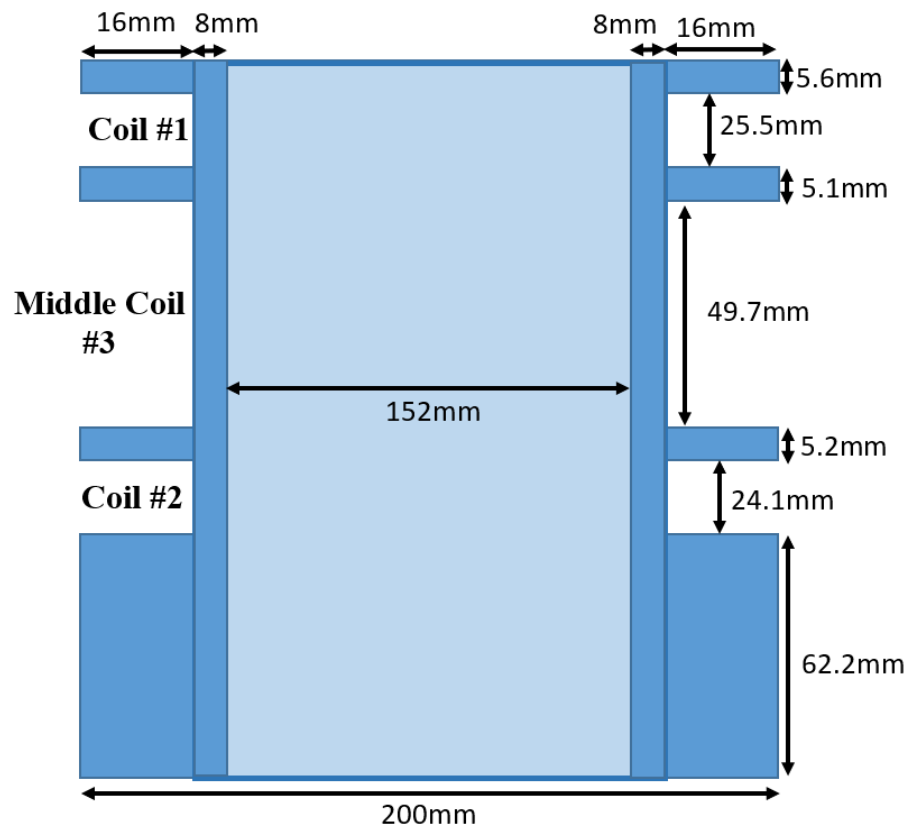


Figure 11: Dimensions of Maxwell Coil

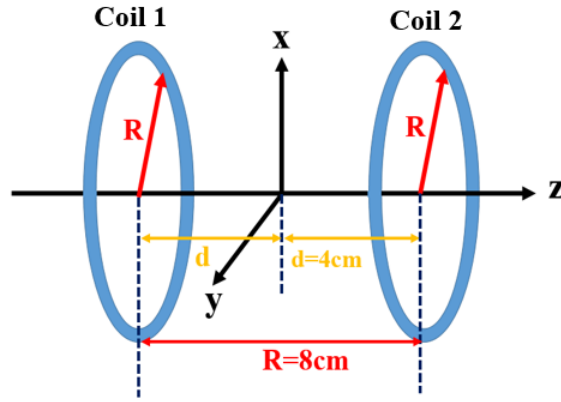


Figure 12: Dimensions of Helmholtz Coil

Magnetic Field Due to Helmholtz coils ($B_{H_{1,2}}$):

Coil 1:

$$B_{H1} = \frac{\mu_0 N R^2 I}{2} \left\{ \frac{1}{[R^2 + (z - d)^2]^{3/2}} \right\}$$

Coil 2:

$$B_{H2} = \frac{\mu_0 N R^2 I}{2} \left\{ \frac{1}{[R^2 + (z + d)^2]^{3/2}} \right\}$$

$$B_{H_{1,2}} = \frac{\mu_0 N R^2 I}{2} \left\{ \frac{1}{[R^2 + (z + d)^2]^{3/2}} + \frac{1}{[R^2 + (z - d)^2]^{3/2}} \right\} \quad (3.4)$$

At the center of a Helmholtz coils, equation (3.4) can be reduced to

$$\frac{B(z)}{I} = \frac{8}{5\sqrt{5}} \left(\frac{\mu_0 N}{R} \right) \quad (3.5)$$

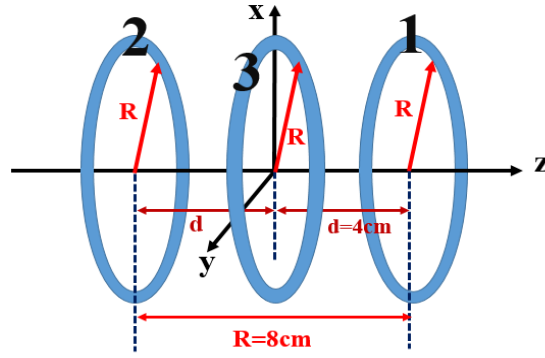


Figure 13: Dimensions of Maxwell Coil

The magnetic field produced by each coil is given as:

Coil 1:

$$BH1 = \frac{\mu_0 N R^2 I}{2} \left\{ \frac{1}{[R^2 + (z - d)^2]^{3/2}} \right\}$$

Coil 2:

$$BH2 = \frac{\mu_0 N R^2 I}{2} \left\{ \frac{1}{[R^2 + (z + d)^2]^{3/2}} \right\}$$

Coil 3:

$$BH3 = \frac{\mu_0 N R^2 I}{2} \left\{ \frac{1}{[R^2 + z^2]^{3/2}} \right\}$$

$$BH_{1,2,3} = \frac{\mu_0 N R^2 I}{2} \left\{ \frac{1}{[R^2 + (z + d)^2]^{3/2}} + \frac{1}{[R^2 + (z - d)^2]^{3/2}} + \frac{1}{[R^2 + z^2]^{3/2}} \right\} \quad (3.6)$$

$BH_{1,2,3}$: Magnetic field due to coil#1, coil#2 and coil#3

At the center of Maxwell's coil, we can use the finite coils approximation formula where :

Coil 3:

$$BH3 = \left(\frac{L}{\sqrt{d^2 + L^2}} \right) \mu_0 n I \quad (3.7)$$

And the total magnetic field at the center of Maxwell's coil will be the summation of equation (3.5) and (3.7) where

$$\frac{B}{I} \approx 0.2 \text{ Oe/mA} \quad (3.8)$$

Using Mathematica to plot the Magnetic Field Due to coils# 1, 2, and 3

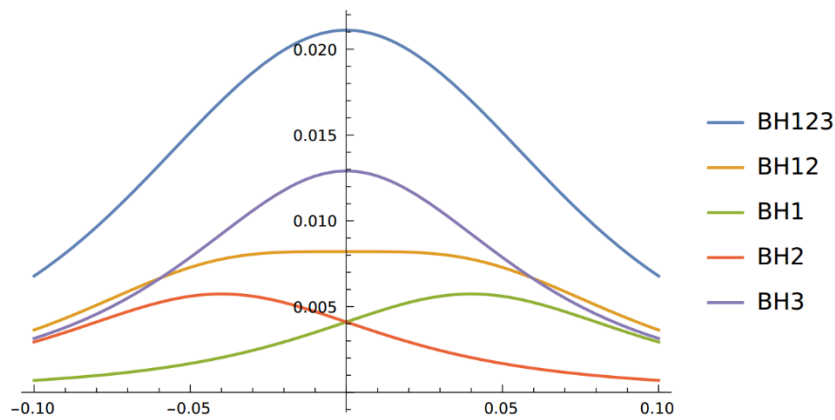


Figure 14: The magnetic field produced by the 3 parts of the Maxwell coil along the coil axis.

$BH_{1,2,3}$: Magnetic field due to coil#1, coil#2 and coil#3

$BH_{1,2}$: Magnetic field due to Helmholtz coils

BH1: Magnetic field due to coil#1

BH2: Magnetic field due to coil#2

BH3: Magnetic field due to coil#3

Some values of magnetic field:

Table 10: Values of The Magnetic Field at a Certain Location

z(m)	Unit	BH1	BH2	BH3	BH _{1,2}	BH _{1,2,3}
0	T/A	0.00410368	0.00410368	0.0129	0.00820735	0.0211073
	Oe/A	41.0368	41.0368	129.00	82.0735	211.073
	Oe/mA	0.0410368	0.0410368	0.129	0.0820735	0.211073
d= 4cm	T/A	0.00573506	0.00202765	0.00923046	0.00776271	0.0169932
	Oe/A	57.3506	20.2765	92.3046	77.6271	169.932
	Oe/mA	0.0573506	0.0202765	0.0923046	0.0776271	0.169932
d= -4cm	T/A	0.00202765	0.00573506	0.00923046	0.00776271	0.0169932
	Oe/A	20.2765	57.3506	92.3046	77.6271	169.932
	Oe/mA	0.0202765	0.0573506	0.0923046	0.0776271	0.169932

CHAPTER 4

Survey of The Transition Temperatures of The Prepared Transition Metal Series

The polycrystalline and several crystalline materials of layered van der Waals crystal MYX_3 series where M is Transition-metal (Cr or V), (Y is Sn or Sb), and X is a chalcogen (S, Se, and Te) have been tested using the ac-susceptibility measurement. The figures below show the results of all samples. Some samples reveal a sharp peak indicating a ferromagnetic phase ($CrSnS_3$, $CrSbS_3$, $CrSbSe_3$). Other samples show a almost symmetrical peak in their behavior which may refer to antiferromagnetism. The vanadium (V) samples reveal no peaks and may need more investigation. In the following chapters we investigated in detail the magnetic behavior of $CrSnS_3$ and $CrSbS_3$. In particular, we report the ac susceptibility, Curie Wise behavior, the critical behavior, the universal scaling behavior and the magnetocaloric behavior.

4.1 CrSnX₃ (X=S, Se and Te) System:

The real part of the ac-susceptibility of CrSnS₃, CrSnSe₃ and CrSnTe₃ are presented in Figure 15. The figure reveals that the CrSnSe₃ sample exhibit a wide maximum near 175K. This may indicate a non uniformly reacting material. The other two samples showed a sharp transition at about 120K for CrSnS₃ sample and at 225K for CrSnTe₃ sample. Both samples also reveal additional shoulders near 79 and 165K for CrSnS₃ and CrSnTe₃, respectively. It is also observed that the transition temperature gradually increases with increasing atomic mass (and the ionic radius) of the chalcogen element.

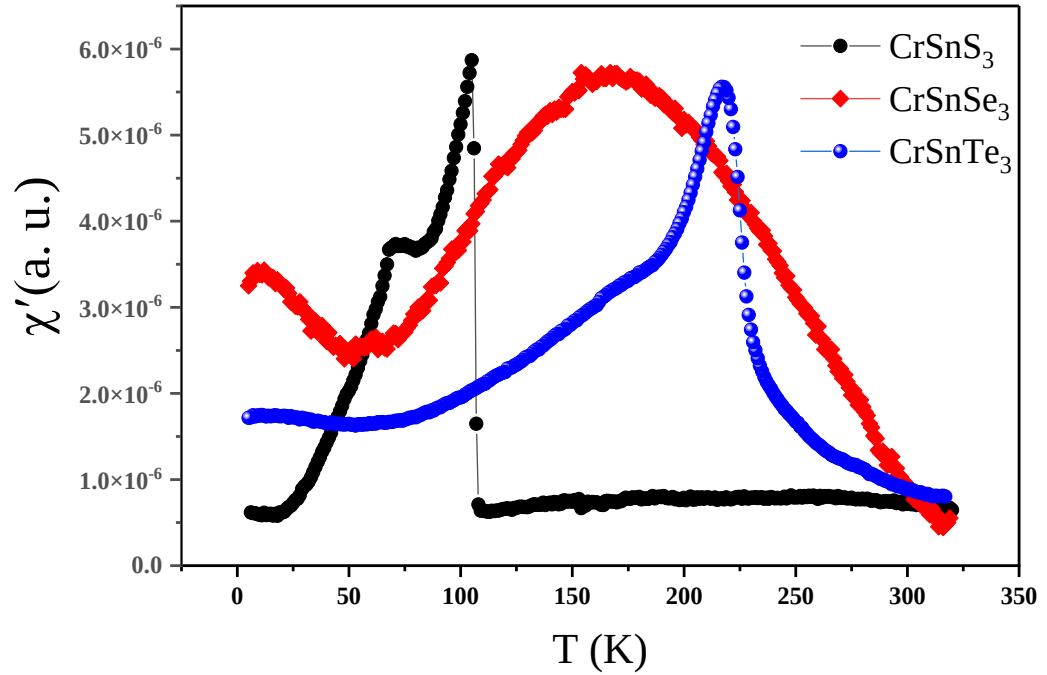


Figure 15: The Dependences of The Real Part of Ac-Susceptibility on The Temperature of CrSnX₃

4.2 CrSbX₃ (X=S, Se and Te) System:

In Fig. 16, we present the real part of the ac-susceptibility of chromium antimony based van der Waals materials, namely: CrSbS₃, CrSbSe₃ and CrSbTe₃. The figure reveals that the CrSbTe₃ sample exhibits a somewhat sharp maximum near 160K. The other two samples showed a sharp transition at about 70K for CrSbSe₃ sample and at 115 K for CrSbS₃ sample. Both samples also reveal very small shoulders near 45 and 90K for CrSbSe₃ and CrSbS₃, respectively. These shoulders are much less pronounced than what we observed in CrSnS₃ and CrSnTe₃. It is also observed that the transition temperature gradually increases with increasing atomic mass (and the ionic radius) of the chalcogen element.

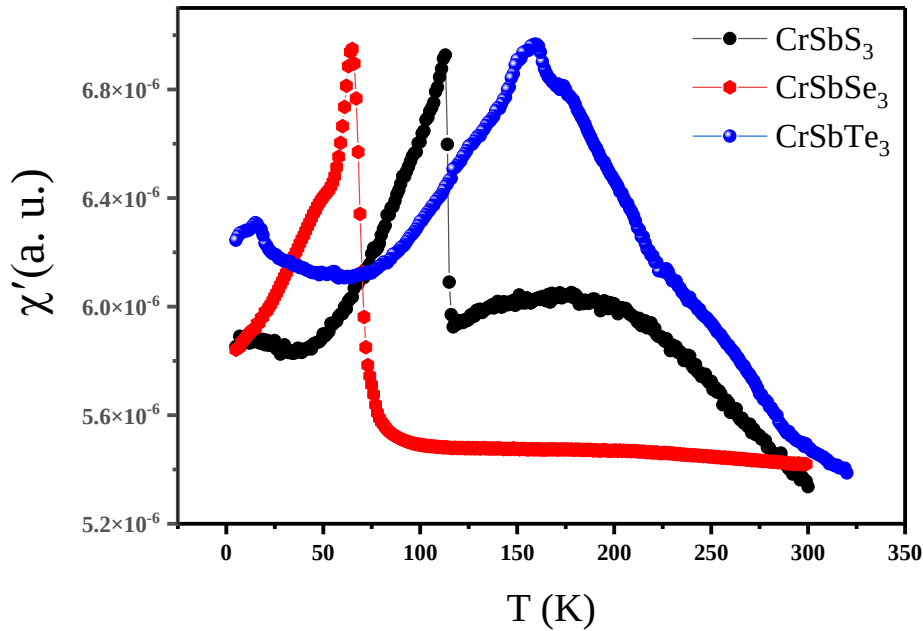


Figure 16: The Dependences of The Real Part of Ac-Susceptibility on The Temperature of CrSbX₃

4.3 VS_nX₃ (X=S, Se and Te) System:

In Fig. 17, we present the real part of the ac-susceptibility of Vanadium Tin based van der Waals materials, namely: VS_nS₃, VS_nSe₃ and VS_nTe₃. The figure reveals that all samples exhibit a somewhat sharp maximum at 14.8 , 20.9 and 35.7 K for VS_nS₃, VS_nSe₃ and VS_nTe₃, respectively. It is also observed that the transition temperature gradually increases with increasing atomic mass (and the ionic radius) of the chalcogen element. It is interesting to observe that the peaks in VS_n-based samples occur at much lower temperatures than what we observed in CrSn samples.

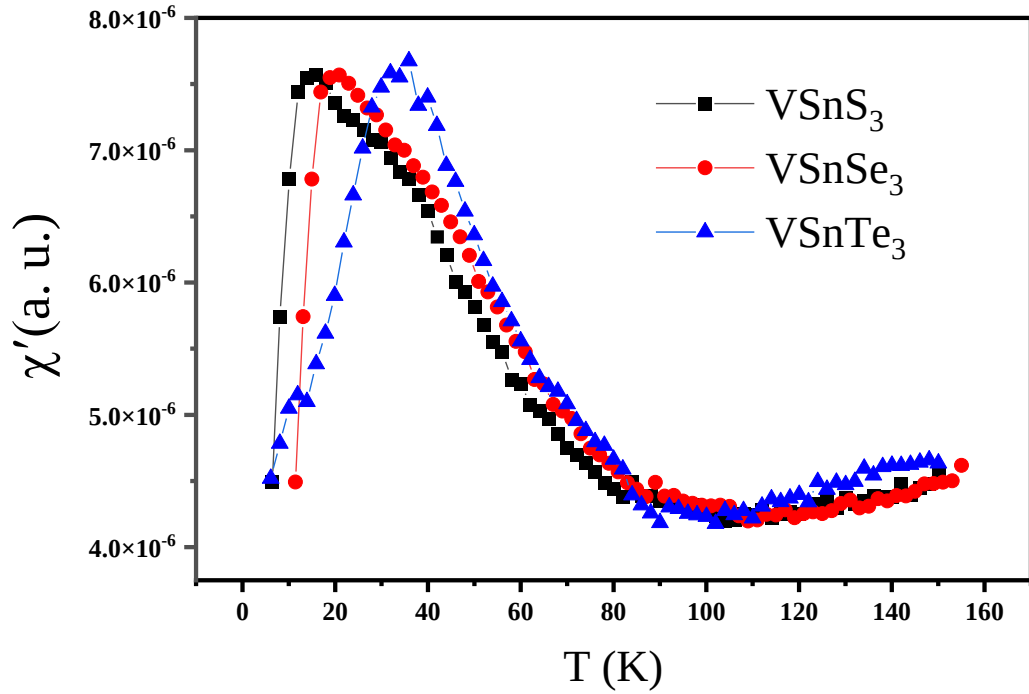


Figure 17: The Dependences of The Real Part of Ac-Susceptibility on The Temperature of VS_nX₃

4.4 VSbX₃ (X=S, Se and Te) System:

In Fig. 18, we present the real part of the ac-susceptibility of Vanadium Antimony based van der Waals materials, namely: VSbS₃, VSbSe₃ and VSbTe₃. The figure reveals that all samples exhibit a somewhat sharp maximum at 14.2, 29.9 and 36.1 K for VSbS₃, VSbSe₃ and VSbTe₃, respectively. It is also observed that the transition temperature gradually increases with increasing atomic mass (and the ionic radius) of the chalcogen element. It is interesting to observe that the peaks in VSb-based samples occur at much lower temperatures than what we observed in CrSb samples.

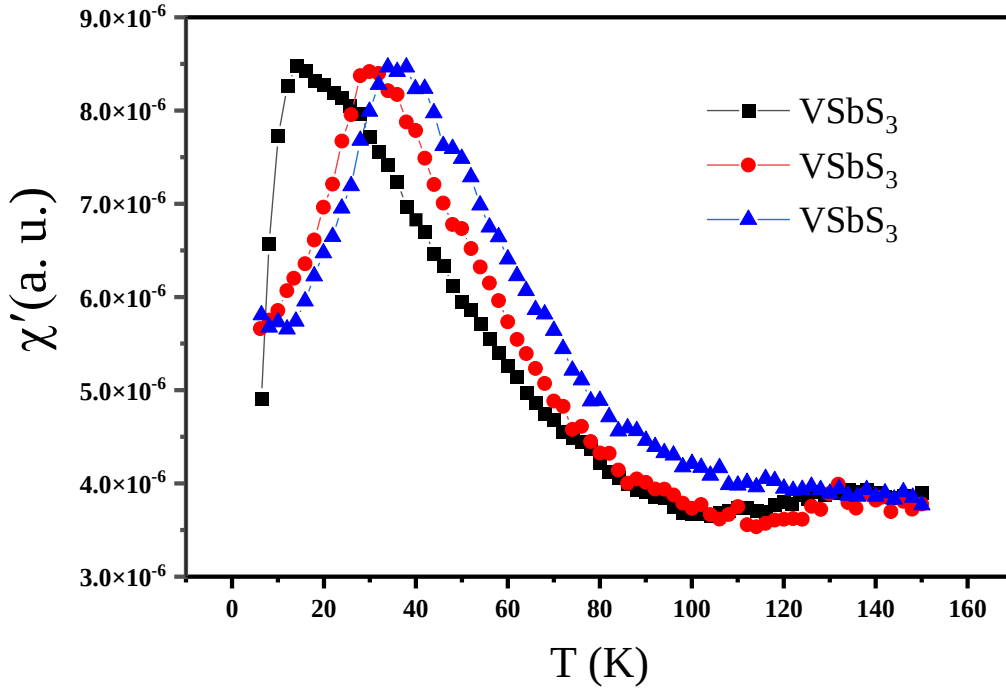


Figure 18: The Dependences of The Real Part of Ac-Susceptibility on The Temperature of VSbX₃

CHAPTER 5

RESULTS AND DISCUSSION FOR CrSnS_3

The discovery of graphene renewed research interest in various 2-dimensional materials and their corresponding properties. These materials are commonly known as van der Waals materials because the coupling between the layers is weak, while the in-plane coupling is mainly strong covalent bonding. In particular, the transition metal based van der Waals materials are of great potential for practical applications. In particular, their corresponding ferromagnetic properties are being intensively investigated for their possible use in spintronics and magnetic semiconductors [149]. Various properties of these materials, such as electrical and magnetic, are also directly influenced by these strong and weak couplings. Recently, ferromagnetism in van der Waals materials was re-discovered in $\text{Cr}_2\text{Ge}_2\text{Te}_6$, CrSbSe_3 , CrI_3 , and VSe_2 [150]. Transition metal trichalcogenides (TMTs) van der Waals materials share the general chemical formula MTX_3 where M is magnetic transition element (V, Cr, Mn, Fe, Co or Ni), T represents either group IV (Si, Ge, Sn) or group V (P, As, Sb) and X is Chalcogens (S, Se, Te) [151]. The compound MAX_3 is a subgroup of the MTX_3 , where A is the group IV element (Si, Ge, Sn) [50]. The general structure of the MAX_3 compounds in their bulk form are single layers as ABC-stacked and are held together mainly by van der Waals force [50]. The bilayer structure of the compound consists of M^{3+} cations and $(\text{A}_2\text{X}_6)^{-6}$ anions. The crystal structure varies depending on how these ions are arranged [151]. The main difference between MAX_3 compounds and MPX_3 compounds (P is group V

element) is that the A atoms have one fewer electron compared to P atoms, yielding compounds with more negativity and larger nominal metal cation valences 3^+ rather than 2^+ in the MPX_3 compounds and the anions $(P_2X_6)^{4-}$ of group V are replaced by $(A_2X_6)^{6-}$ of group IV. This change is responsible for essential modifications in the resulting electronic and magnetic properties and may lead to more in-plane negativity hence stronger 2-dimensional behavior such as stronger anisotropy effects [50]. Chittari et al. DFT calculations for an Ising model predicted that $CrSnS_3$ is a metallic ferromagnet with $T_C = 116$ K [50]. A similar enhancement of T_C has been predicted for $CrSnSe_3$ and $CoSnS_3$.

The MAX_3 structures are expected to have a quasi-two-dimensional layered crystal structure rather than a pseudo-one-dimensional crystal structure, with edge-sharing and double rutile chains in MPX_3 compounds [50][152][153]. The quasi-two-dimensional layered crystal structure shows a distinctive phase diagram in an applied field. According to what follows from the Mermin-Wagner theorem, the transition to the ordered state can only occur at $T_C = 0$ in a two-dimensional isotropic Heisenberg magnet. This contrasts with the topological Kosterlitz Thouless transition, which is caused by the unbinding of vortex-antivortex pairs. It may occur at a critical temperature $T_C \neq 0$ K in a two-dimensional system with XY anisotropy [25].

5.1 X-ray Diffraction

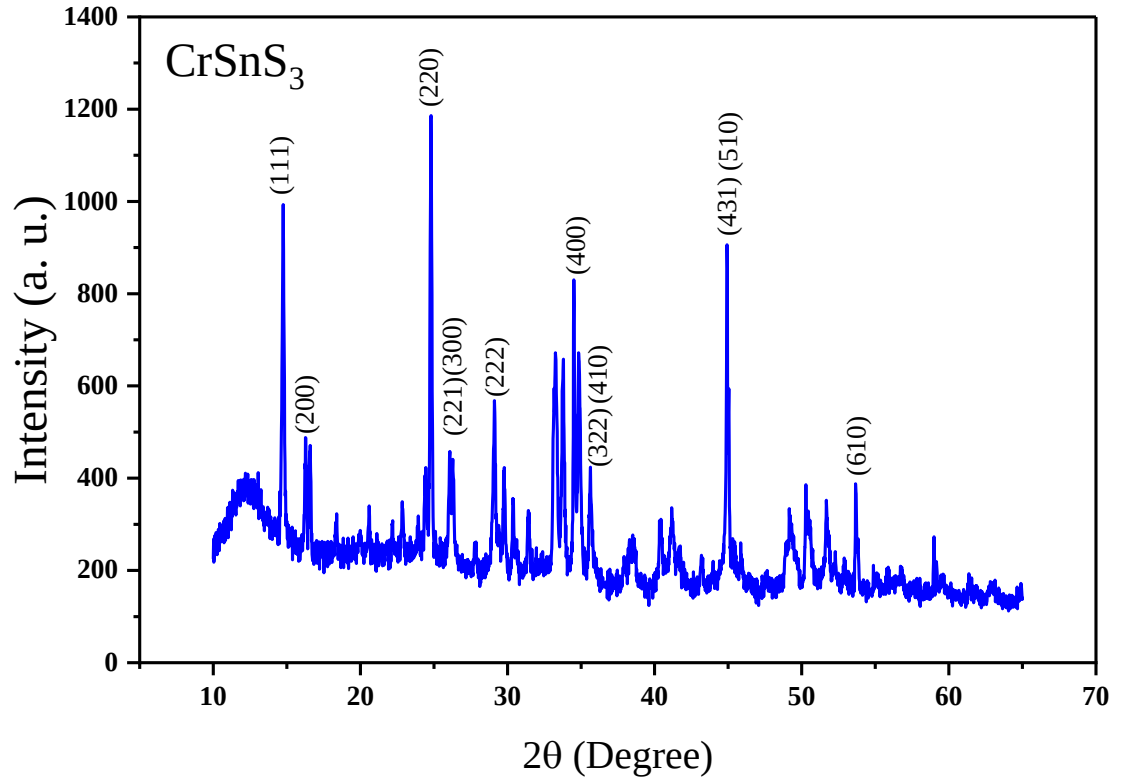


Figure 19: Powder X-Ray Diffraction (XRD) Pattern of CrSnS₃

The X-ray diffraction pattern of CrSnS₃ is presented in Fig. 19, using the Cu K α line ($\lambda=1.5405\text{\AA}$). Most of the XRD peaks were fitted to an orthorhombic structure. The minority phases of SnS and SnS₂ have been detected. To find the lattice parameter, we use the equation of an orthorhombic structure which is given by:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (5.1)$$

The XRD data has been corrected for the $\kappa\alpha_2$ lines then used to calculate the lattice parameters using analytical method. Fullproof software has been used to perform refinement of the lattice parameters, the obtained values are:

$$a = 10.377 \text{ \AA}, b = 10.216 \text{ \AA} \text{ and } c = 10.898 \text{ \AA}.$$

5.2 Magnetic Ac-Susceptibility (χ_{ac})

AC-susceptibility is a very sensitive technique and very useful in studying phase transition and magnetization dynamics in a variety of magnetic materials. In the following, we present both components of ac-susceptibility; namely the real and the imaginary parts that we obtained for the Cr-based van der Waals ferromagnetic samples. AC-susceptibility measurements (χ_{ac}) performed under various DC-ferromagnetic fields will be presented in another section.

5.2.1 The Real and Imaginary Parts of Ac-Susceptibility (χ_{ac})

The temperature dependence of the real and imaginary parts of magnetic ac-Susceptibility (χ_{ac}) of CrSnS₃ are shown in Figures 20 and 21. The inset shows the first derivative of the real part of the susceptibility (χ'). The rapid increase in the susceptibility at $T_C \sim 119\text{K}$ indicates the onset of FM order. The susceptibility derivative reveals a very sharp ferromagnetic transition at $T_C = 119\text{K}$ and FWHM $\sim 0.2\text{K}$. The sudden rise of the ac-susceptibility to a sharp peak indicates a first-order phase transition. As the temperature decreases below T_C , the susceptibility decreases rapidly. Then it rises to another maximum value near 90K (Fig. 20). This peculiar behavior is also reflected in the susceptibility derivative (Fig. 20.), which reveals another maximum at 90 K, indicating yet another transition to a possible antiferromagnetic state; however, a spin reorientation of spin cannot be ruled out. Below 90K, the susceptibility continues to drop, becoming almost constant below 25 K. The imaginary part of ac-susceptibility (χ'') has similar behavior to the real part (χ') as shown in figure 21.

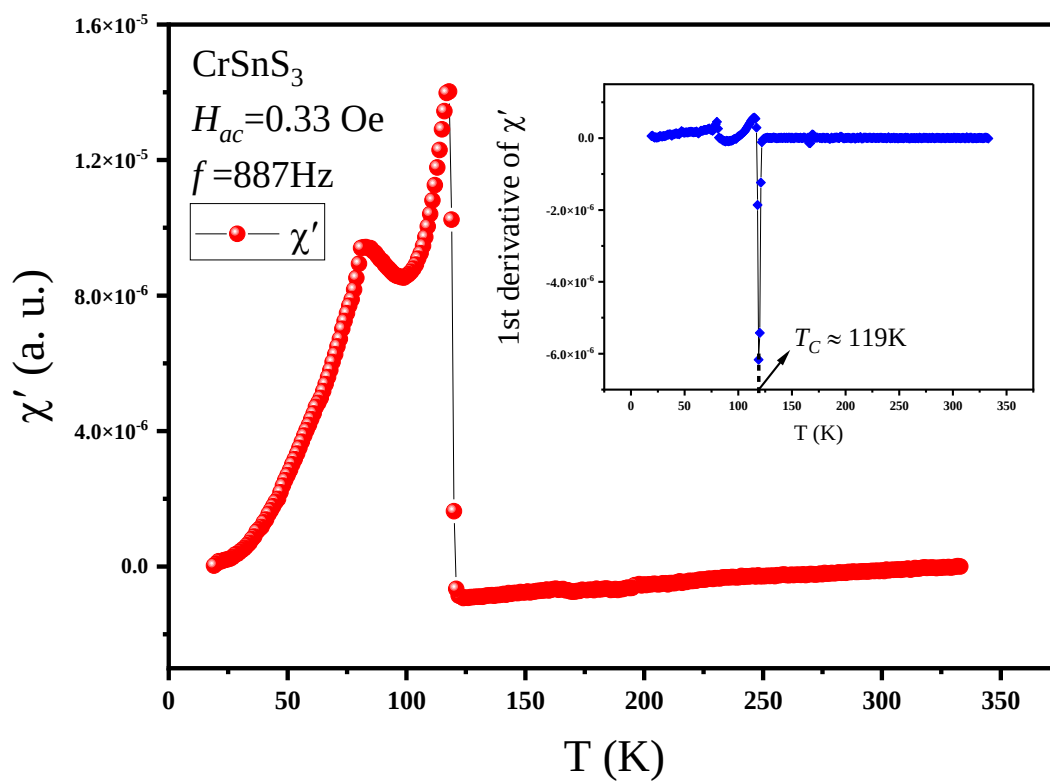


Figure 20: Temperature-dependence of the Real Part of Magnetic Ac-Susceptibility(χ'). Inset shows The First Derivative of (χ') for CrSnS₃

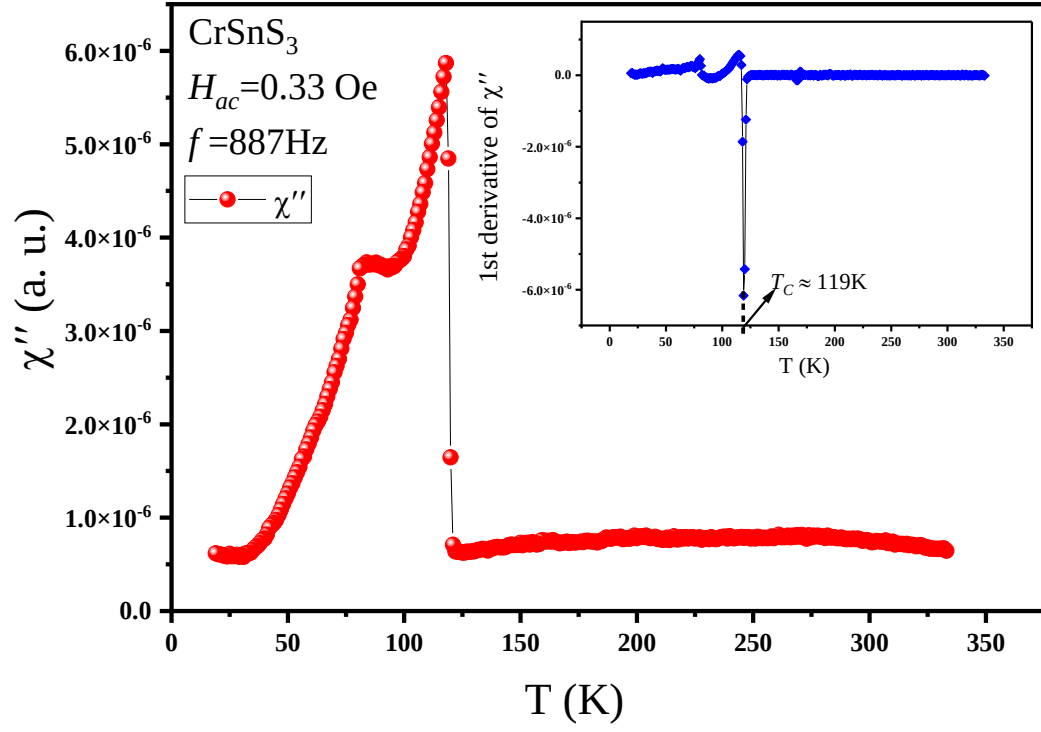


Figure 21: Temperature-dependence of The Imaginary Part of Magnetic Ac-Susceptibility(χ'') . Inset shows The First Derivative of (χ'') for CrSnS₃

5.2.2 Effects of The DC-bias Field on The Ac-Susceptibility

The effect of dc-magnetic field bias on the ac-susceptibility can further be used to investigate the magnetic state. The results are presented in Fig. 22. The applied dc-field gradually suppresses the sharp peak and shifts it to lower temperatures. As the dc-field increases, the ac-Susceptibility shows a wide maximum in the temperature range (~85-110K) such a behavior is commonly seen in ferromagnetic dc-susceptibility. As the temperature decreases, the drop in the susceptibility reaches a minimum near 30 K. This drop can be the result of spin reorientation, which may be caused by antiferromagnetic exchange interaction (see Fig. 22.). As the applied dc-field increases, the width of the FM transition increases (Fig. 22.), indicating that the material becomes less responsive to the low H_{ac} (~ 0.33 Oe) , and the ac-susceptibility in large dc-fields (~40 Oe) looks much similar to the dc-susceptibility (see Fig. 25.).

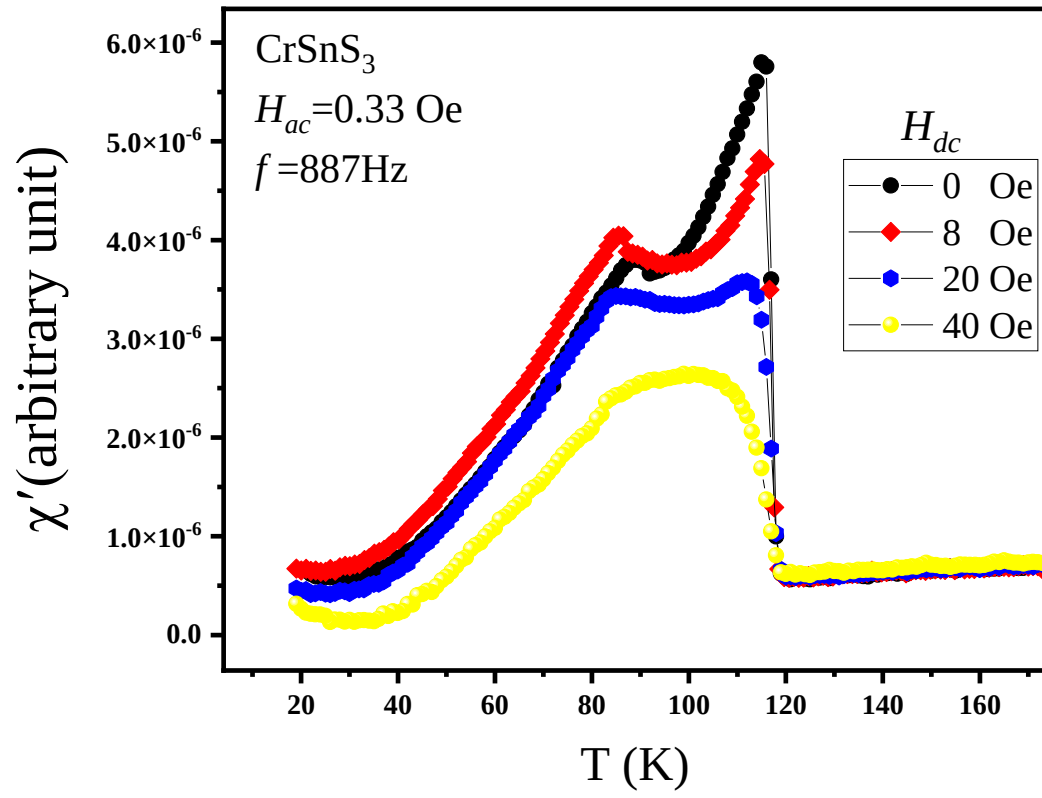


Figure 22: Effect of Applied DC Field in-phase (χ') of Ac-Susceptibility for CrSnS₃

The effects of dc-bias field on the transition temperature can be further investigated by measuring the ac-susceptibility as a function of the dc-field cycled between two maxima (± 45 Oe) at various temperatures near T_C . The result is presented in Fig. 23. A maximum in the susceptibility can be seen in the figure when $H_{dc} = 0$. This maximum value has totally vanished by the time the temperature reaches 120K, but it shows a little peak when the temperature is $T = 119$ K. This would imply that the onset of the transition occurs somewhere between (118-119K).

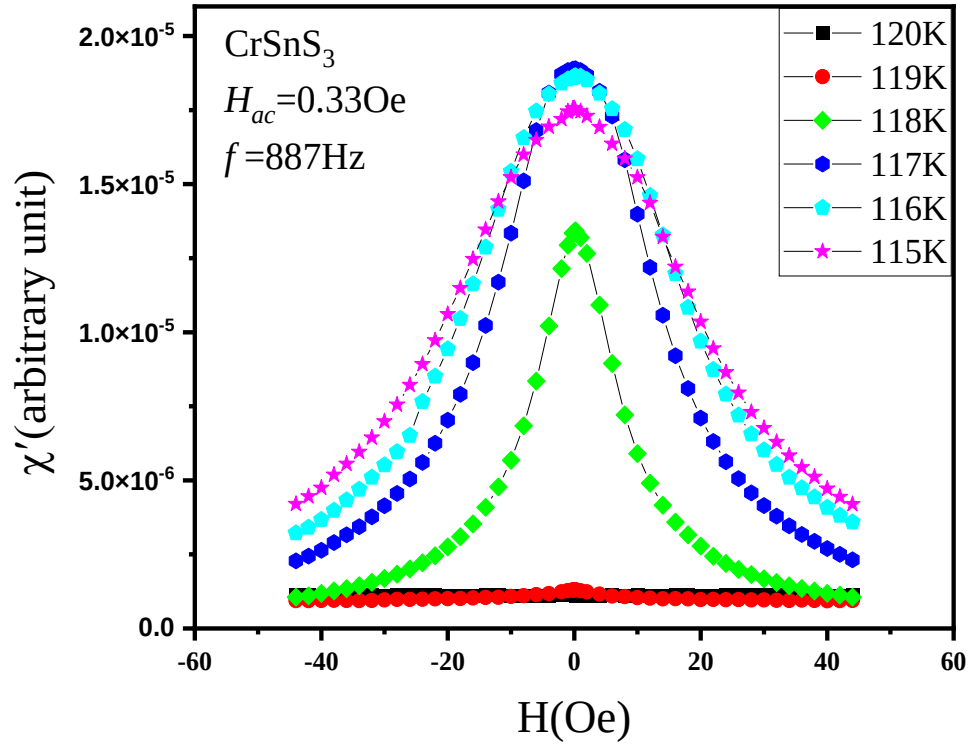


Figure 23: DC bias Fields Variation of in-phase (χ') of Ac-Susceptibility at Different Temperatures for CrSnS₃.

5.2.3 The Frequency Dependence of Magnetic Ac-Susceptibility (χ_{ac})

The AC-susceptibility measurements (χ_{ac}) obtained for the polycrystalline sample of CrSnS₃ are displayed in Figure 24. These data were measured at different frequencies. As can be seen in Figure 24, the real part of the ac-susceptibility, denoted by (χ'), is independent of frequency. Using the Arrhenius law, one may calculate the activation energy by observing the shift in the ac-susceptibility peak as a function of frequency. [25]. The relaxation time $\tau(T) = 1/f$ is expressed as:

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right) \quad (5.2)$$

After a characteristic time (τ), also known as the relaxation time, the magnetization M of a spin system will reach a new equilibrium state as the applied magnetic field shifts from H to $H \pm \Delta H$. The relaxation process is effected by a number of factors, including the motion of domain walls, the rotation of magnetic moments and other parameters. So equation (5.2) converts to:

$$\ln f = \frac{-\Delta E}{k_B} \frac{1}{T} + \ln f_0 \quad (5.3)$$

As a result, it would appear that the transition to the ferromagnetic phase is the immediate process, and the fact that the relevant reorganization of the domain structure is not a relaxation effect indicates that the moments are unable to follow the oscillating field. This is in agreement with the results seen in conventional or ferromagnetic

materials, in which the frequency dependency of susceptibility was only seen in the MHz range. In addition, the quasi-1D molecular magnets have a frequency dependence, whereas here, it is absent, suggesting that the materials' structure tends to be quasi-2D molecular magnetic.

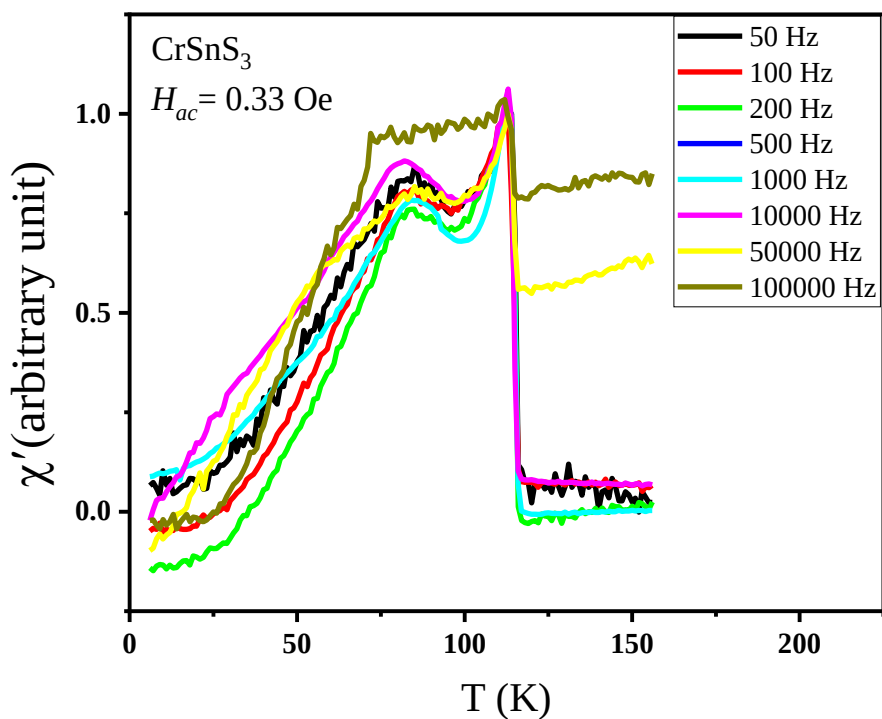


Figure 24: Frequency-dependence of in-phase (χ') of Ac-Susceptibility for CrSnS₃

5.3 Magnetic Isotherms and The Dc-Susceptibility

The variations of the magnetization with the temperature at a constant magnetic field $H_{dc} = 200 \text{ Oe}$ is presented in Fig. 25. The figure shows a sudden rise in the magnetization at $T_C \sim 120\text{K}$, reaching a maximum near 90K, then further drops with a shoulder near 15K. The derivative of the susceptibility is shown in the insert of Fig. 25. The derivative shows a very sharp transition indicating a first order FM phase transition. Further analysis of the order of the phase transition will be presented in the following sections on critical behavior analysis.

The isothermal magnetization versus different values of the magnetic field is presented in Fig. 26. At the lowest temperature ($T = 4 \text{ K}$), the magnetization nearly increases linearly, with a slight reduction in the slope near 4 K, then continues to increase with no sign of saturation. This indicates an antiferromagnetic behavior at a low temperature. At higher temperatures ($\sim 50\text{K}$), the magnetization rapidly increases, reaching saturation near one kOe, indicative of a ferromagnetic ordering. Similar behavior continues up to just below $T \approx 120\text{K}$. At $T = 120 \text{ K}$ and above, the magnetic state is in paramagnetic order, and the magnetization increases linearly with the applied magnetic field. The behavior of the isothermal magnetization changes close to 120 K implying that the transition from a ferromagnetic to paramagnetic occurs close to 120K, which is in line with the result obtained for ac-susceptibilities (see Fig. 20.).

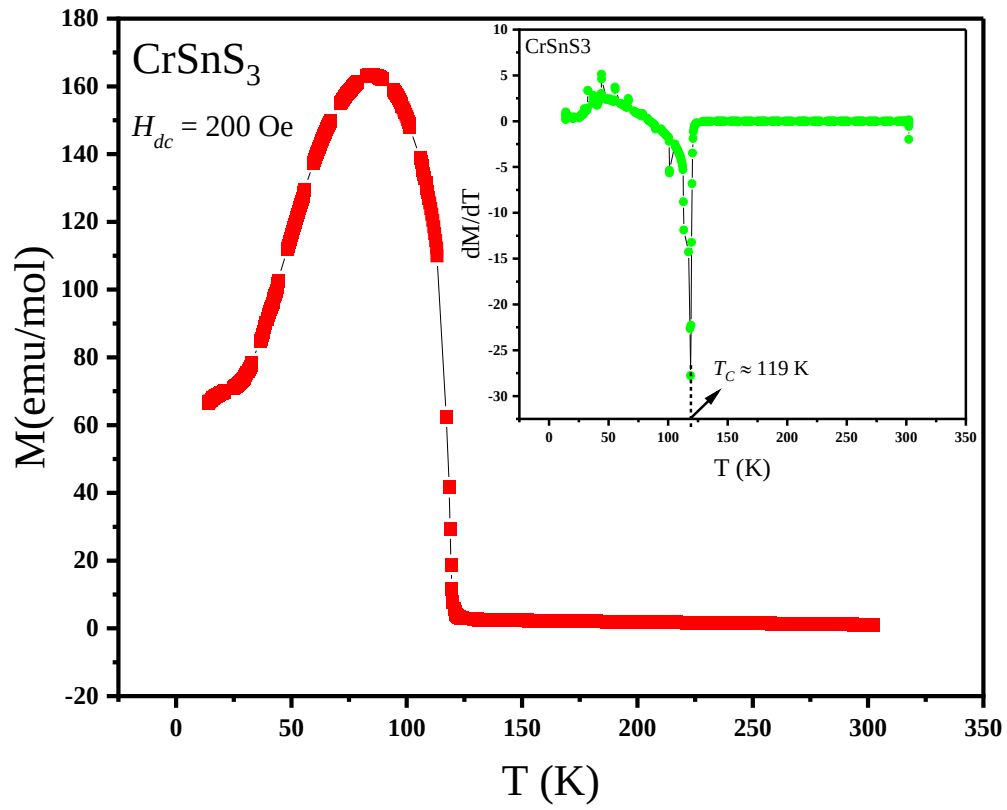


Figure 25: Temperature-dependence Magnetization $M(T)$ measured at $H_{dc} = 200$ Oe for CrSnS_3 .
Inset shows The First Derivative of $M(T)$ for CrSnS_3 .

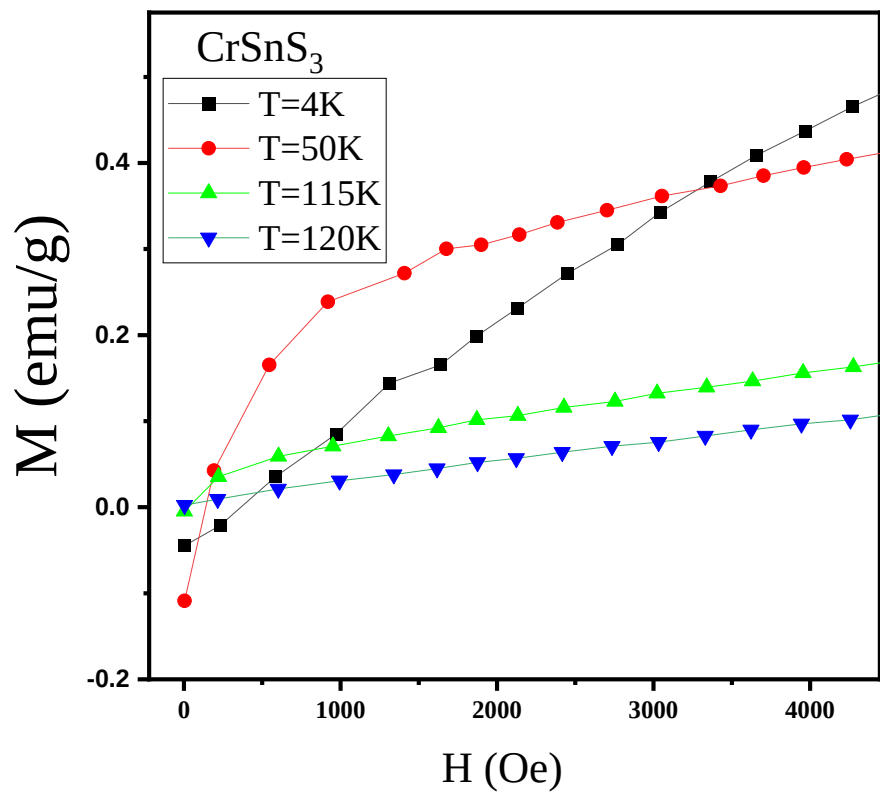


Figure 26: Isothermal Magnetization Curves Measured at selected Temperatures for CrSnS_3 .

5.4 The Curie-Weiss Law

The relationship between inverse magnetic susceptibility and temperature is depicted in figure 27. The figure exhibits a linear behavior above 240K, way above T_C ($\sim 120K$). Moreover, the figure reflects typical Ferrimagnetic behavior with positive θ_N . The linear part of the inverse susceptibility is fitted to the Curie-Weiss relation (in the paramagnetic temperature range) The Neel temperature is $\theta_N \sim 80 K$, and the molar Curie constant is $C_m = 1.3 \text{ emu. K/mol}$.

The effective magnetic moment of the Cr-ion is calculated using the relation:

$$\mu_{eff} = 2.828 \sqrt{C_m} \mu_B \quad (5.4)$$

where the constant 2.828 is calculated using $\sqrt{3 k_B / N_A \mu_B^2} = 2.828$, $k_B = 1.380649 \times 10^{-16} \text{ erg/K}$, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ and $\mu_B = 9.274 \times 10^{-21} \text{ erg/G}$, these are the Boltzmann constant, Avogadro's number, and the Bohr magneton, respectively.

The calculated effective magnetic moment (μ_{eff}) per Cr^{3+} ions in CrSnS_3 is equal to $3.2\mu_B$. This value for the CrSnS_3 is significantly lower than the observed value of the effective magnetic moment of free Cr^{3+} ions ($\mu_{eff, \text{Cr}^{3+}} = 3.85 \mu_B$). This reflects a moderate degree of itinerant ferromagnetism in this material. Moreover, this may also indicate a complex magnetic ordering (ferro, ferri, and antiferromagnetic) in CrSnS_3 below T_C and exhibits an impurity phase in the sample.

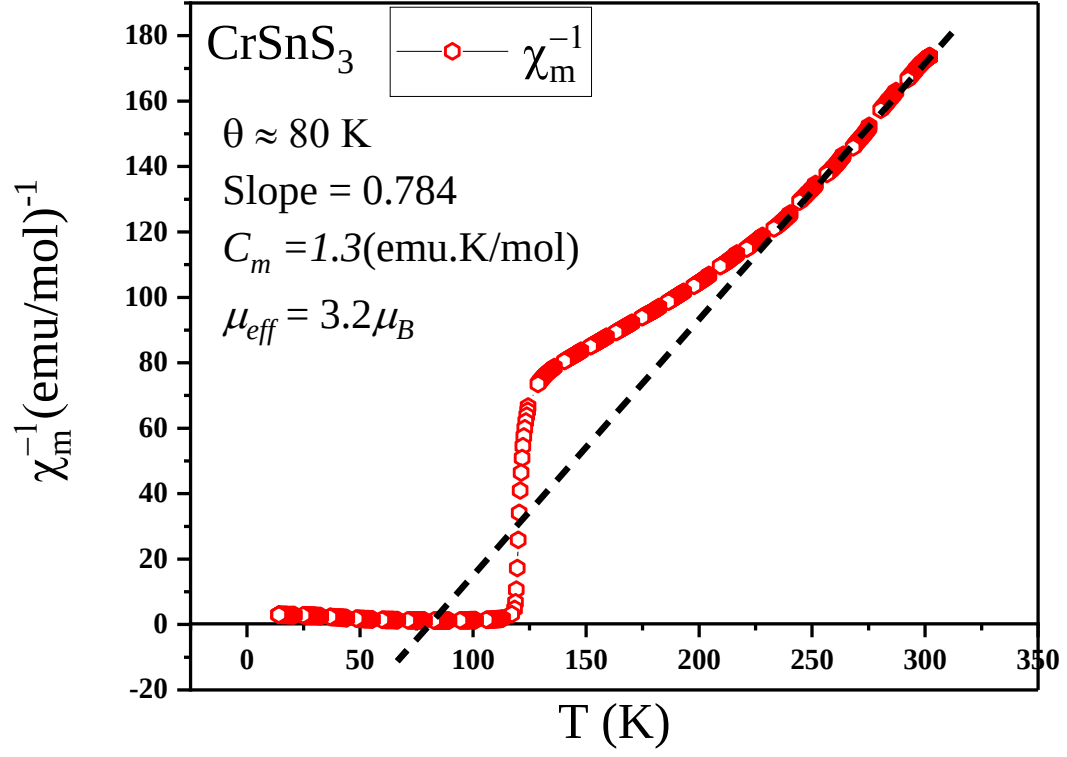


Figure 27: Variation of the Inverse of The Molar Magnetic Susceptibility (χ_m^{-1}) as a Function of Temperature for CrSnS3 at $H_{dc} = 200 \text{ Oe}$

5.5 Critical Behavior

By analyzing the magnetic isotherms $M(H)$ using an Arrott plot (Fig. 28.), we were able to gain some understanding of the magnetic transitions in CrSnS_3 . According to Banerjee, the order of the phase transition can be determined by the slope of the lines in the Arrott plot. Negative curvatures correspond to a first-order magnetic transition (FOMT), whereas positive curvatures belong to a second-order magnetic transition (SOMT). The intercept values were determined using linear fits, allowing the order of phase transitions to be distinguished.

For the CrSnS_3 sample, the value of intercept at 118 K, the one closer to spin reorientation, is found to be negative for the high field area, suggesting the possibility of a first-order magnetic transition. The Arrott plot analysis of CrSnS_3 reveals that the sample undergoes a ferromagnetic-paramagnetic (FM-PM) transition upon first-order spin reorientation.

The mean-field critical exponents $\beta = 0.5$ and $\gamma = 1.0$ are involved in the Arrott plot. Accordingly, the isotherm at T_C should pass through the origin, and the magnetization isotherms M^2 versus H/M should be a collection of parallel straight lines. The Arrott plot of CrSnS_3 shows that all curves have a downward curvature and are nonlinear (Fig. 30.), proving that the mean-field model is inapplicable to CrSnS_3 . We use the modified Arrott plot to better understand the PM-FM transition in CrSnS_3 because the mean-field model is unsuccessful.

Figures 31 , 32 and 33 exhibit the modified Arrott plots using possible exponents from 3D Ising ($\beta = 0.325, \gamma = 1.24$), 3D Heisenberg ($\beta = 0.365, \gamma = 1.386$), and tricritical

mean-field ($\beta = 0.25, \gamma = 1.0$) models. The modified Arrott plot should consist of parallel lines in the high-field zone with the same slope $S(T) = dM^{1/\beta}/d(H/M)^{1/\gamma}$. The relative slope (RS) [$RS = S(T)/S(T_C)$], which compares with the ideal value of unity, is used to choose the model that best matches the data.

The plot of relative slope (RS) versus temperature (T) for each model is also presented in (Fig. 29). The highest deviation from unity is observed for the RS of the tricritical mean-field model. Above T_C , the RS of the tricritical mean-field model is very close to $RS = 1$, whereas, below T_C , the RS of the mean-field model is optimal. Since the standard Arrott plot analysis does not allow us to determine which one of these models is closer to matching the data of the sample. Therefore, we applied the original technique to find the critical exponents of the Sample. In this way, we find the fitting of $M(H)$ curves at the high field where we have straight lines, the slope represents the magnetic susceptibility, and the y-intercept represents the spontaneous magnetization.

The spontaneous magnetization (M_S) for a first-order PM-FM phase transition is below the transition temperature (T_C), the initial magnetic susceptibility (χ_o^{-1}) is above T_C , and the field-dependent magnetization (M) at T_C can be described by a set of critical exponents β , γ , and δ , respectively. The exponents derived from magnetization measurements are defined mathematically below:

$$M_S(T) = M_o(-\varepsilon)^\beta \quad (5.5)$$

$$\chi_o^{-1} = (h_o/m_o)(\varepsilon)^{-\gamma} \quad (5.6)$$

$$M = D H^{\frac{1}{\delta}} \quad (5.7)$$

$$\varepsilon \equiv \frac{T-T_c}{T_c} \quad (5.8)$$

where M_o , (h_o/m_o) and D are the critical amplitudes. To obtain the anisotropic critical exponents β , γ , and δ , the values of spontaneous magnetization (M_S) and the inverse initial magnetic susceptibility (χ_o^{-1}) are extracted from isothermal magnetization curves (Fig. 34.) and shown in Table 11. From the Kouvel-Fisher method where $M_S(T)/(dM_S(T)/dT)$ and $\chi_o^{-1}(T)/(\chi_o^{-1}(T)/dT)$ plotted against temperature should be straight lines with slopes of $1/\beta$ and $1/\gamma$, respectively.

$$\frac{M_S(T)}{dM_S(T)/dT} = \frac{T}{\beta} - \frac{T_C}{\beta} \quad (5.9)$$

$$\frac{\chi_o^{-1}(T)}{d\chi_o^{-1}(T)/dT} = \frac{T}{\gamma} - \frac{T_C}{\gamma} \quad (5.10)$$

The linear fit of the plots (Fig. 35.) yield $\beta = 0.236$ with $T_C = 116.3$ K and $\gamma = 0.135$ with $T_C = 121.1$ K.

The Widom relation gives:

$$\delta = 1 + \frac{\gamma}{\beta} \quad (5.11)$$

From β and γ obtained with the Kouvel-Fisher method, δ is calculated to be 1.572. According to Eq. (5.7), the critical isotherm analysis $M(H)$ at T_C should be a straight line in the log-log scale with the slope of $1/\delta$ (Fig. 36.). Such fitting yields $\delta = 1.621$ which is close to that obtained from The Widom relation.

The accuracy of the calculated critical exponents can be roughly estimated by means of a scaling analysis. The magnetic equation of state at the critical area is said to obey a scaling relation, as proposed by the scaling hypothesis, and this relation can be represented as:

$$M(H, \varepsilon) = \varepsilon^\beta f_\pm\left(\frac{H}{\varepsilon^{\beta+\gamma}}\right) \quad (5.12)$$

where f_+ for $T > T_C$ and f_- for $T < T_C$, respectively, are the regular functions. In terms of the variable $m \equiv \varepsilon^{-\beta} M(H, \varepsilon)$ and $h \equiv \varepsilon^{-(\beta+\gamma)} H$, renormalized magnetization, and renormalized field, respectively, equation (4.10) can be simplified to the following form:

$$m = f_\pm(h) \quad (5.13)$$

It suggests that for a true scaling relation with the right choices for β , γ , and δ , the renormalized m versus h data will fall onto two different universal curves: $f_+(h)$ for temperatures above T_C and $f_-(h)$ for temperatures below T_C . In order to create the renormalized m vs. h plots, we used the values of β , γ , and δ obtained from the Kouvel-Fisher plot see (Fig. 37. And Fig. 38.). All experimental data were observed to collapse onto two distinct branches, one above T_C and the other below T_C , demonstrating adequate handling of the critical regime.

Table 11: Values of Spontaneous Magnetization (M_S) and The Initial Magnetic Susceptibility (χ_o^{-1})

T	M_S	T	χ_o^{-1}
106	0.55717	124	26410.69
108	0.53022	126	28149.89
110	0.49485	128	29348.3
112	0.44907	130	30383.24
114	0.38905	132	31134.54

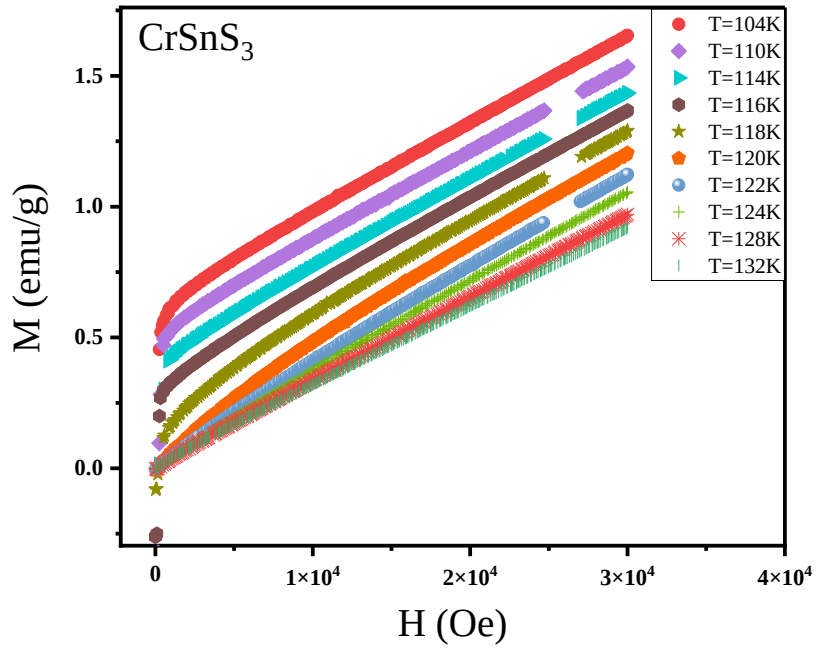


Figure 28: Magnetization-Field Curves $M(H)$ for Different Temperatures around T_C for CrSnS_3

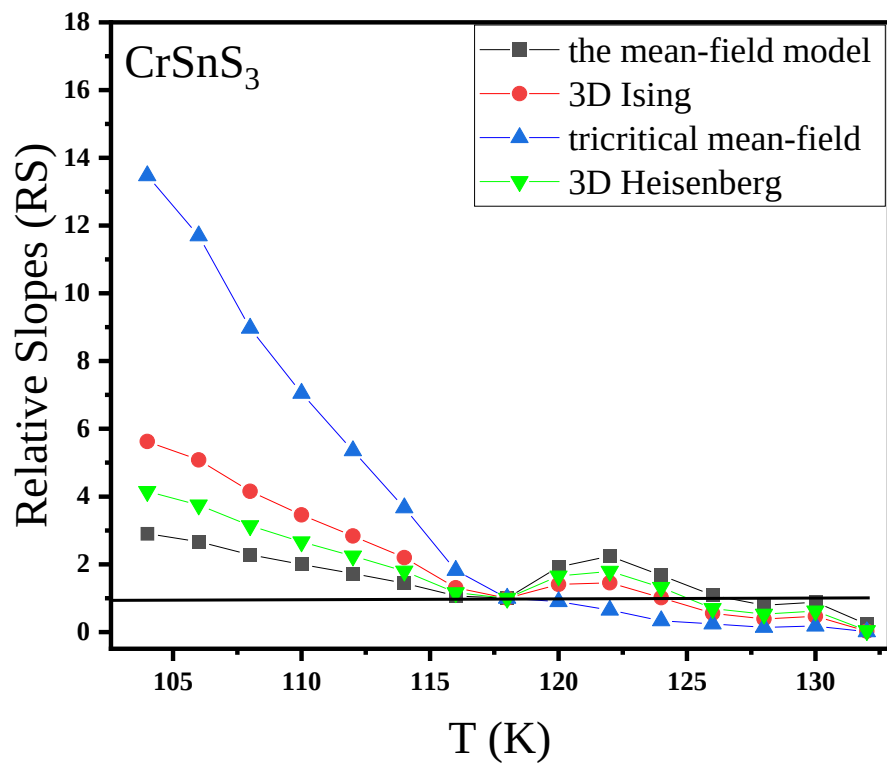


Figure 29: Relative Slope (RS) for CrSnS_3 as a Function of Temperature

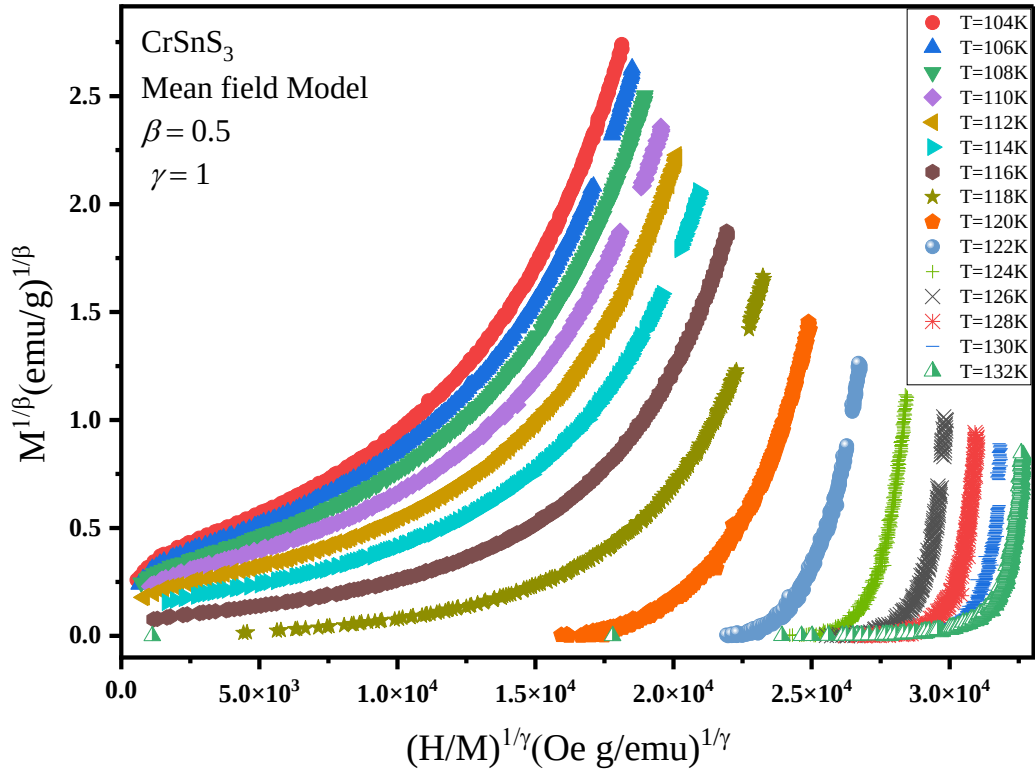


Figure 30: The Isotherms of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ with Parameters of The Mean-Field Model for CrSnS₃.

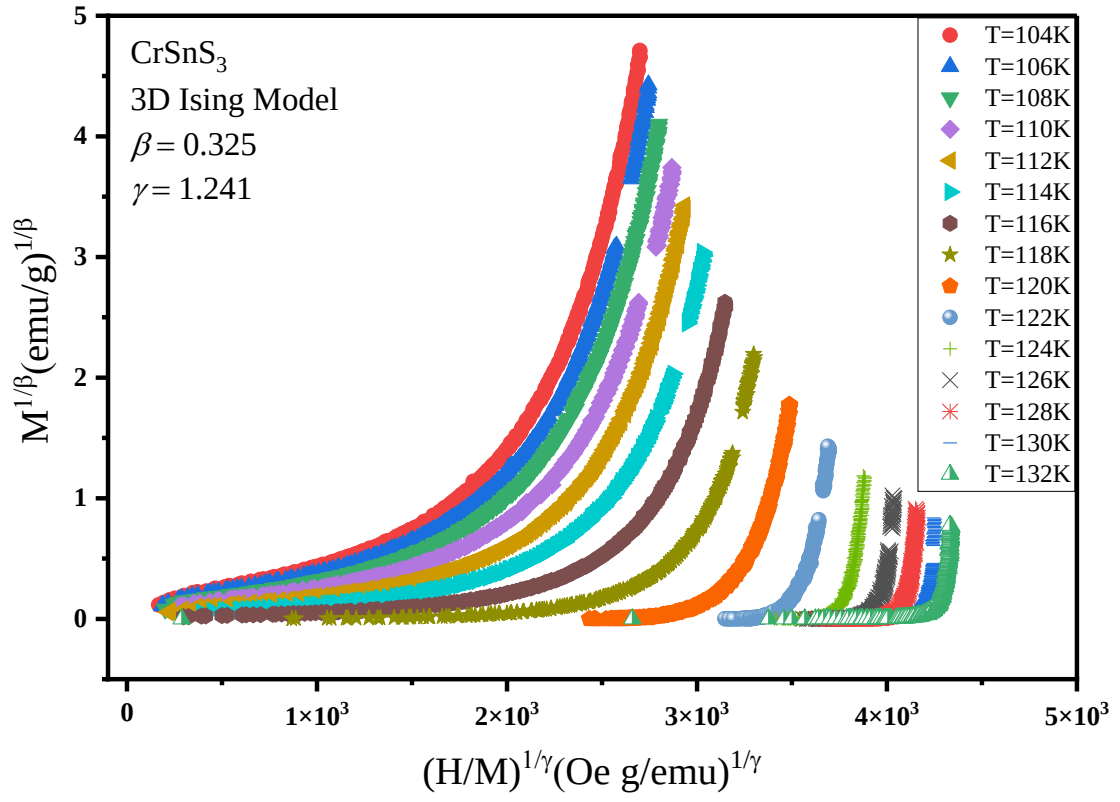


Figure 31: The Isotherms of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ with Parameters of 3D Ising Model for CrSnS₃.

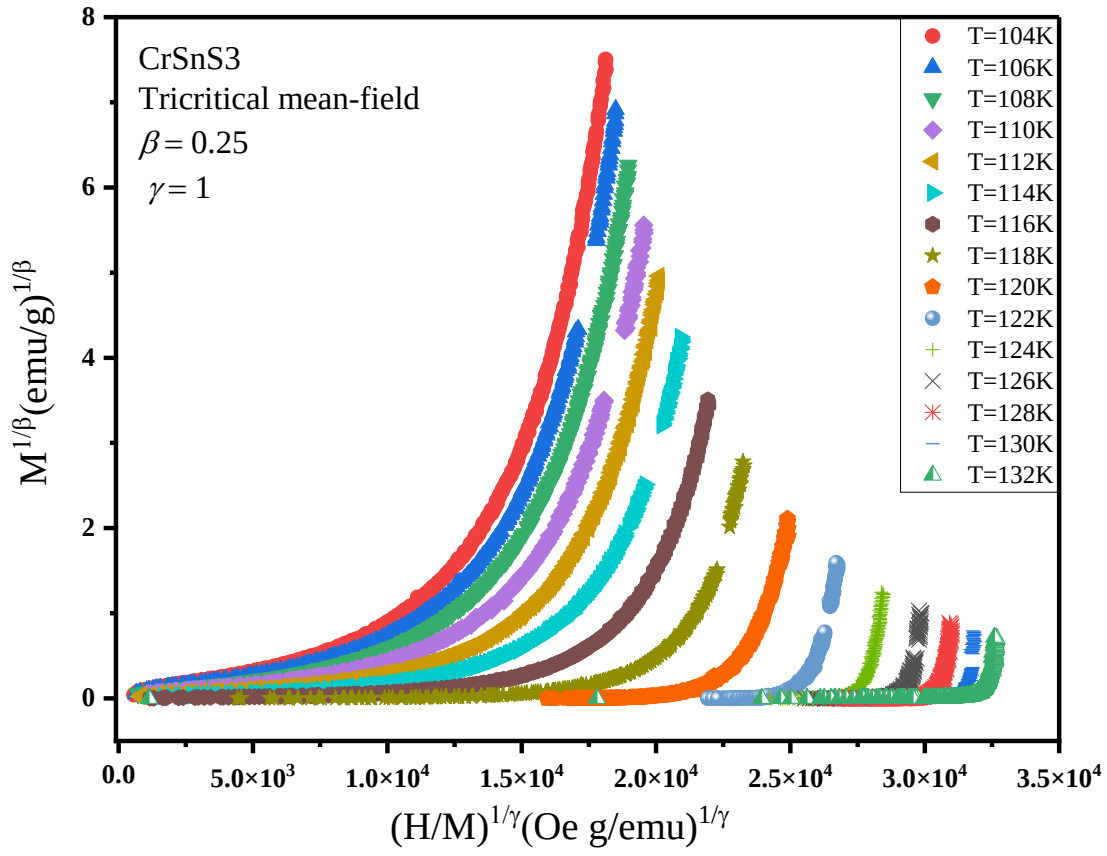


Figure 32: The Isotherms of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ with Parameters of Tricritical Mean-Field Model for CrSnS₃.

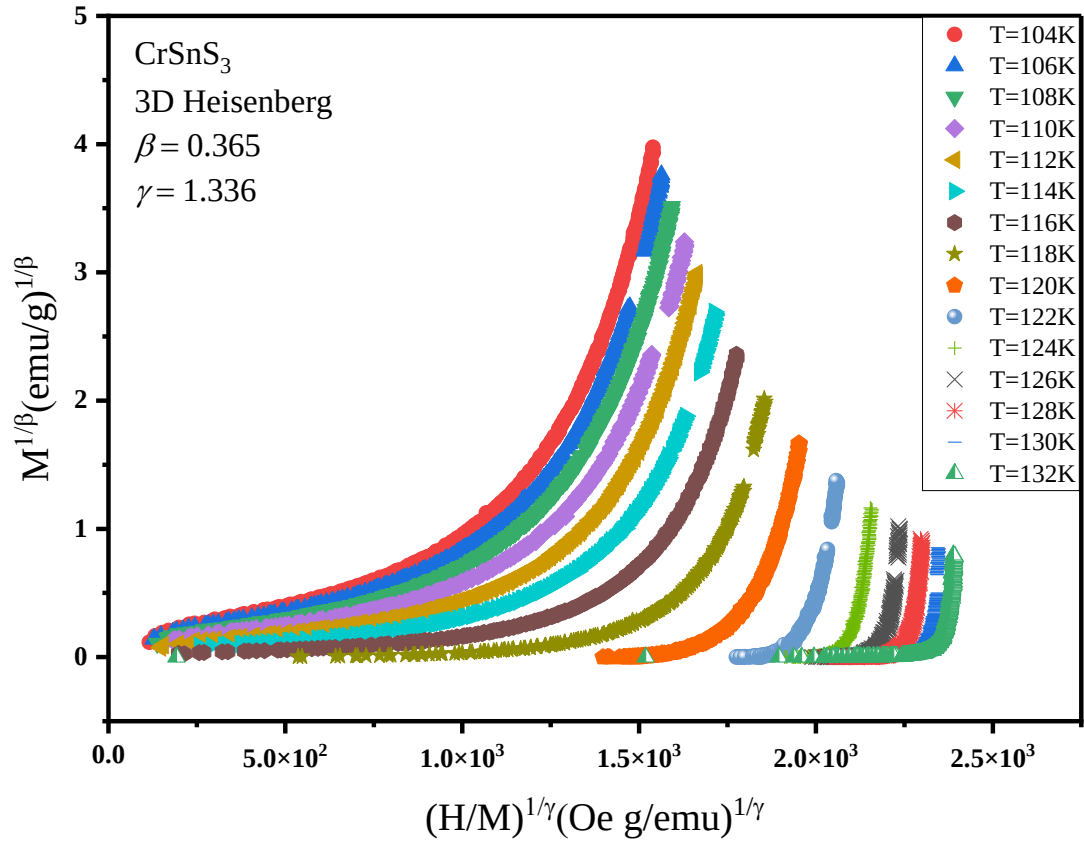


Figure 33: The Isotherms of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ with Parameters of 3D Heisenberg Model for CrSnS₃.

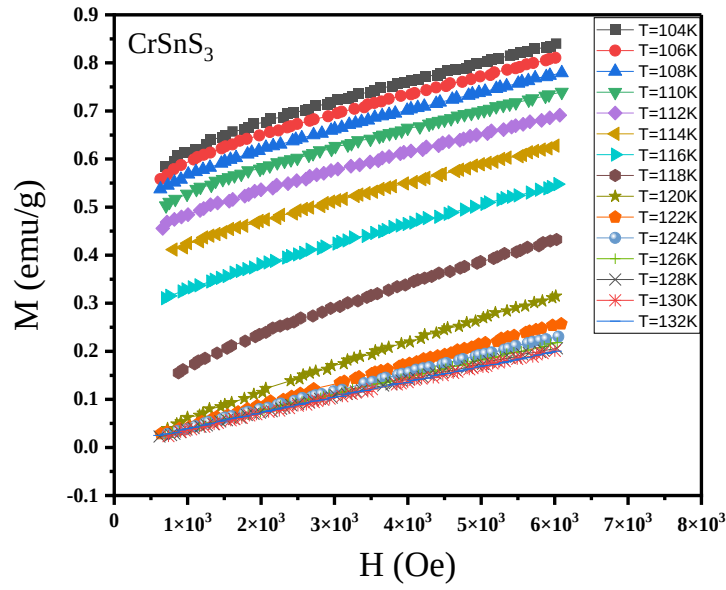


Figure 34: The Straight Lines of Isothermal Magnetization at Different Temperatures for CrSnS_3 .

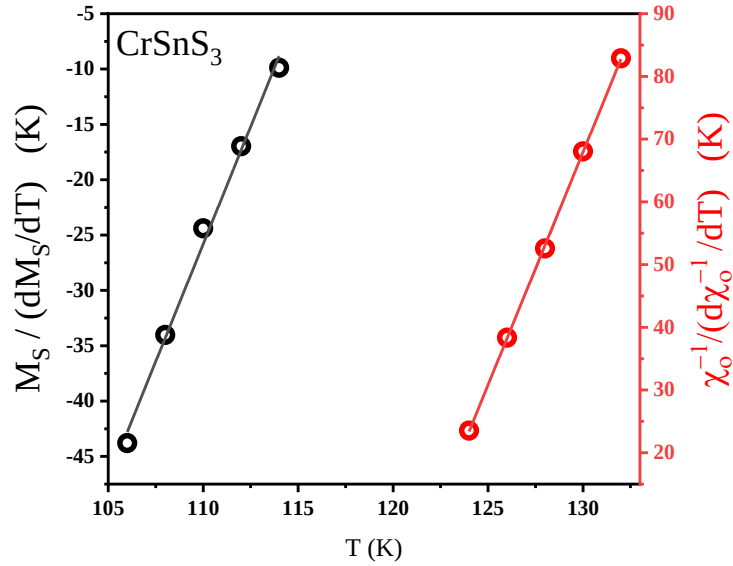


Figure 35: Kouvel-Fisher Plots with the Fitting Curve for CrSnS_3 .

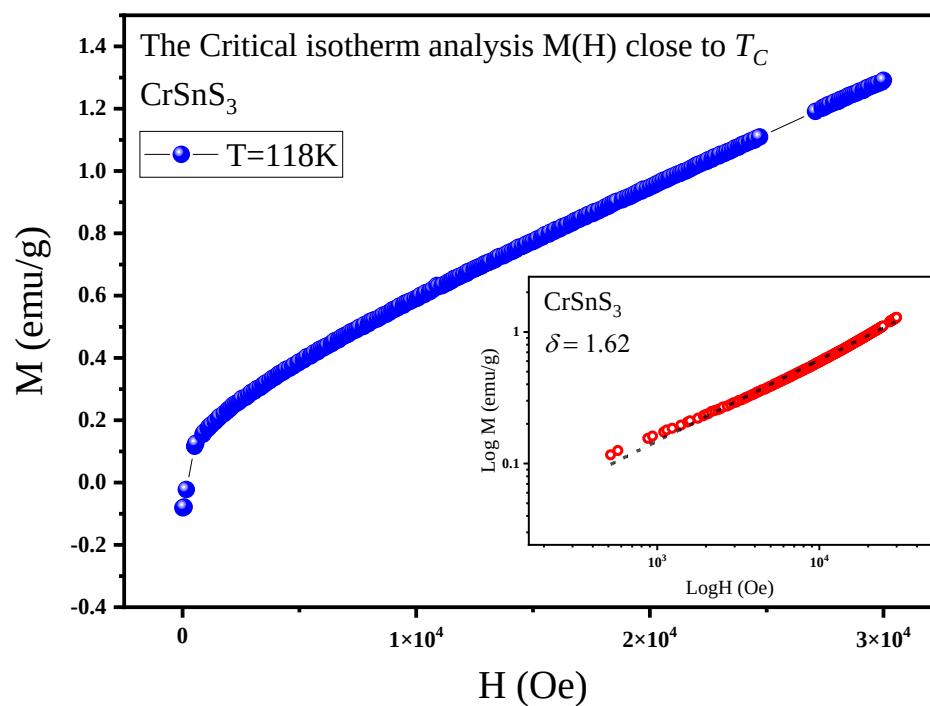


Figure 36: The Isotherm $M(H)$ Plot Collected at $T = 118$ K for CrSnS_3 . Inset: The Same Plot in the Log-Log Scale with the Fitting Curve.

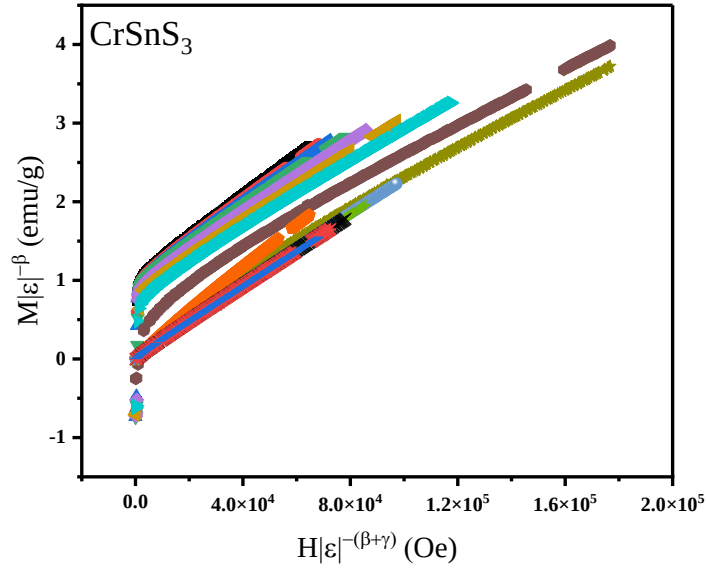


Figure 37: Scaling Plots of Renormalized Magnetization m vs. Renormalized Field h Below and above T_C for CrSnS_3

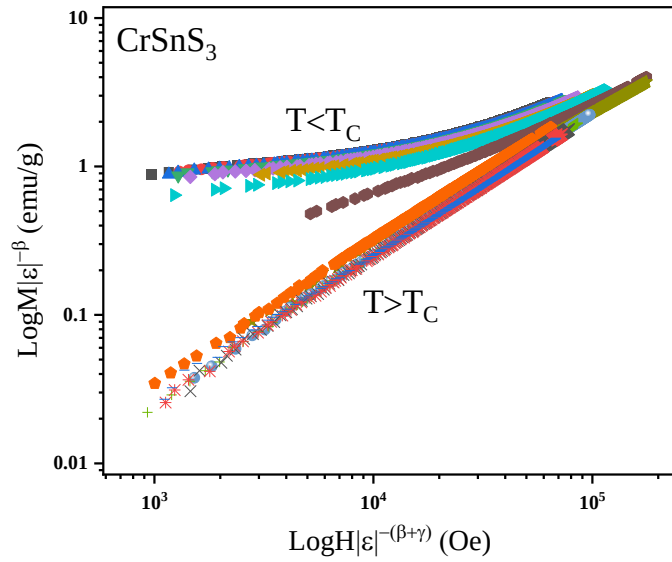


Figure 38: Scaling Plots of Renormalized Magnetization m vs. Renormalized Field h in Log-Log Scale for CrSnS_3 .

5.6 Magnetocaloric Effect

Plots in figures 39 and 40 show the corresponding temperature changes in $-\Delta S_M$ and ΔT_{ad} for various magnetic field changes up to (3 T), respectively. Regardless of the change in magnetic field strength (H) it has been found that this particular compound exhibits a positive MCE across the whole temperature range that was examined. In most cases, it has been found that ordinary ferromagnets have positive MCE. Figures 39 and 40 show that both peaks of $-\Delta S_M$ and ΔT_{ad} occur around T_C , and their magnitudes increase with increasing ΔH .

The relative cooling power (RCP) represents the amount of heat that could be transported in an ideal thermodynamic cycle between the hot and cold parts of the refrigerator. The calculated RCP values of CrSnS_3 using the magnitude of the change in magnetic entropy curves ($-\Delta S_M$ Versus T) reach maxima at 3T of 1.9 J kg^{-1} . In addition, the field dependence of $(-\Delta S_M^{max})$ and RCP can be well-fitted using the power-law relations $(-\Delta S_M^{max}) = aH^n$ and $RCP = bH^m$ (see figure 41) [136]. Fitting of $(-\Delta S_M^{max})$ and RCP give that $n = 1.06$ and $m = 1.64$. As is known, the exponents n and m are correlated with the critical exponents as: $n = 1 + \frac{\beta-1}{\beta+\gamma}$ and $m = 1 + \frac{1}{\delta}$ [138]–[140].

The measured results of the specific heat change (ΔC_P) versus temperature under various field variations are shown in Figure 42. These findings were determined by applying Equation (1.42). The (ΔC_P) shows a sudden transition from a negative to a positive value somewhere in the vicinity of T_C , with a negative value below T_C and a positive value above T_C . The negative or positive values of (ΔC_P) that are close to or above T_C have the potential to significantly influence the total specific heat, which in turn impacts the magnetic refrigerator's capacity for either cooling or heating.

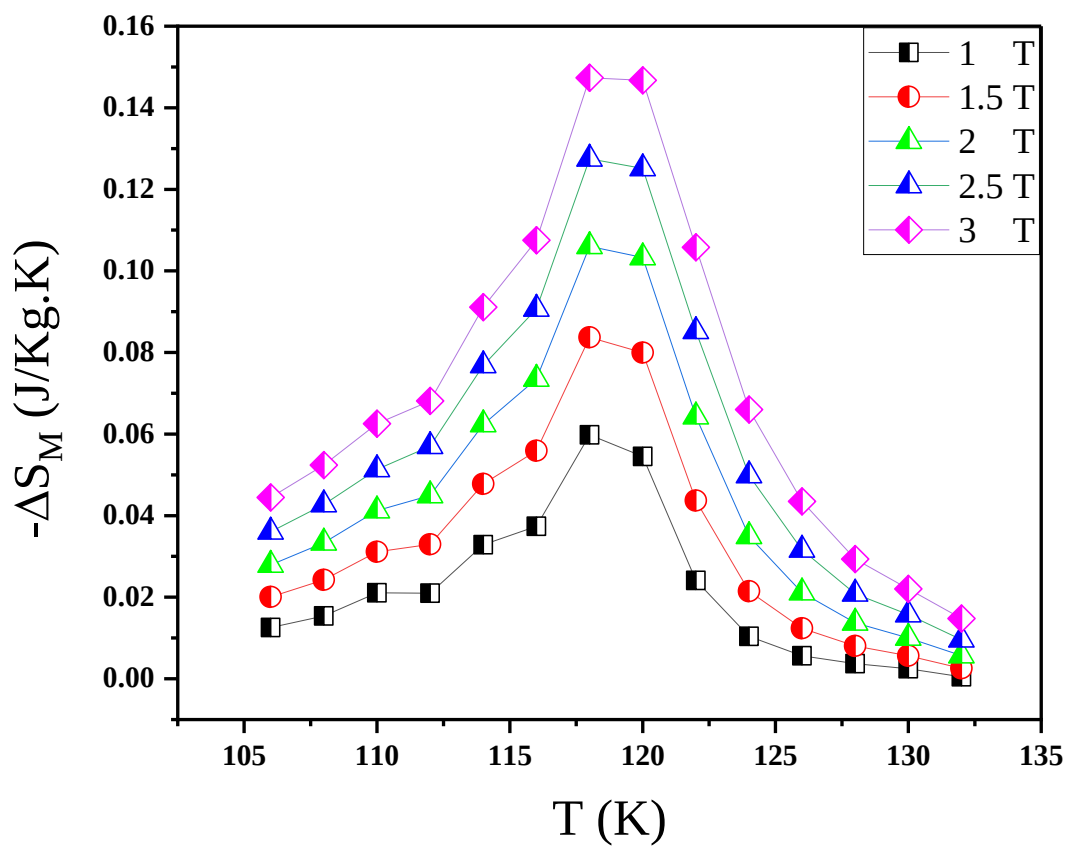


Figure 39: Magnetic Entropy Change ($-\Delta S_M$) as a Function of Temperature at Magnetic Field Changes of ΔH 1, 1.5 , 2 , 2.5 and 3 T for CrSnS₃.

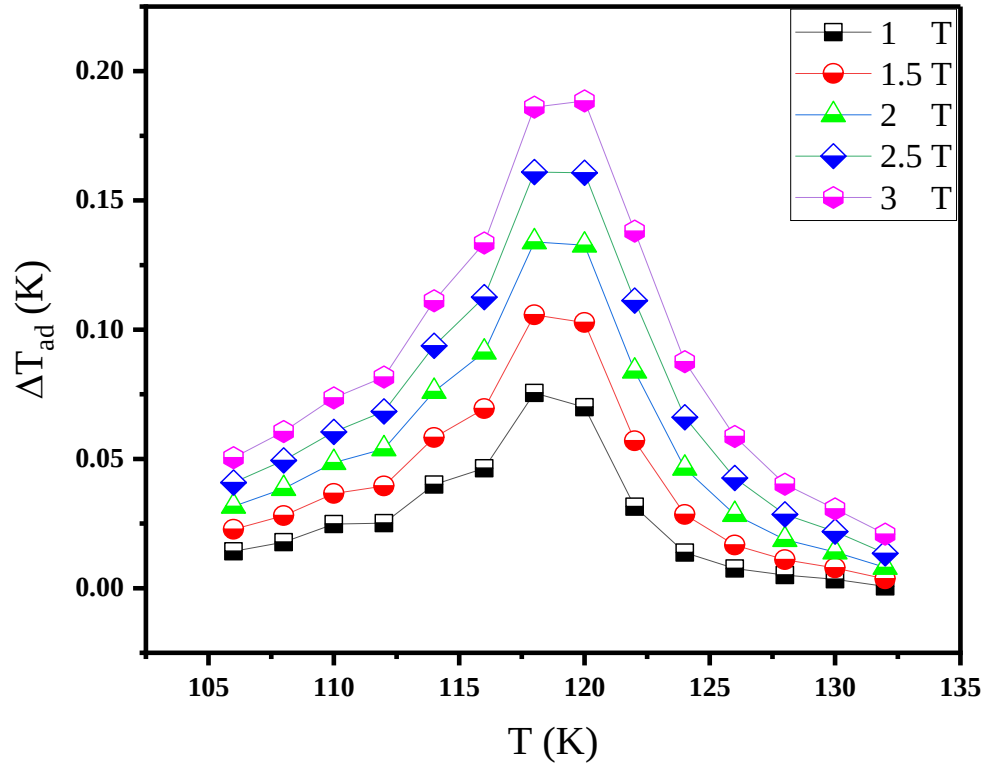


Figure 40: Adiabatic Temperature Change (ΔT_{ad}) Curves of ΔH 1, 1.5 , 2 , 2.5 and 3 T for CrSnS₃.

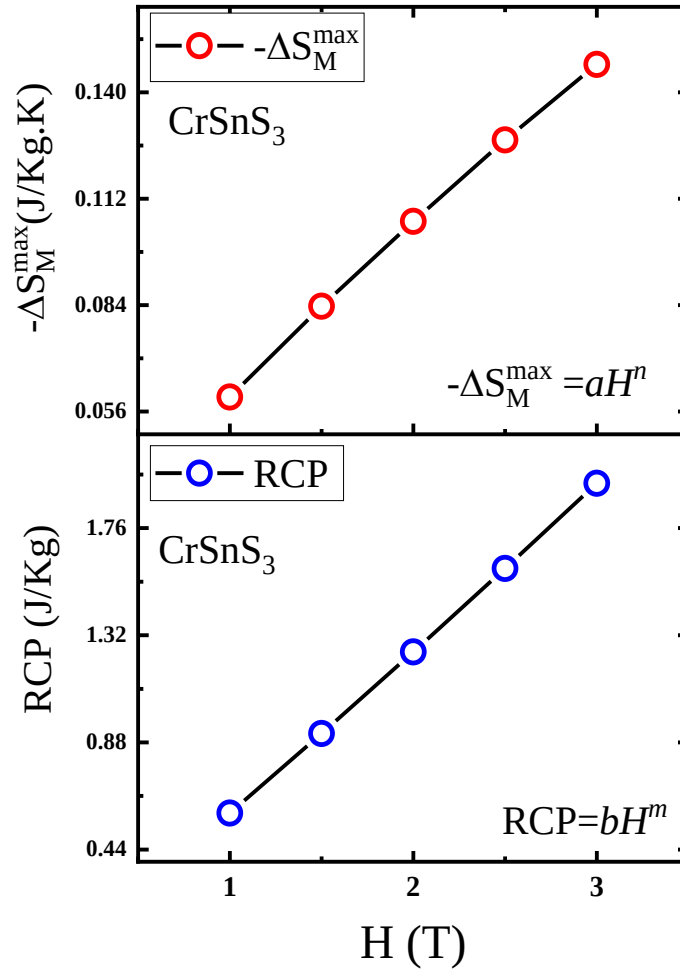


Figure 41: Relative Cooling Power (RCP) and The Maximum Magnetic Entropy Change ($-\Delta S_M$) as a Function of Magnetic Field for CrSnS_3 .

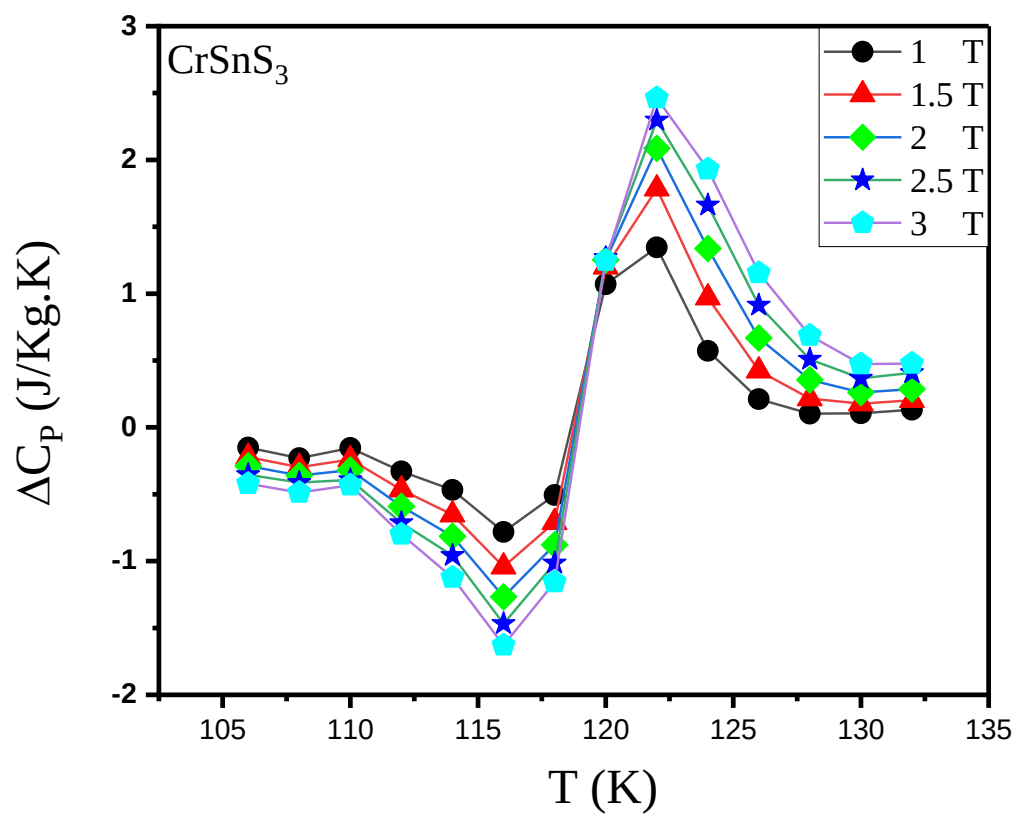


Figure 42: The Specific Heat Change (ΔC_p) Versus Temperature for CrSnS_3 .

5.7 The Resistivity of CrSnS₃

The variations of the resistivity of CrSnS₃ with temperature is shown in Fig. 43. on a semi-log plot versus $1000/T$. At room temperature (300K), the resistivity is about 75 $\Omega\text{-cm}$ and increases with decreasing temperature. The resistivity shows a linear Arrhenius-type behavior. This indicates a semiconducting behavior with a band gap of ~ 0.2 eV.

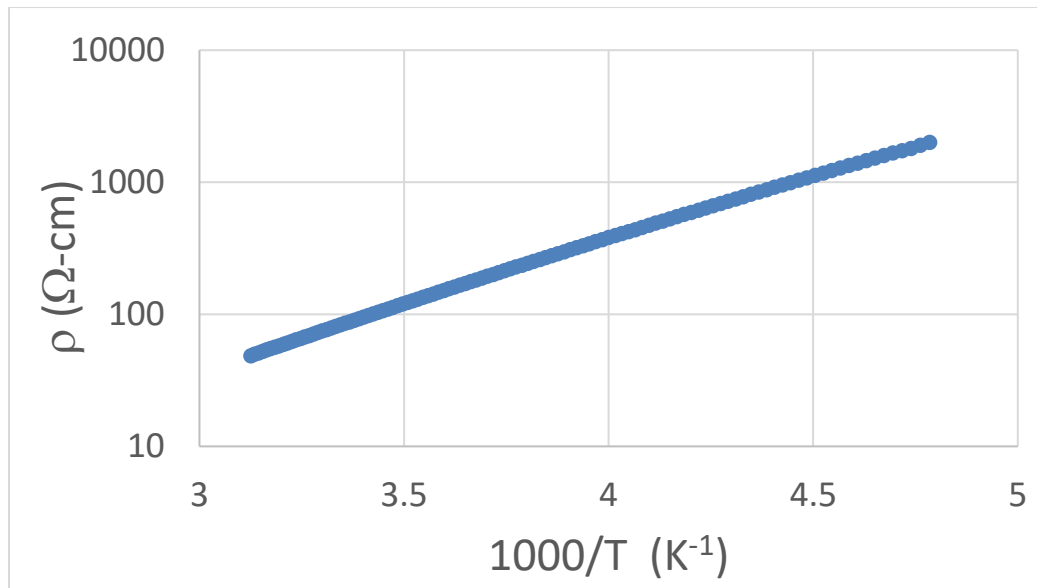


Figure 43: The Variation of The Resistivity of CrSnS₃ with Temperature

CHAPTER 6

RESULTS AND DISCUSSION FOR CrSbS₃

The emergence of cutting-edge technologies driven by diverse needs has led to a wide range of materials synthesized in many different dimensions. In spintronic applications, for instance, two-dimensional (2D) materials, have displayed great potential due to their peculiar physical properties [154]. Therefore, many attempts have been conducted to control magnetism in low-dimensional semiconducting materials. Several 2D magnetic semiconductors have been suggested to maintain their ferromagnet properties at an atomic-layer level [153]. However, the studies are still preliminary because their Curie temperatures (T_C) are insufficient for practical applications [155]. Therefore, it is an essential challenge for materials scientists to improve functional semiconductor systems with curie temperatures (T_C) exceeding room temperature comfortably.

The occurrence of interesting magnetic properties in the new phases motivated us to examine the low dimensional chromium ternary chalcogenides (CrMX_3 , with M being a non-transition metal, $X = \text{S, Se}$). They are expected to possess interesting magnetic properties related to 1D - 3D magnetism because Cr belong to 3d transition element [152]. These properties are obtained by a structural kind of the compound and by the M cations. In this case, structures are formed by CrX_6 polyhedral stacked in different ways [152]. In principle, it may lead to the formation of either 3D,

2D, or 1D infinite network of CrX_6 octahedral, which is accounted for the dimensionality and the category of magnetic interactions. Moreover, Cr-based materials play an important role in superconductivity in reduced dimensional systems. When $M = \text{Sb}$ and $X = \text{S}$, CrMX_3 becomes CrSbS_3 compounds. Bulk CrSbS_3 is a quasi-layered material: the neighboring two CrSbS_3 layers are linked by weak Sb–S bonds which display a pseudo-one-dimensional crystal structure, with CrX_6 octahedral forming infinite, edge-sharing, and double chains. In addition, M atoms link to the relative angle, and neighboring chains between double chains will be changed for different M atoms [153], [156]. Accordingly, the compounds are likely to have 1D ferromagnetic properties.

6.1 X-ray Diffraction

The powder X-ray diffraction pattern of CrSbS₃ recorded with Cu K α line ($\lambda=1.5405\text{\AA}$) radiation is shown in Figure 44. The black solid circles are experimental data, the red line is the fitted curve, and the blue line is the difference between them. The lattice parameter of the sample was determined using Fullproof Software and calculation. The crystal system (which is defined as orthorhombic and belong to the space group pnma no. 62) are analyzed by indexing the peaks based on the value of the peaks from Fullproof software. The graph shows that the model does not account for some experimental peaks. These peaks can be due to other phases that may be present in the sample.

The results of the lattice parameters are presented in the following Table (12). The values obtained are compared with the published values as shown below:

Table 12: Comparison Between Lattice Parameters Obtained From Fullproof, Calculation, and The Published Values.

S/N		a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)
1	Published values	8.879	3.661	12.847
2	Fullproof	8.86479	3.6647	12.83302
2	Calculation	8.722	3.665	12.672

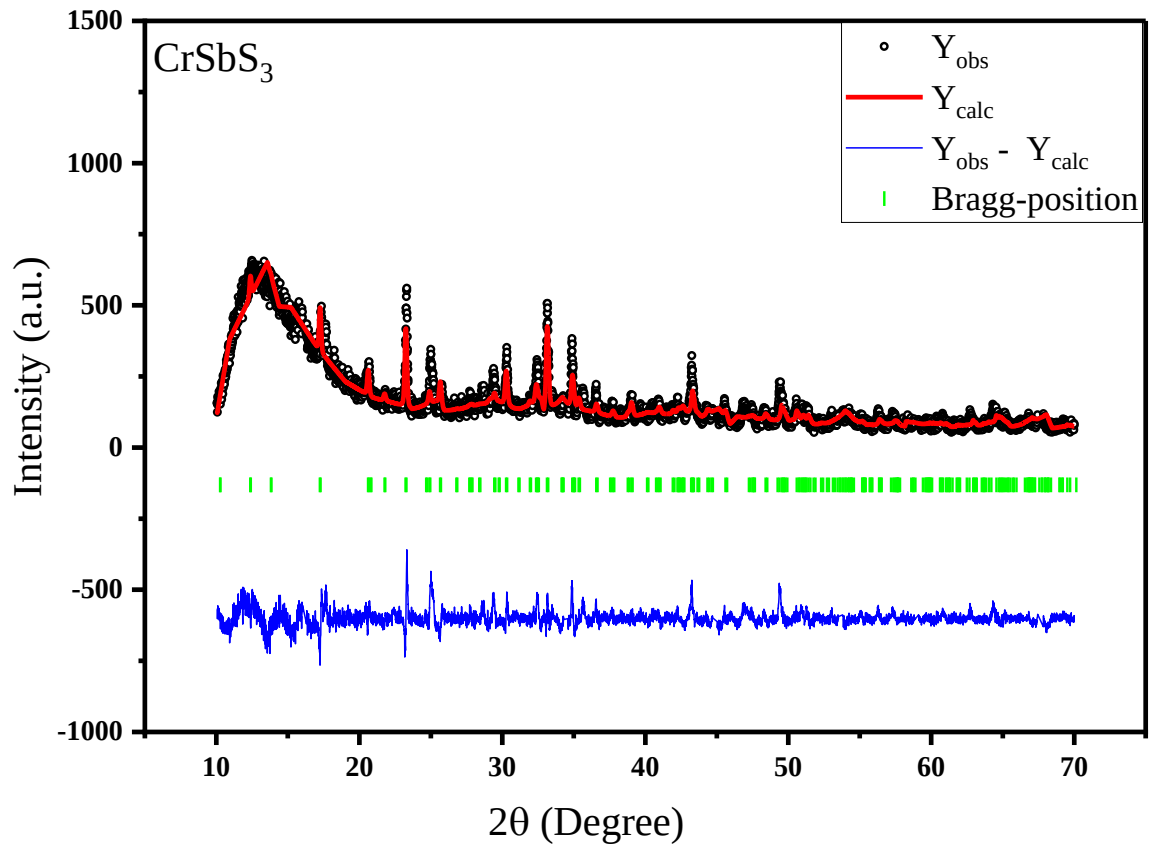


Figure 44: Powder X-ray Diffraction Pattern of CrSbS₃. Red line shows the fitted curve. Black crosses are measured data, Blue line indicates the difference between measured and calculated values, and Magenta Ticks indicate the Bragg Reflection Positions.

6.2 Magnetic Ac-Susceptibility (χ_{ac})

Dynamic magnetic susceptibility technique, often known as AC-susceptibility technique or simply AC-susceptibility (χ_{ac}) is sensitive and a relatively less used tool for identifying new materials. In particular, for studies of phase transitions and magnetic relaxation, (χ_{ac}) is a powerful addition to observations in static (DC) magnetic field measurements.

The differential dM/dH response of the sample's magnetization (M) to an oscillating magnetic field (H) is defined as AC-susceptibility (χ_{ac}). Most frequently, operating frequencies f range from 1 Hz to 10 KHz. In addition to the oscillating magnetic field, it is also possible to apply a DC bias field.

In the following, we present both components of ac-susceptibility; namely the real and the imaginary parts that we obtained for the Cr-based van der Waals ferromagnetic samples. AC-susceptibility measurements (χ_{ac}) performed under various DC-ferromagnetic fields will be presented in another section.

6.2.1 The Real and Imaginary Parts of Ac-Susceptibility (χ_{ac})

Figures 45 and 46 demonstrate the temperature variation of the in-phase (χ') and the out-of-phase (χ'') components of ac magnetic susceptibility from 10 K to 320 K at fixed $H_{ac} = 0.33$ Oe and $H_{dc} = 0$. The reorientation of domain magnetization and the alteration of domain wall motion in the oscillating magnetic field control how (χ')

behaves. The domain magnetization reorientation is insignificant in low ac magnetic field, so the domain wall motion mainly governs the magnetization. The domain structure originates from the magneto-crystalline anisotropy and is affected by the defects of the crystal lattice. The peak in the (χ'') plot reflects energy absorption linked to domain wall motion and rotation, suggesting that these losses are significant in the current situation at temperatures below T_C . Figures 44 and 45 show that a sharp kink in both components was observed at the Curie temperature T_C . By taking the first derivative of both components, we can accurately determine the Curie temperature T_C and show the inflection point, which is $T_C \approx 115\text{ K}$ and FWHM $\sim 2.5\text{ K}$ (see inset in figures 45 and 46). A sudden drop in both components indicates that the FM-PM magnetic phase transition is a first-order magnetic transition. As the temperature decreases below T_C , the susceptibility decreases rapidly. Then it reaches another maximum value near 90 K. This peculiar behavior is also reflected in the susceptibility derivative, which reveals another maximum at 90 K, indicating yet another transition to a possibly antiferromagnetic state.

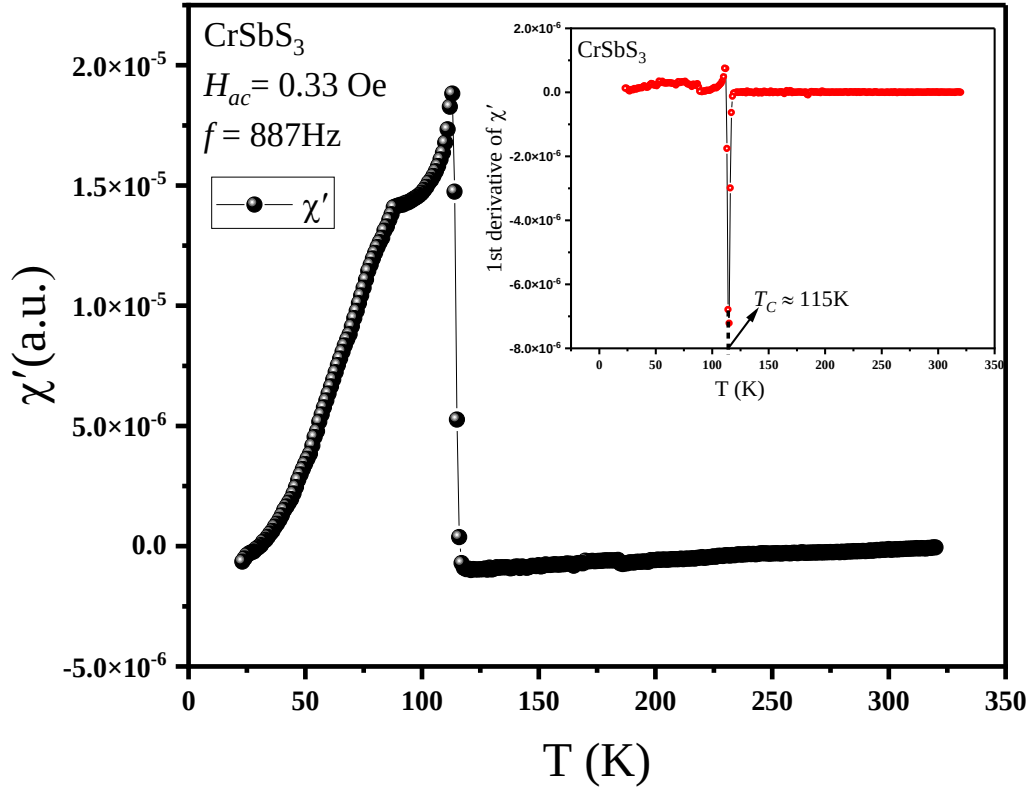


Figure 45: Temperature-Dependence of The Real Part of Magnetic Ac-Susceptibility(χ'). Inset shows The First Derivative of (χ') for CrSbS₃.

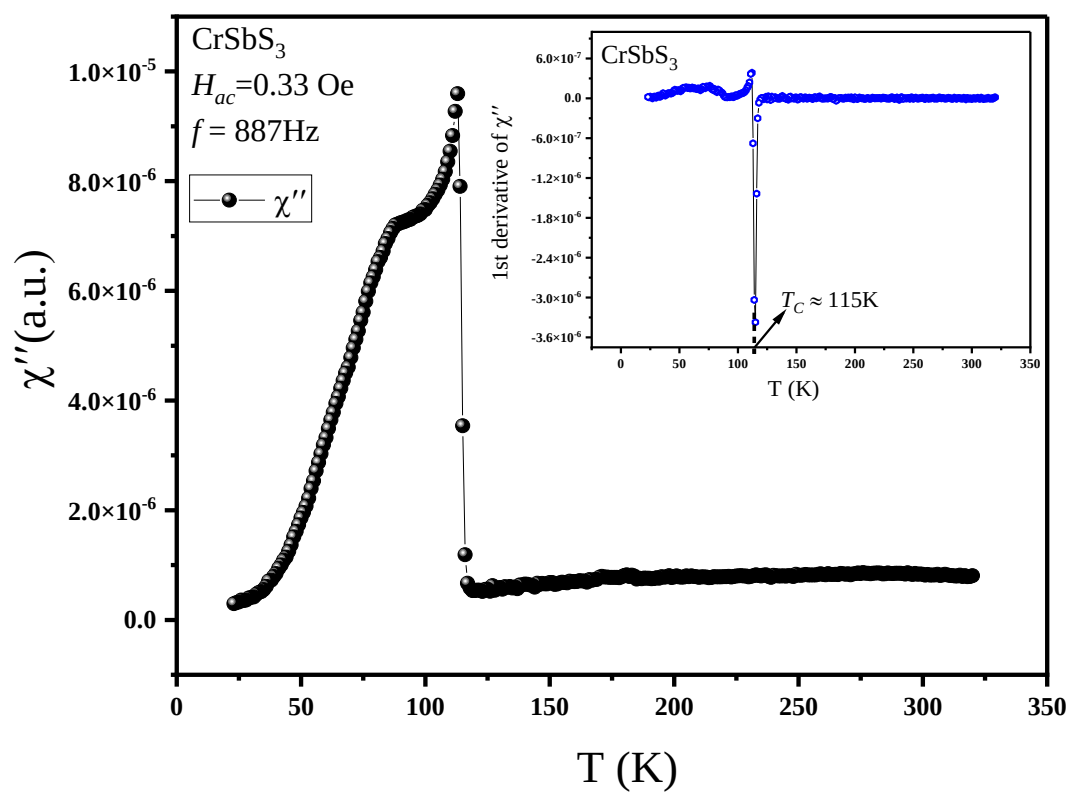


Figure 46: Temperature-Dependence of The Imaginary Part of Magnetic Ac-Susceptibility(χ'') . Inset shows The First Derivative of (χ'') for CrSbS₃

6.2.2 Effects of The DC-biased Field on The Ac-Susceptibility

The effect of dc-magnetic field bias on the ac-susceptibility can further be used to investigate the magnetic state. By applying a dc bias field (H_{dc}), the response of the ac susceptibility diminishes with significant modification in its behavior, which can be seen in Fig. 47. The magnitude of χ' is strongly suppresses the sharp peak and slightly shifts it to lower temperatures by applying the dc bias field. As can be seen in figure 46, the magnetic phase changes from a paramagnetic phase to a ferromagnetic phase about $T_C \approx 115\text{ K}$, this state of affairs persists until approximately $T \approx 80\text{ K}$ with behavior commonly seen in ferromagnetic dc-susceptibility. The susceptibility begins to fall below $T \approx 80\text{ K}$, possibly due to spin reorientation generated by antiferromagnetic exchange interaction. As the applied dc-field increases, the width of the FM transition increases (Fig. 47.), indicating that the materials become less responsive to the low H_{ac} ($\sim 0.33\text{ Oe}$).

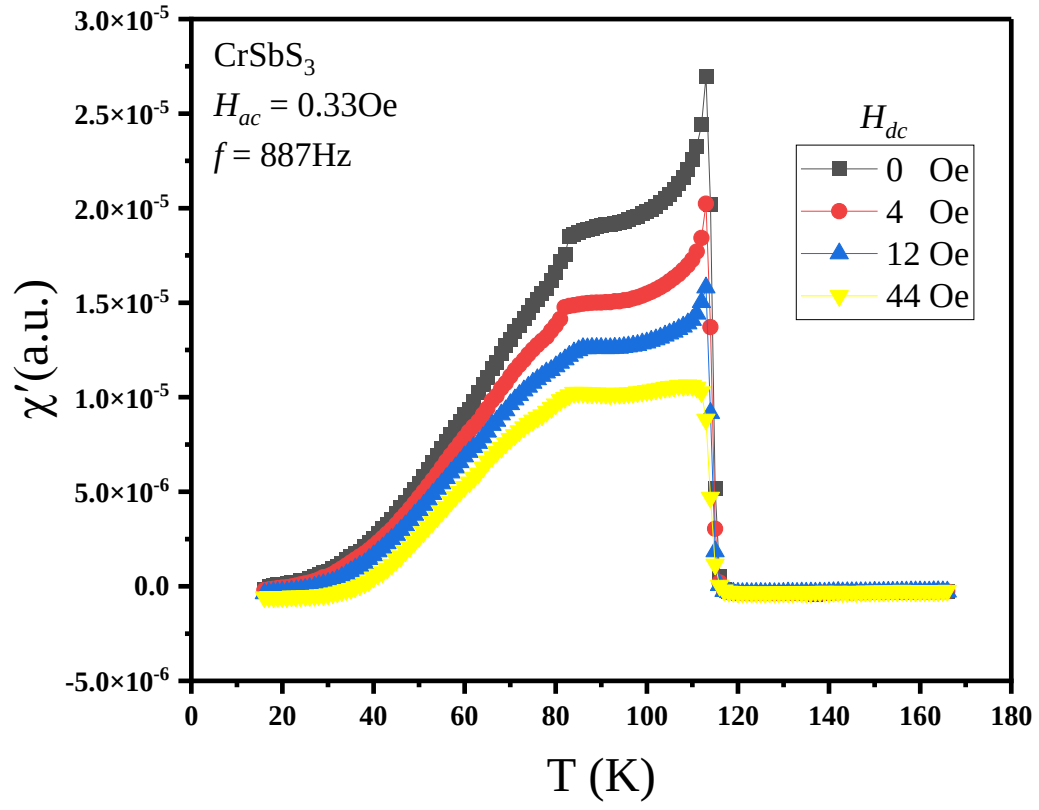


Figure 47: Temperature Variation of in-phase(χ') of Ac-Susceptibility for CrSbS₃ at Different Applied Dc-Magnetic Field H_{dc} (0 , 4 , 12 , 44 Oe) at Fixed H_{ac} =0.33 Oe and f = 887 Hz

The effects of the dc-bias field on the transition temperature can be further investigated by measuring the ac-susceptibility as a function of the dc-field cycled between two maxima (± 45 Oe) at various temperatures near T_C . Figure 48 shows the result. According to the figure, the susceptibility reaches its maximum at ($H_{dc} = 0$). It totally disappears at 117 K, with a tiny peak at $T = 115$ K. This indicates that the transition occurred between these two points (115-116K).

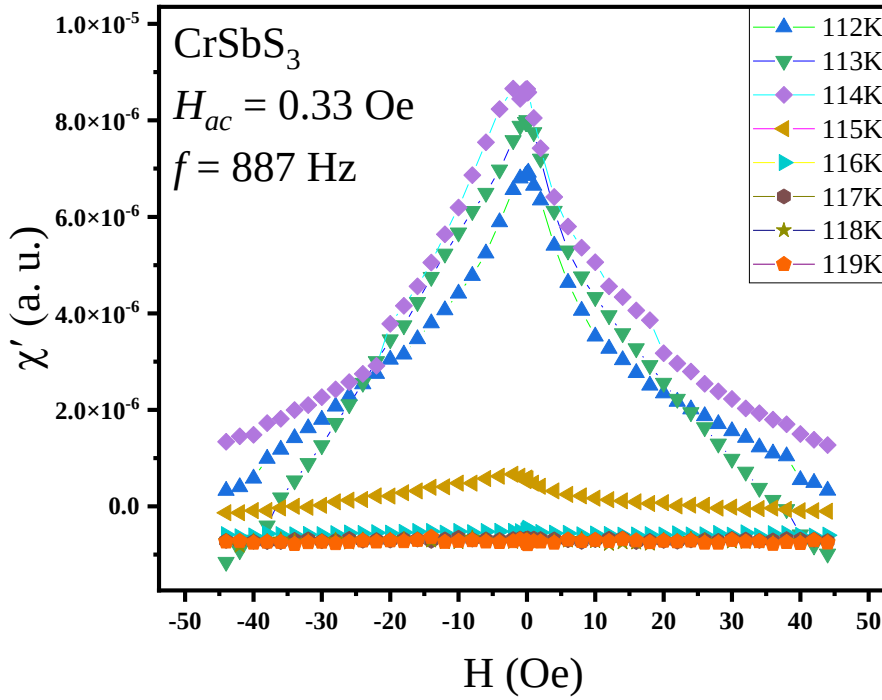


Figure 48: DC Bias Fields Variation of in-phase (χ') of AC-Susceptibility at Different Temperatures for CrSbS_3 .

6.2.3 The Frequency Dependence of Magnetic Ac-Susceptibility (χ_{ac})

The temperature change of the in-phase (χ') of ac magnetic susceptibility at various frequencies over a wide temperature range is depicted in Figure 49. This is the result when the values of $H_{ac} = 0.33$ Oe and $H_{dc} = 0$. The magnetization M of a spin system will relax to a new equilibrium state after a characteristic time (τ), called the relaxation time, as the applied magnetic field shifts from H to $H \pm \Delta H$.

The real part of ac-susceptibility (χ') as depicted in Figure 49, is frequency dependent. Since the moments can follow the oscillating field, it appears that the relevant reconfiguration of the domain structure is a relaxing effect. Furthermore, the frequency dependence of the ac magnetic susceptibility supports the pseudo-one-dimensional structure of the CrSbS_3 sample, in which the magnetic-moment-bearing Cr sublattice forms double chains. Furthermore, peak shifts in the ac-susceptibility (χ') as a function of frequency follow the Arrhenius law, which can be used to calculate the activation energy.

a)

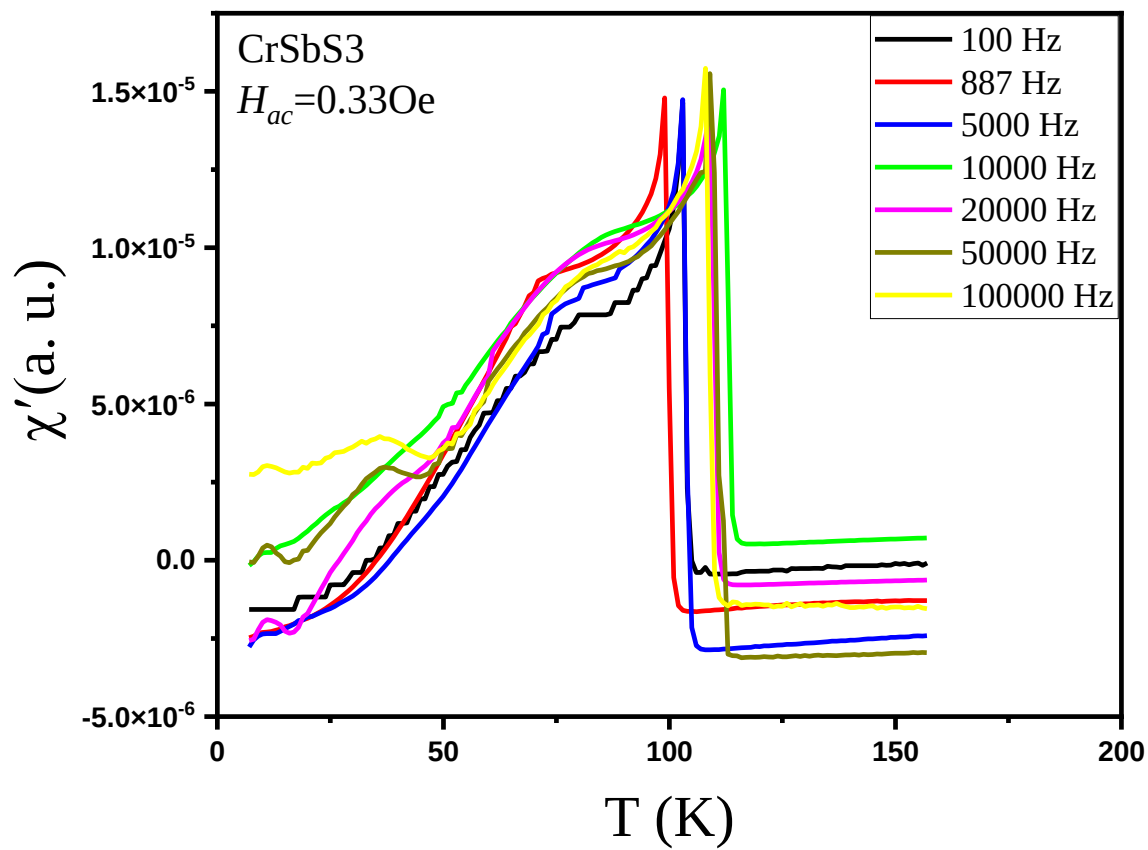


Figure 49: a) Frequency Dependent on in-phase (χ') of AC-Susceptibility for CrSbS₃.

6.2.4 The activation energy

Using the Arrhenius law, one may calculate the activation energy by observing the shift in the ac-susceptibility peak as a function of frequency (see Fig. 49b and c.) [25].

The relaxation time $\tau(T) = 1/f$ is expressed as:

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right) \quad (6.1)$$

After a characteristic time (τ), also known as the relaxation time, the magnetization M of a spin system will reach a new equilibrium state as the applied magnetic field shifts from H to $H \pm \Delta H$. The relaxation process is effected by a number of factors, including the motion of domain walls, the rotation of magnetic moments and other parameters. So equation (6.1) converts to:

$$\ln f = \frac{-\Delta E}{k_B} \frac{1}{T} + \ln f_0 \quad (6.2)$$

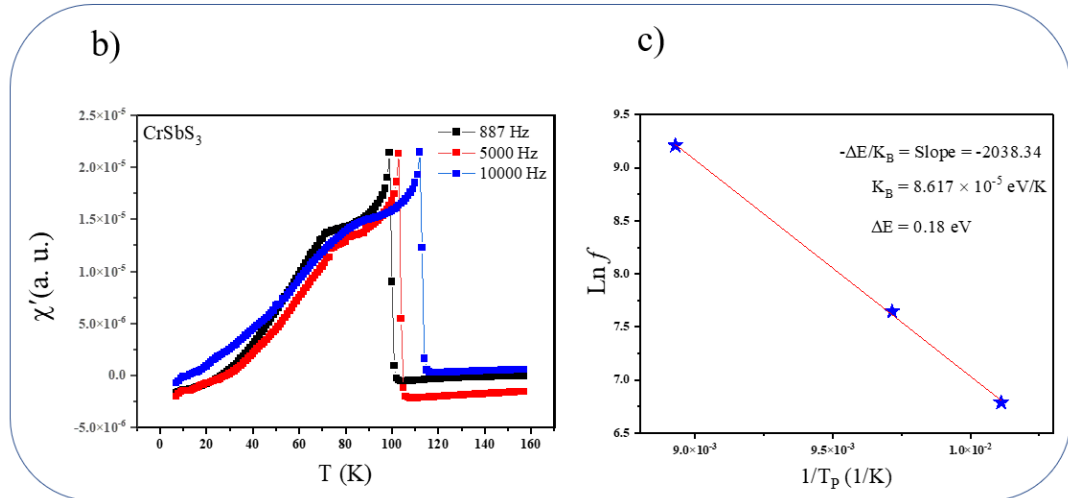


Figure 49: b),c) Activation Energy

6.3 Magnetic Isotherms and The Dc-Susceptibility

The variations of the magnetization with the temperature at a constant magnetic field $H_{dc} = 200 \text{ Oe}$ is presented in Fig. 50. It is evident that the CrSbS3 sample undergoes paramagnetic (PM) to ferromagnetic transition. A rapid increase in $M(T)$ at $T_C \sim 115 \text{ K}$ indicates an onset of FM-type order. Inset in figure 50 shows the first derivative of $M(T)$ to determine the critical temperature (inflection point) where the critical temperature $T_C \approx 115 \text{ K}$. The temperature dependence of the magnetization $M(T)$ reaches a maximum near 85K, then gradually decreases at low temperatures indicating that a spin re-orientation occurs below 85K. A sharp peak at the critical temperature $T_C \approx 115 \text{ K}$ can be described as a first-order magnetic transition.

Isothermal magnetization was measured at various temperatures to further explore the complex magnetic behavior. Figure 51 displays few of the results. When temperatures decrease below 118 K, the shape of the $M(H)$ curves changes from the straight lines expected for a PM state to significantly bent curves indicative of an FM ordering. Nevertheless, the shape of the $M(H)$ curve at low temperatures is very similar to those that are predicted for antiferromagnetic order (AFM). Figure 52 shows the dc-magnetic susceptibility (χ_{dc}) versus temperature at constant $H_{dc} = 200 \text{ Oe}$.

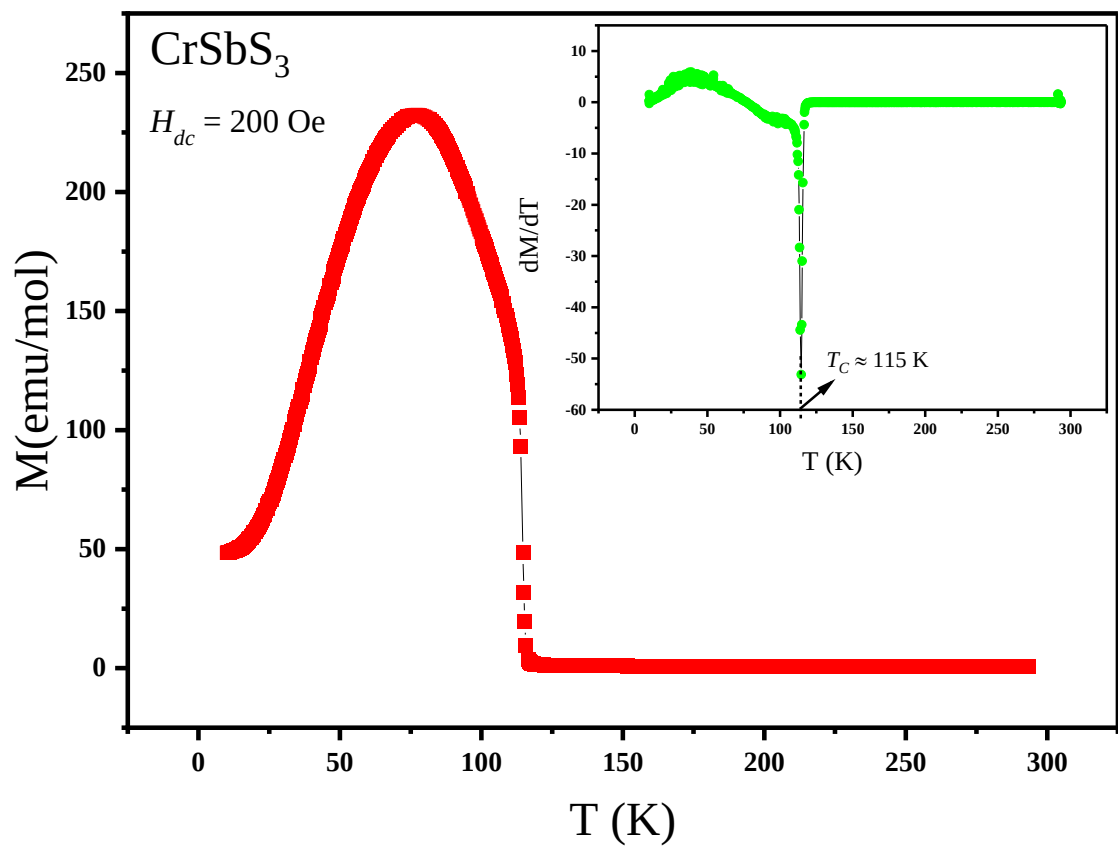


Figure 50: Temperature-Dependent Magnetization $M(T)$ measured in $H_{dc} = 200\text{Oe}$ for CrSbS₃. Inset shows The First Derivative of $M(T)$ for CrSbS₃.

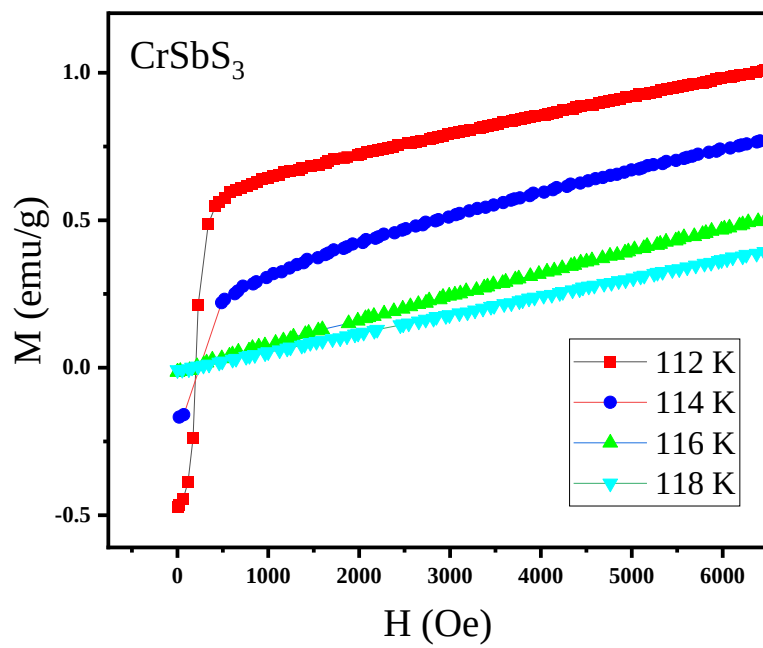


Figure 51: Isothermal Magnetization Curves measured at selected Temperatures for CrSbS_3 .

6.4 The Curie-Weiss Law

The relationship between inverse magnetic susceptibility and temperature is depicted in figure 52. Figure 52 shows how the Curie-Weiss law describes the experimental curve over the whole range of PM temperatures. The figure reflects typical ferrimagnetic behavior with negative θ_N . The linear part of the inverse susceptibility is fitted to the Curie-Weiss relation (The paramagnetic temperature range). The Neel temperature is $\theta_N \approx -30 \text{ K}$, and the molar Curie constant is ($C_m = 0.86 \text{ emu. K/mol}$).

For the effective magnetic moment of the Cr-ion, the following equation was used to determine the effective magnetic moment of the Cr^{3+} ions ($\mu_{eff, \text{Cr}^{3+}}$) in the temperature range of application of the Curie-Weiss law:

$$\mu_{eff} = 2.828 \sqrt{C_m} \mu_B \quad (6.3)$$

Where $\sqrt{3 K_B / N_A \mu_B^2} = 2.828$, in which $K_B = 1.380649 \times 10^{-16} \text{ erg/K}$, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$, $\mu_B = 9.274 \times 10^{-21} \text{ erg/G}$ are the Boltzmann constant, Avogadro's number, and the Bohr magneton, respectively.

It is found that the effective magnetic moment of Cr^{3+} ions ($\mu_{eff, \text{Cr}^{3+}}$) in CrSbS_3 is $2.61\mu_B$. This value is smaller than the observed value of the effective magnetic moment of free Cr^{3+} ions ($\mu_{eff, \text{Cr}^{3+}} = 3.85 \mu_B$). This fact also indicates a complex magnetic ordering (ferro, ferri, and antiferromagnetic) in CrSbS_3 below T_C and exhibits an impurity phase in the sample.

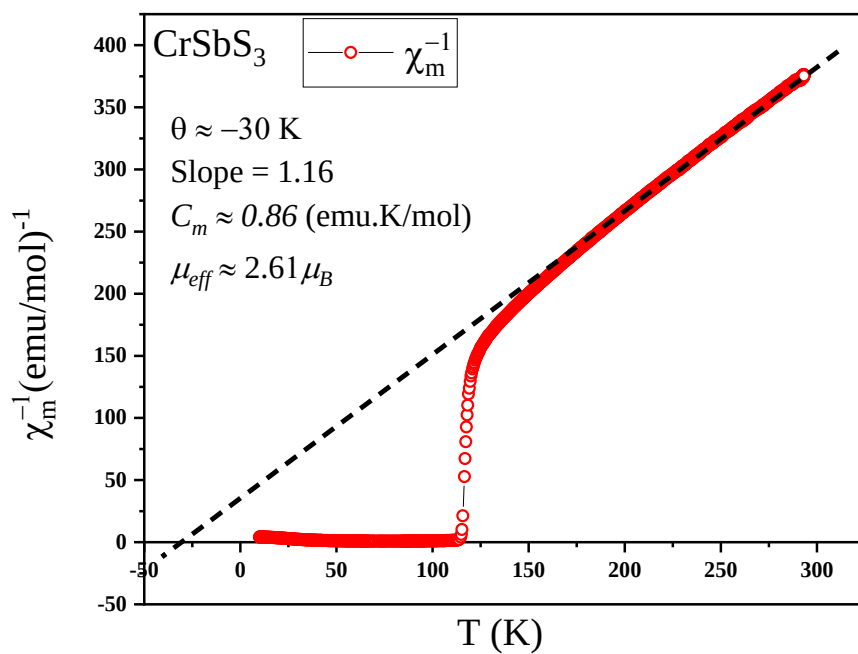


Figure 52: Variation of The Inverse of The Molar Magnetic Susceptibility (χ_m^{-1}) as a Function of Temperature for CrSbS₃ at $H_{dc} = 200$ Oe.

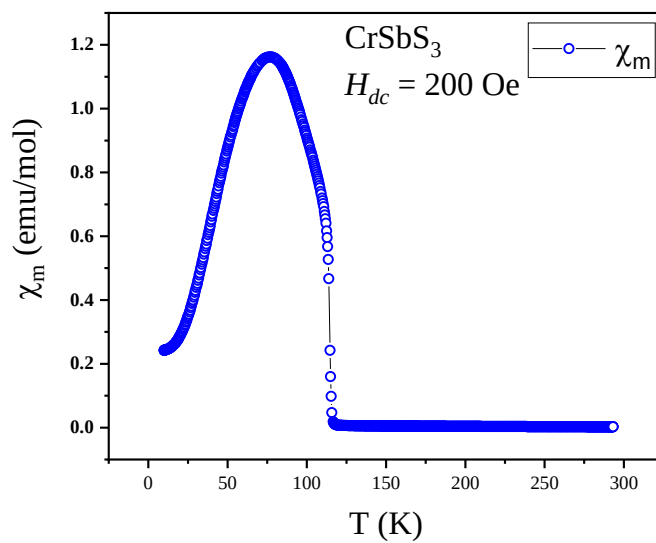


Figure 53: Variation of the Molar Magnetic Susceptibility (χ_m) as a Function of Temperature at $H_{dc} = 200$ Oe for CrSbS₃

6.5 Critical Behavior

Arrott plot analysis of $M(H)$ curves (Fig. 54.) was performed to get an understanding of the nature of the magnetic transitions in CrSbS_3 . Banerjee argues that the slope in the Arrott plot reveals the order of the phase transition: negative curvatures correlate to a first-order transition, while positive curvatures imply a second-order transition. The intercept values were used to differentiate the order of phase transitions and these calculated using linear fits. For CrSbS_3 , the possibility of a first-order magnetic transition is indicated by the fact that the value of the y-intercept at 115 K, the one closer to spin reorientation, is negative for the high field region. We may deduce that the sample undergoes an FM-PM change upon first-order spin re-orientation by analyzing the Arrott plot.

In the Mean-field model, the critical exponents $\beta = 0.5$ and $\gamma = 1$ are used in the Arrott plot. Consequently, the M^2 against H/M magnetization isotherms should be a series of parallel straight lines, and the T_C magnetization isotherm should be a straight line through the origin. We can observe that the mean-field model is not applicable to CrSbS_3 because all of the curves in the Arrott plot are nonlinear and have a downward curvature (see Fig. 55.). Because of the inadequacy of the mean-field model, we resort to the modified Arrott plot in order to learn more about the PM-FM transition in CrSbS_3 .

Exponents from the 3D Ising model ($\beta = 0.325$, $\gamma = 1.24$), 3D Heisenberg model ($\beta = 0.365$, $\gamma = 1.386$), and tricritical mean-field model ($\beta = 0.25$, $\gamma = 1.0$) are shown in Figures 56 , 57 and 58 to illustrate the updated Arrott plots. In the high-field region, the modified Arrott plot should consist of a series of parallel lines with the same slope $S(T) =$

$dM^{1/\beta}/d(H/M)^{1/\gamma}$. The relative slope (RS) [$RS = S(T)/S(T_C)$] helps us decide which model offers the best fit for the data. The best model will have a Relative slope (RS) that tends toward unity. Figure 59 displays the RS versus T values for several models. It is noted that the RS of the tricritical mean-field model shows the largest deviation from unity below T_C . The RS of the tricritical mean-field model is close to $RS = 1$, mostly above T_C , while that of the 3D Heisenberg model is the best below T_C . Since the standard Arrott plot analysis does not allow us to determine which one of these models is closer to describing the critical behavior in the sample therefore, we applied the original technique to find the critical point of the samples using the Kouvel-Fisher method. In this way, we find the fitting of $M(H)$ curves at the high field where we have straight lines in which the slope represents the magnetic susceptibility, and the y-intercept represents the spontaneous magnetization.

For a first-order PM-FM phase transition, the spontaneous magnetization (M_S) occurs at temperatures lower than the transition temperature (T_C), the inverse initial magnetic susceptibility (χ_o^{-1}) occurs at temperatures higher than the (T_C), and the field-dependent magnetization (M) at T_C can be described by a set of critical exponents consisting of β , γ , and δ and, respectively. The mathematical definitions of the exponents from magnetization measurement are given below:

$$M_S(T) = M_o(-\varepsilon)^\beta \quad (6.4)$$

$$\chi_o^{-1} = (h_o/m_o)(\varepsilon)^{-\gamma} \quad (6.5)$$

$$M = D H^{\frac{1}{\delta}} \quad (6.6)$$

$$\varepsilon = \frac{T-T_c}{T_c} \quad (6.7)$$

where M_O , (h_o/m_o) and D are the critical amplitudes.

As discussed before, the order of phase transition is the first order. So, to obtain the anisotropic critical exponents β , γ , and δ , the values of spontaneous magnetization (M_S) and the inverse initial magnetic susceptibility (χ_o^{-1}) are extracted from isothermal magnetization curves (Fig. 60.) and shown in Table (13). From the Kouvel-Fisher method where $M_S(T)/(dM_S(T)/dT)$ and $\chi_o^{-1}(T)/(\chi_o^{-1}(T)/dT)$ plotted against temperature should be straight lines with slopes $1/\beta$ and $1/\gamma$, respectively.

$$\frac{M_S(T)}{dM_S(T)/dT} = \frac{T}{\beta} - \frac{T_c}{\beta} \quad (6.8)$$

$$\frac{\chi_o^{-1}(T)}{d\chi_o^{-1}(T)/dT} = \frac{T}{\gamma} - \frac{T_c}{\gamma} \quad (6.9)$$

The linear fits of the plots (Fig. 61.) yield $\beta = 0.263$ with $T_c = 113.3$ K and $\gamma = 0.171$ with $T_c = 115.3$ K.

The Widom relation gives:

$$\delta = 1 + \frac{\gamma}{\beta} \quad (6.10)$$

The value of δ is determined to be 1.65 based on the results of the Kouvel-Fisher method applied to obtain β and γ . The critical isotherm analysis $M(H)$ at T_c should be a straight line on the log-log scale with a slope of $1/\delta$, according to Eq. (6.6)(see Fig. 62.).

This type of fitting gives a value of $\delta = 1.71$, which is comparable to the value obtained from the Widom relation.

The accuracy of the calculated critical exponents can be estimated via scaling analysis. Assuming that the magnetic equation of state in the critical area follows a scaling relation, we get the following:

$$M(H, \varepsilon) = \varepsilon^\beta f_\pm\left(\frac{H}{\varepsilon^{\beta+\gamma}}\right) \quad (6.11)$$

where f_+ for $T > T_C$ and f_- for $T < T_C$, respectively, are the regular functions. In terms of the renormalized magnetization (m) where $m \equiv \varepsilon^{-\beta} M(H, \varepsilon)$ and the renormalized field (h) where $h \equiv \varepsilon^{-(\beta+\gamma)} H$, Eq.(4.20) reduces to a simple form:

$$m = f_\pm(h) \quad (6.12)$$

It proposes that for a correct scaling relation with the right choices for β , γ , and δ , the renormalized m versus h data will fall onto two different universal curves: $f_+(h)$ for temperatures above T_C and $f_-(h)$ for temperatures below T_C . We have created the renormalized m vs. h plots using the values of β , γ , and δ derived from the Kouvel-Fisher model (Fig. 63. And Fig. 64.). All experimental data are easily noticed to collapse onto two distinct branches, one above T_C and the other below T_C , confirming proper treatment of the critical regime.

Table 13: Values of Spontaneous Magnetization (M_s) and The Initial Magnetic Susceptibility (χ_o^{-1})

T	M_s	T	χ_o^{-1}
102	1.01617	116	12996.47125
104	0.97521	118	16060.41177
106	0.91479	120	18015.56586
108	0.84114	122	19210.39859
110	0.74806	124	20271.16699
112	0.59586	126	20715.18257

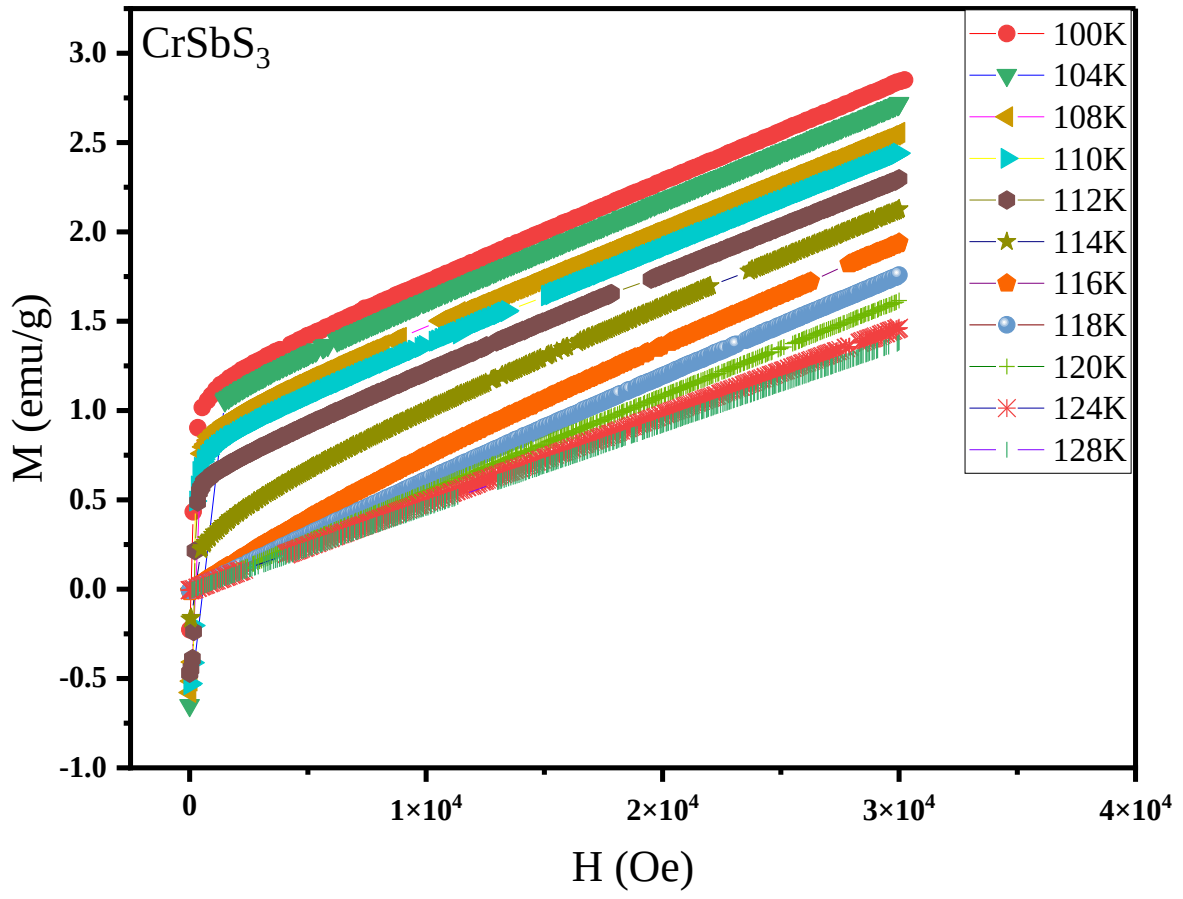


Figure 54: Magnetization-Field Curves $M(H)$ for Different Temperatures Around T_C for CrSbS_3 .

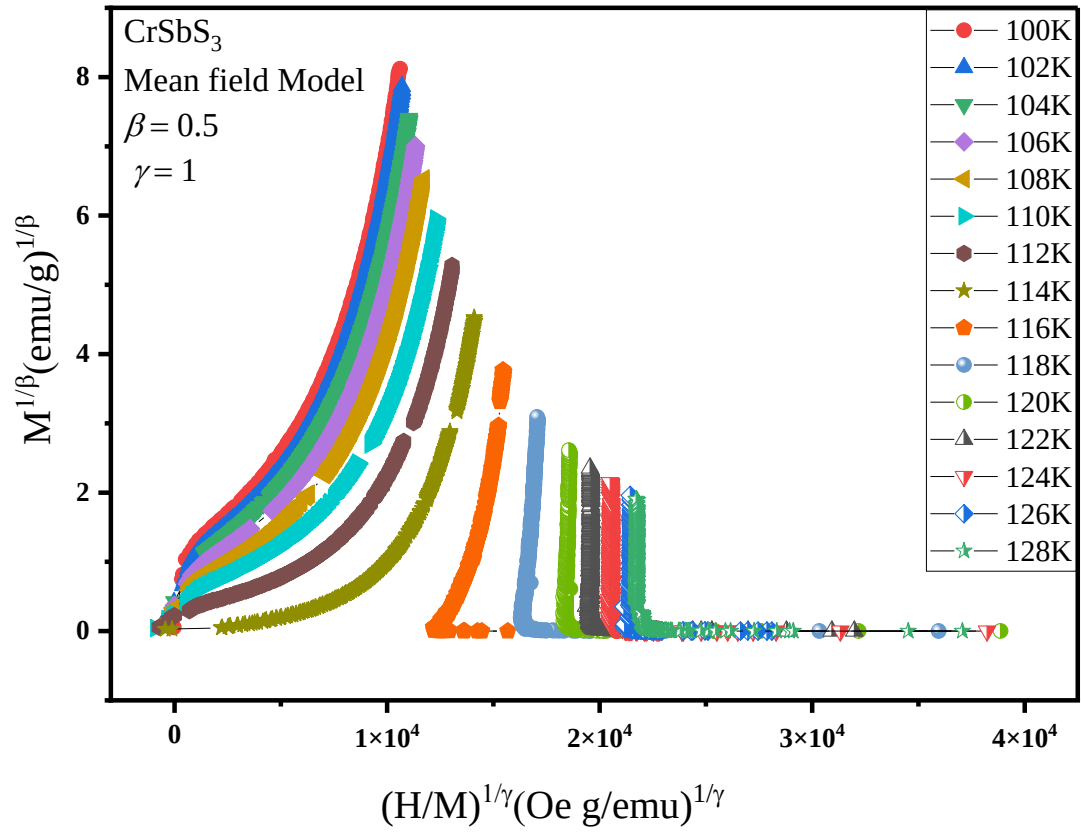


Figure 55: The Isotherms of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ with Parameters of The Mean-Field Model for CrSbS₃.

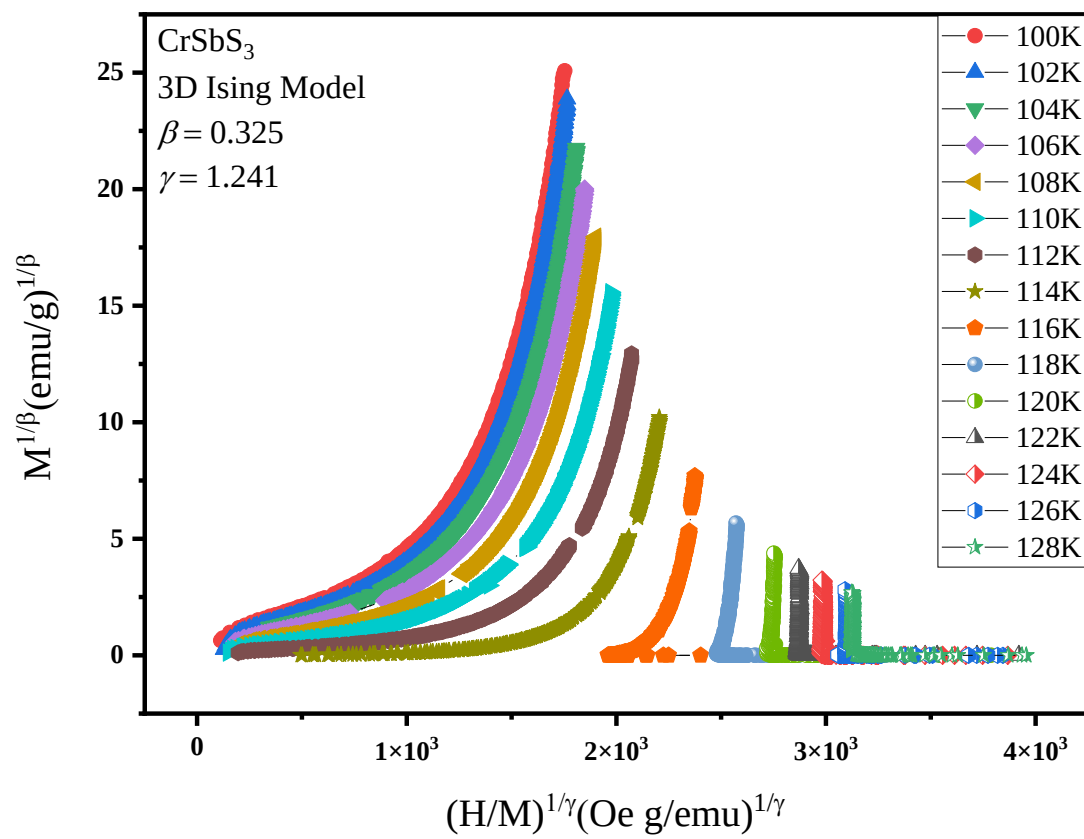


Figure 56: The Isotherms of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ with Parameters of 3D Ising Model for CrSbS₃.

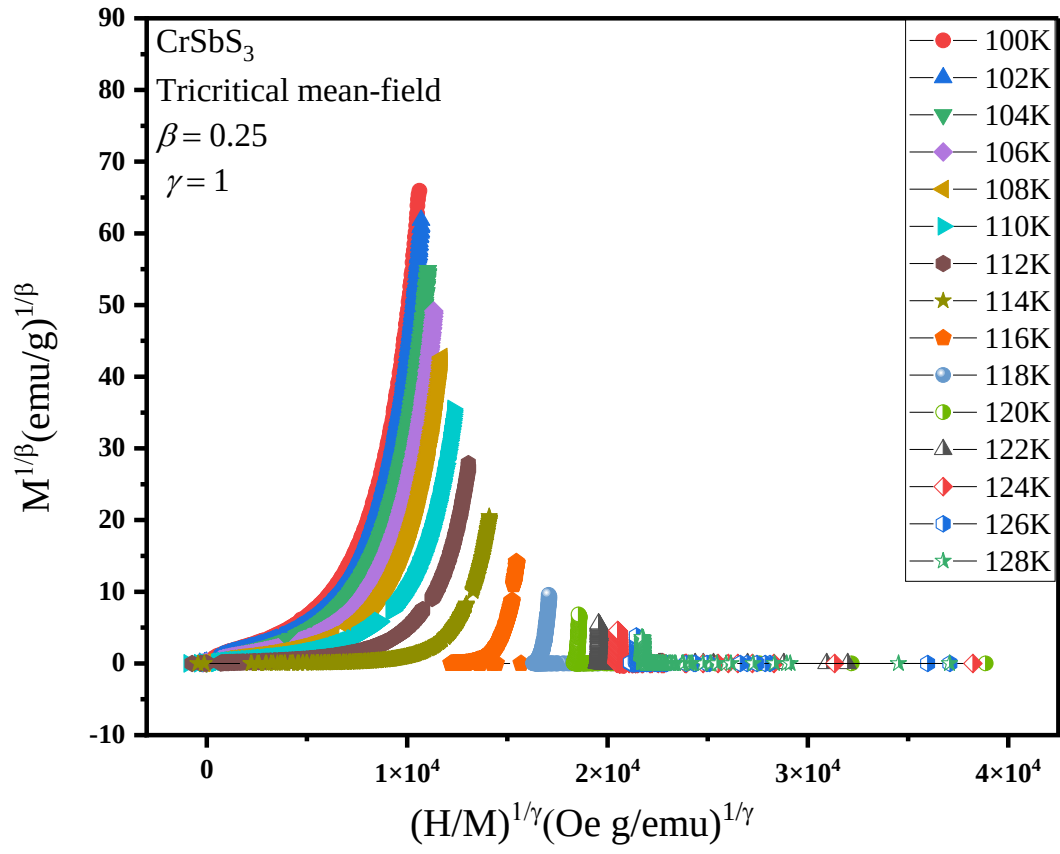


Figure 57: The Isotherms of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ with Parameters of Tricritical Mean-Field Model for CrSbS₃.

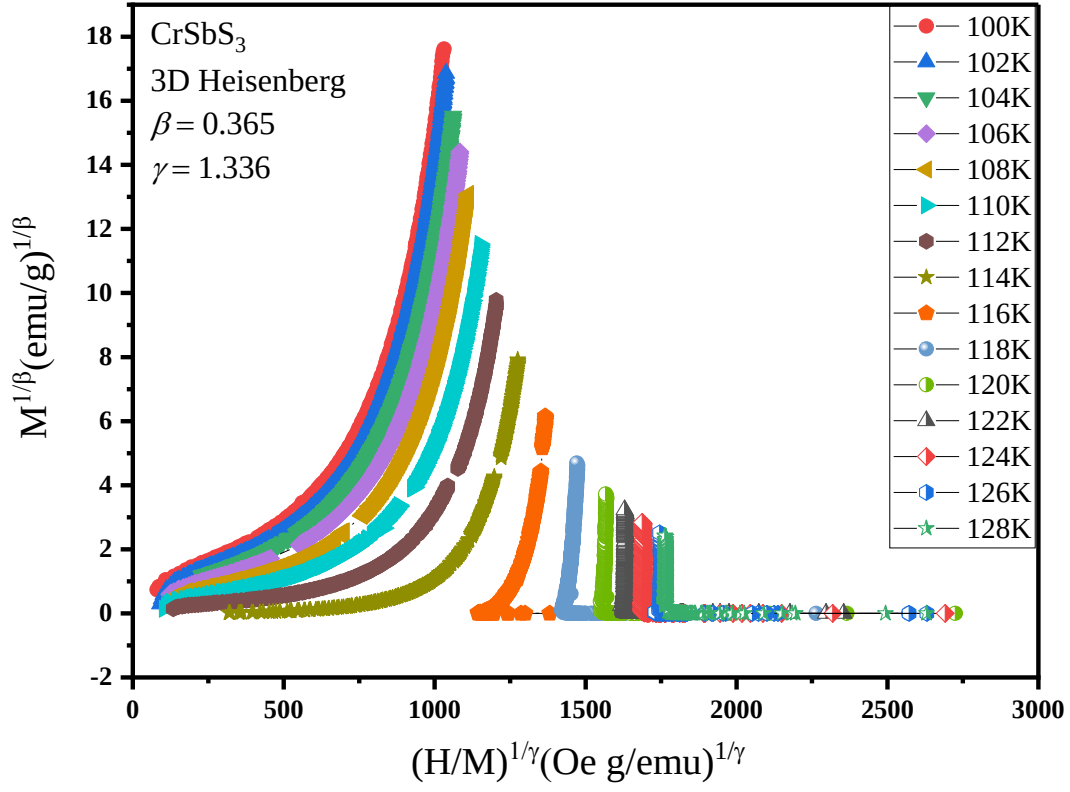


Figure 58: The Isotherms of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ with Parameters of 3D Heisenberg Model for CrSbS₃.

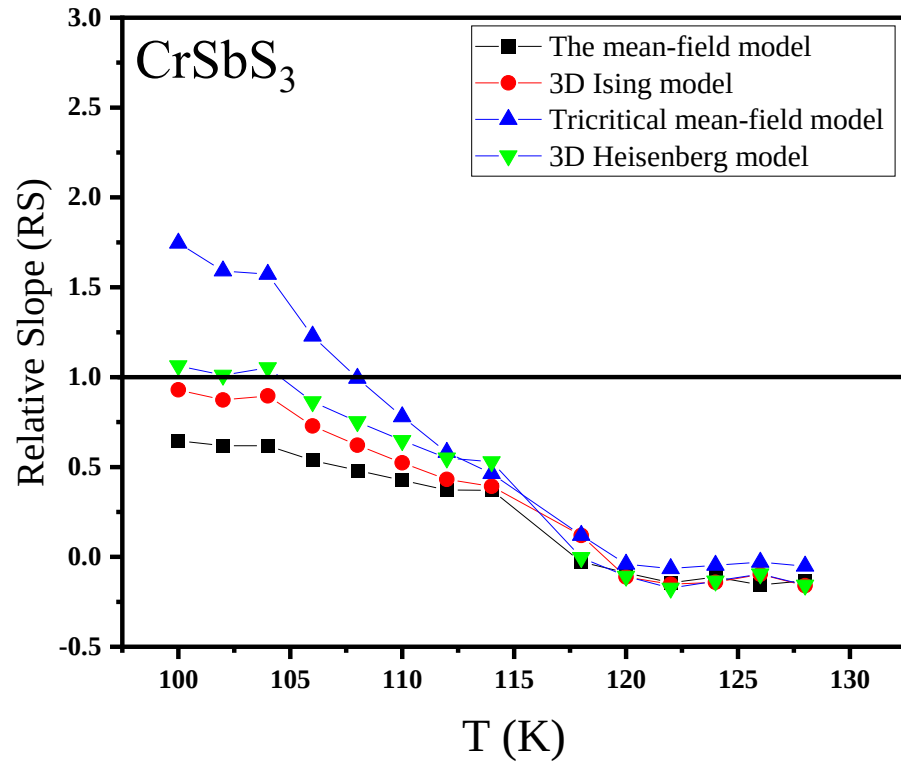


Figure 59: Relative Slope (RS) for CrSbS₃ as a Function of Temperature.

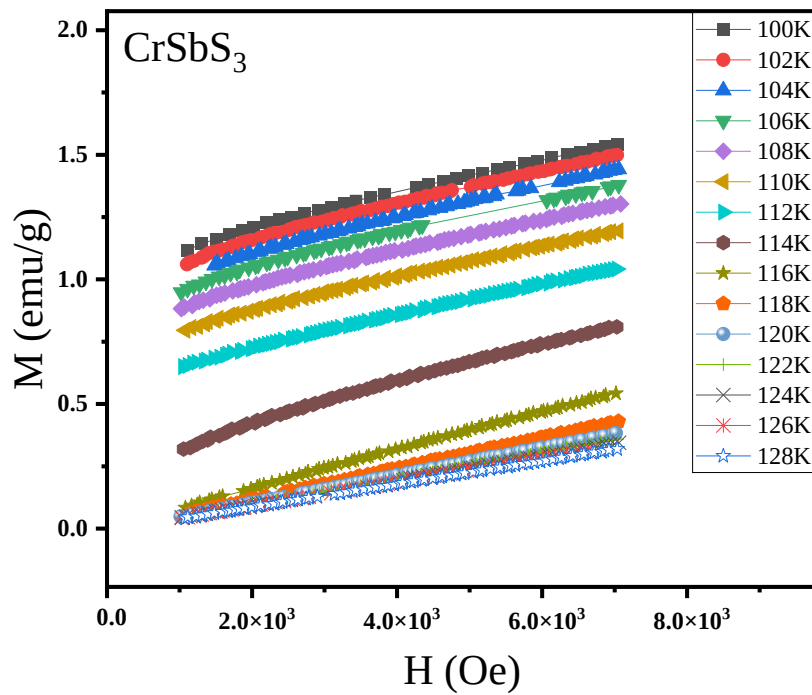


Figure 60: The Straight Lines of Isothermal Magnetization at Different Temperatures for CrSbS_3 .

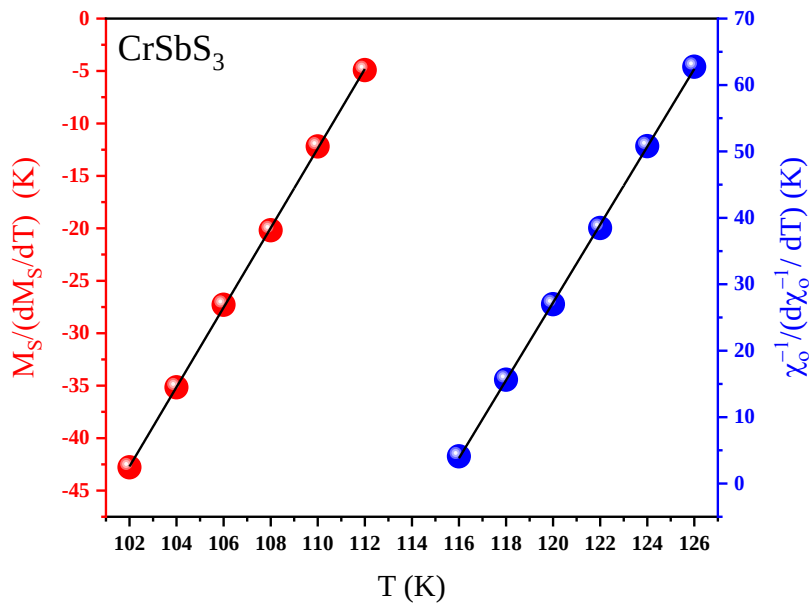


Figure 61: Kouvel-Fisher Plots with The Fitting Curve for CrSbS_3 .

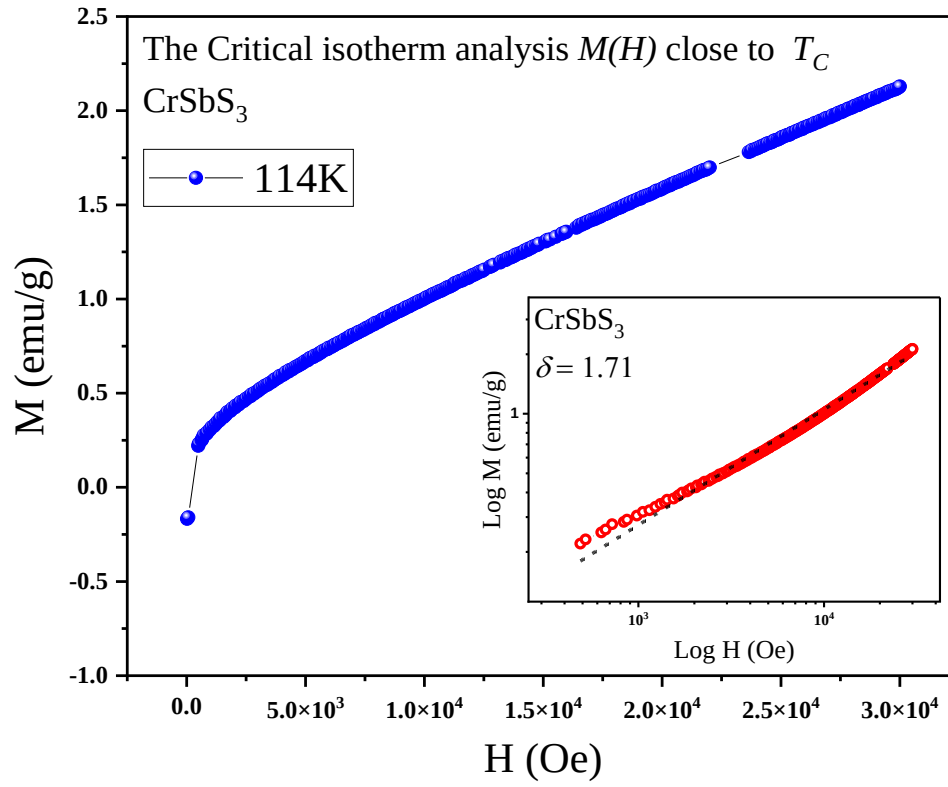


Figure 62: The Isotherm $M(H)$ Plot collected at $T = 114$ K for CrSbS_3 . Inset: The Same Plot in The Log-Log Scale with The Fitting Curve.

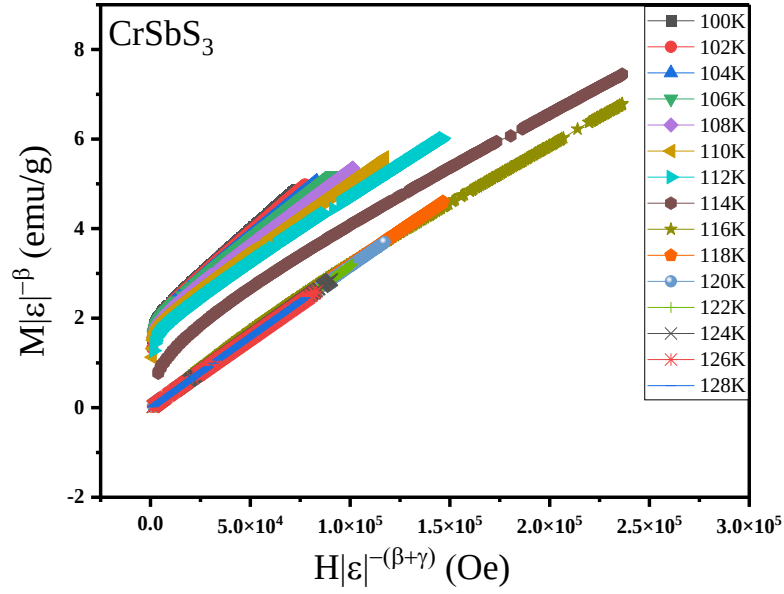


Figure 63: Scaling Plots of Renormalized Magnetization M vs. Renormalized Field h Below and Above T_C for CrSbS_3

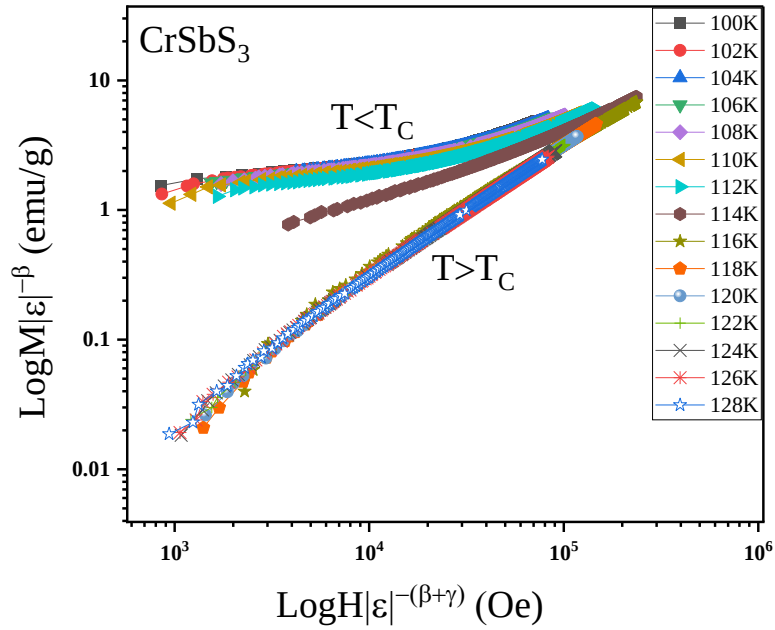


Figure 64: Scaling Plots of Renormalized Magnetization M vs. Renormalized Field h in Log-Log Scale for CrSbS_3 .

6.6 Magnetocaloric Effect

Figures 65 and 66 show the resulting temperature variations of $-\Delta S_M$ and ΔT_{ad} for various magnetic field changes up to 3 T, respectively. Regardless of the magnetic field change (ΔH), it is noted that this compound exhibits positive MCE across the whole tested temperature range. Conventional ferromagnets have been found to generally display positive MCE. As can be concluded from Figures 65 and 66, both $-\Delta S_M$ and ΔT_{ad} exhibit a peak at T_C with a magnitude that systematically increases with increasing (ΔH).

The most important property is the capacity to generate beneficial cooling, which may be measured by a parameter calculated from the temperature dependence of the isothermal magnetic entropy change and referred to the relative cooling power (RCP). In an ideal thermodynamic cycle, RCP is a measurement of the amount of heat that is transported between cold and hot parts of the refrigerator.

The calculated RCP value of CrSbS_3 using the magnitude of the change in magnetic entropy curves ($-\Delta S_M$ Versus T) reaches maxima at 3T of 3.65 J kg^{-1} . In addition, the field dependence of ($-\Delta S_M^{max}$) and RCP can be well-fitted by using the power-law relations ($-\Delta S_M^{max} = aH^n$ and $RCP = bH^m$) as noted in figure 67. Fitting of ($-\Delta S_M^{max}$) and RCP give that $n = 0.81$ and $m = 1.61$. As is known, the exponents n and m are correlated with the critical exponents as: $n = 1 + \frac{\beta-1}{\beta+\gamma}$ and $m = 1 + \frac{1}{\delta}$.

The expected results of the specific heat change (ΔC_P) vs. temperature under various field variations are represented in Figure 68. These outcomes were calculated by applying Equation (1.42). The (ΔC_P) reveals a sudden transition from a negative to a positive value

at around T_C , with a value that is negative below T_C and positive above T_C . The negative or positive values of (ΔC_P) close to or above T_C can significantly alter the total specific heat, which modifies the magnetic refrigerator's cooling or heating performance.

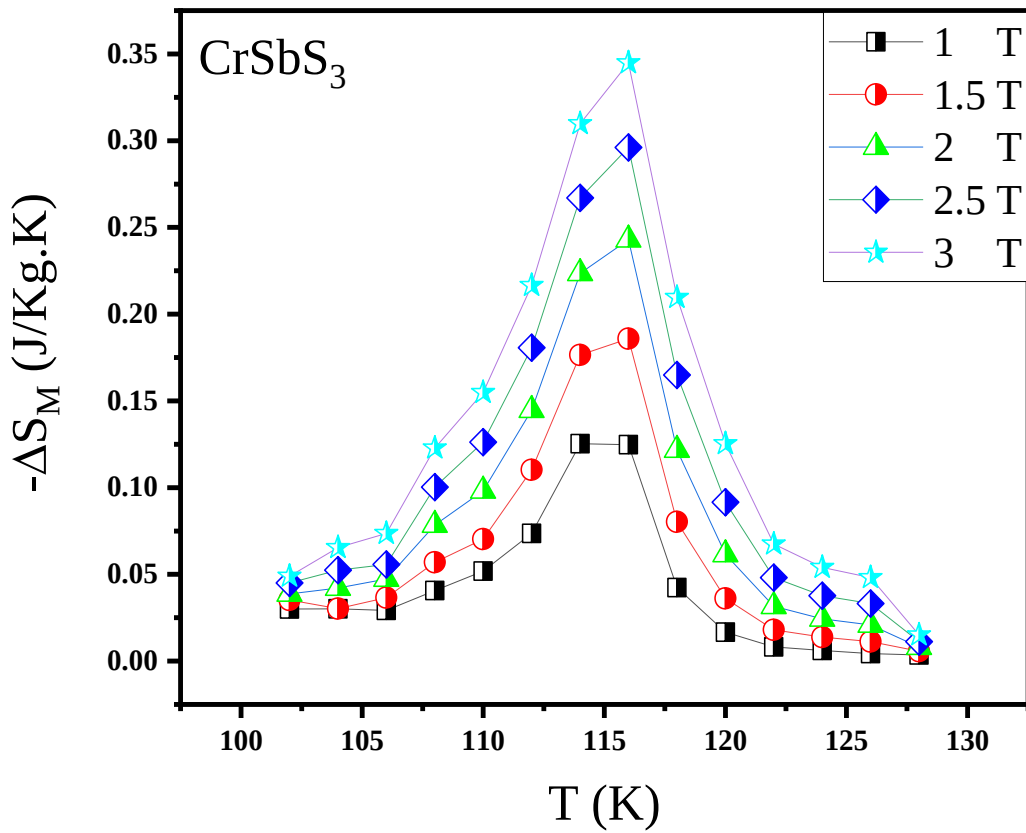


Figure 65: Magnetic Entropy Change ($-\Delta S_M$) as a Function of Temperature at Magnetic Field Changes of ΔH 1, 1.5, 2, 2.5 and 3 T for CrSbS₃.

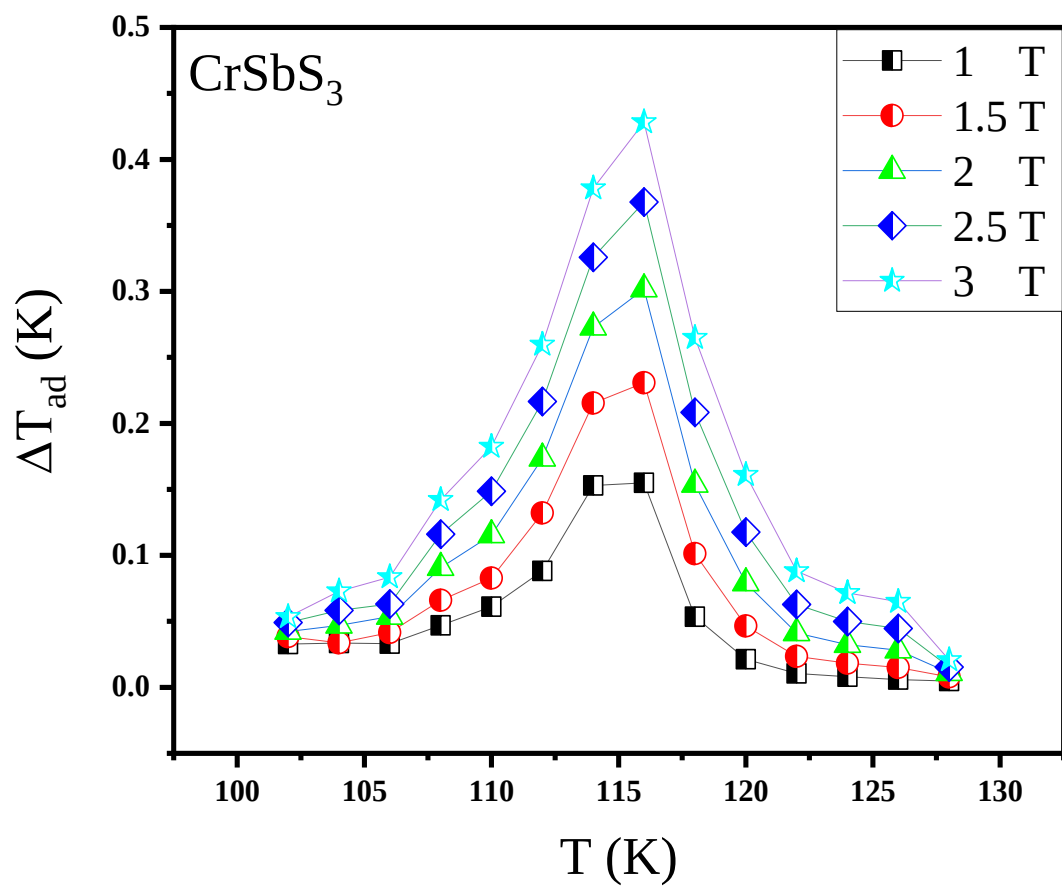


Figure 66: Adiabatic Temperature Change (ΔT_{ad}) curves of ΔH 1, 1.5 , 2 , 2.5 and 3 T for CrSbS₃.

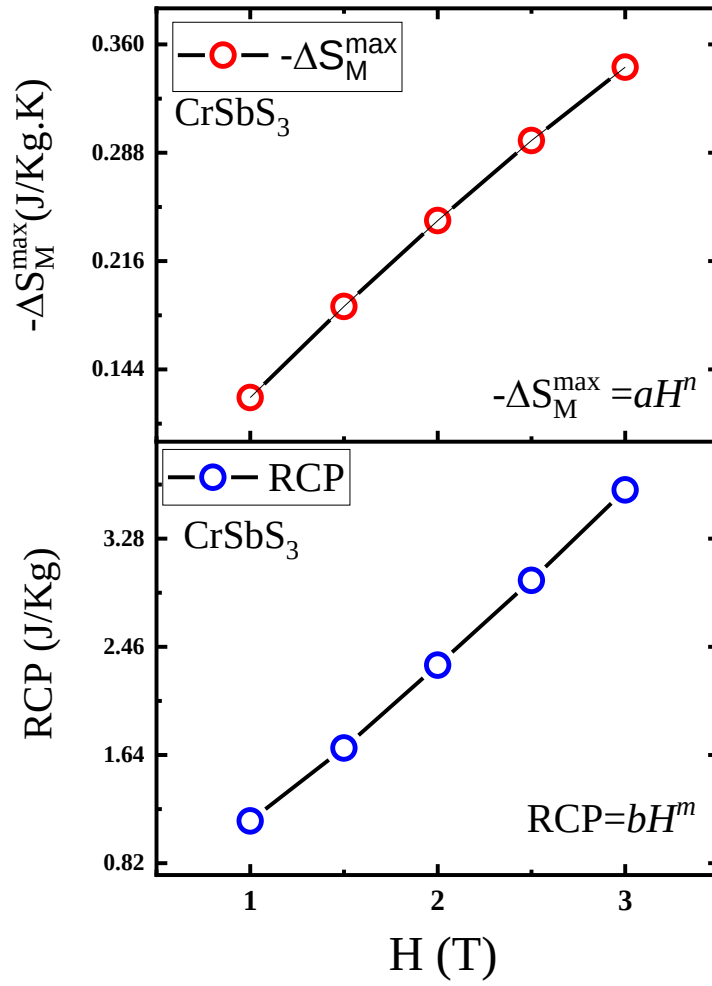


Figure 67: Relative Cooling Power (RCP) and The Maximum Magnetic Entropy Change ($-\Delta S_M$) as a Function of Magnetic Field for CrSbS_3 .

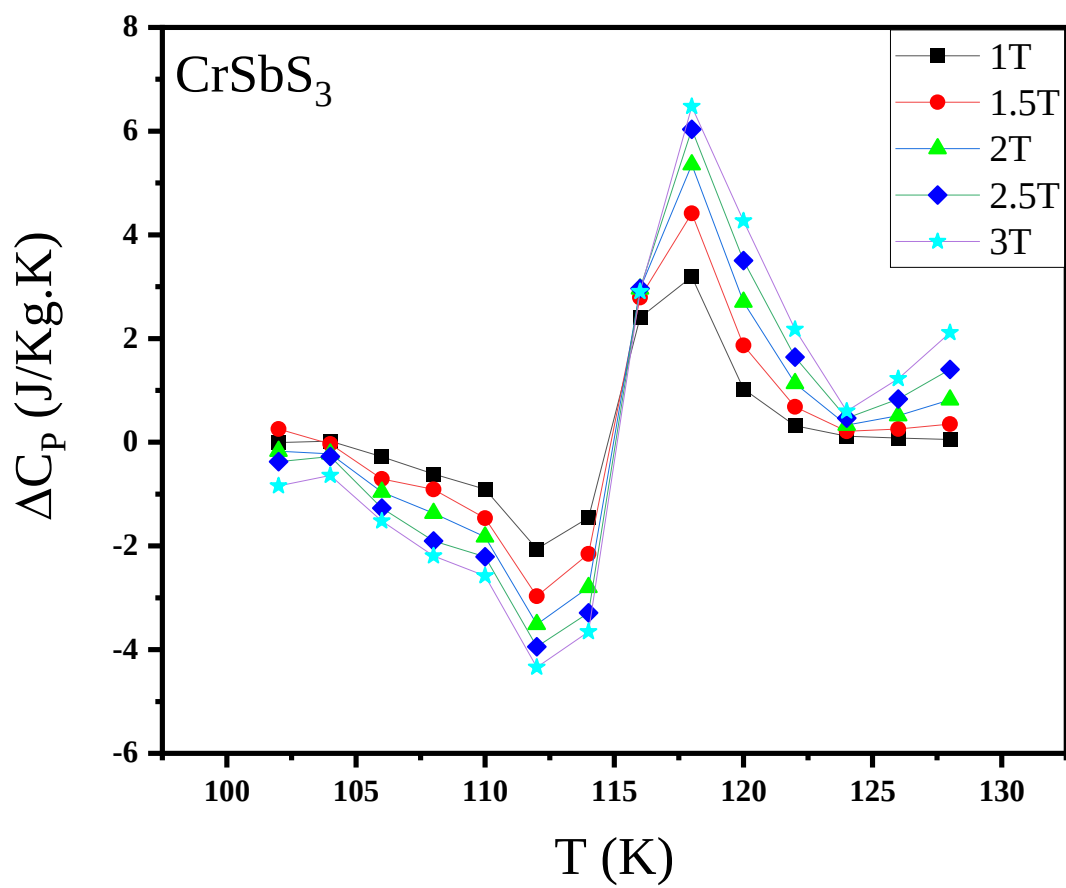


Figure 68: The Specific Heat Change (ΔC_p) versus Temperature for CrSbS₃.

6.7 Frustration index

In magnetism, the frustration index is a measure of the degree of frustration in a magnetic system. It is defined as the ratio of the Curie Weiss temperature, θ_{cw} , to the ordering temperature, T^* . The Curie Weiss temperature is a measure of the energy difference between the ferromagnetic and paramagnetic states, while the ordering temperature is the temperature at which the magnetic system orders.

A high frustration index indicates that the magnetic system is strongly frustrated, and that it is difficult for the system to find a ground state that minimizes the energy of all of the spins. This can lead to a variety of unusual magnetic properties, such as spin glass behavior, heavy fermion behavior, and unconventional superconductivity.

The frustration index can be used to classify magnetic systems and to predict their behavior. It is a valuable tool for understanding the physics of frustrated magnets.

The frustration index can be calculated using the following equation [157]:

$$f = \frac{\theta_{cw}}{T^*} \quad (6.13)$$

where:

- θ_{cw} is the Weiss temperature
- T^* is the ordering temperature

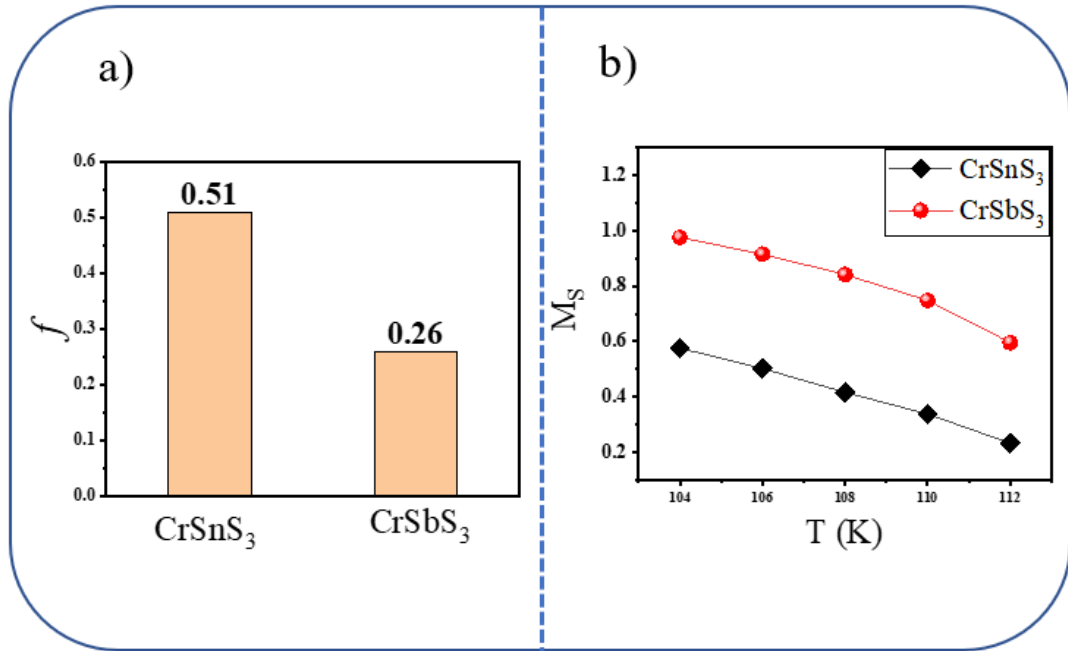


Figure 69: *a)* Frustrated index for CrSnS_3 and CrSbS_3 . *b)* Spontaneous Magnetization at different Temperature

Figure 69 shows that the frustrated index of CrSnS_3 is double that of CrSbS_3 . As a result, the spontaneous magnetization of CrSnS_3 is reduced to half its value relative to CrSbS_3 .

CHAPTER 7

CONCLUSION

In this thesis, we investigated the critical magnetic behavior, magnetocaloric effect, and structural properties of a set of transition-metal based chalcogenides samples with the general formula MYX_3 where M is Transition-metal (Cr or V), (Y is Sn or Sb) and X is a chalcogen (S, Se, and Te). It was observed that the transition temperature gradually increases with increasing atomic mass (and the ionic radius) of the chalcogen element. Three of these samples revealed magnetic order phase transition according to ac-susceptibility measurements. We chose only two samples ($CrSnS_3$, $CrSbS_3$) to study the magnetic behavior in detail. The Paramagnetic-Ferromagnetic transition in ($CrSnS_3$ and $CrSbS_3$) is found to be a first-order magnetic transition at a critical temperature close to 119 K and 115 K, respectively. Reliable values of critical exponents (β , γ) were obtained from the Kouvel-Fisher method, and δ was generated by critical isotherm analysis. Using these exponents, the field dependence of $M(T, H)$ curves splits into two universal branches below and above T_c . The frustration index was calculated where the frustrated index of $CrSnS_3$ is double that of $CrSbS_3$. As a result, the spontaneous magnetization of $CrSnS_3$ is reduced to half its value relative to $CrSbS_3$.

The maximum values of the parameters of the magnetocaloric effect were obtained at 3T around T_C from isothermal magnetization data. The maximum change in magnetic entropy $\Delta S_M^{max} = 0.15 \text{ and } 0.34 \text{ J/Kg.K}$ for CrSnS_3 and CrSbS_3 , respectively. The maximum change in the adiabatic temperature $\Delta T_M^{max} = 0.19\text{K and } 0.43\text{K}$ for CrSnS_3 and CrSbS_3 , respectively. The maximum relative cooling power $\text{RCP} = 1.95 \text{ and } 3.79 \text{ J Kg}^{-1}$ for CrSnS_3 and CrSbS_3 , respectively, which is much smaller than that of CrSbSe_3 . In addition, The (ΔC_P) of both samples revealed a sudden transition from a negative to a positive value around T_C , with a value that is negative below T_C and positive above T_C . The current goal is to find cheap and efficient magnetocaloric materials that can operate around room temperature. So the materials need to improve their behaviour maybe using substitution. For example $\text{Cr}_{1-x}\text{Mn}_x\text{YX}_3$, MnZnSb .

References

- [1] D. L. Duong, S. J. Yun, and Y. H. Lee, “Van der Waals Layered Materials: Opportunities and Challenges,” *ACS Nano*, vol. 11, no. 12. American Chemical Society, pp. 11803–11830, Dec. 26, 2017. doi: 10.1021/acsnano.7b07436.
- [2] B. Shabbir *et al.*, “Long range intrinsic ferromagnetism in two dimensional materials and dissipationless future technologies,” *Applied Physics Reviews*, vol. 5, no. 4. American Institute of Physics Inc., Dec. 01, 2018. doi: 10.1063/1.5040694.
- [3] H. Li, S. Ruan, and Y. J. Zeng, “Intrinsic Van Der Waals Magnetic Materials from Bulk to the 2D Limit: New Frontiers of Spintronics,” *Advanced Materials*, vol. 31, no. 27. Wiley-VCH Verlag, Jul. 05, 2019. doi: 10.1002/adma.201900065.
- [4] Q. Li *et al.*, “Patterning-Induced Ferromagnetism of Fe₃GeTe₂ van der Waals Materials beyond Room Temperature,” *Nano Lett*, vol. 18, no. 9, pp. 5974–5980, Sep. 2018, doi: 10.1021/acs.nanolett.8b02806.
- [5] Sivadas, Nikhil. First-principles and Wannier-function-based study of two-dimensional electronic systems. Diss. Carnegie Mellon University, 1916. [Online]. Available: <http://repository.cmu.edu/dissertations/990>
- [6] D. Torelli and T. Olsen, “First Principles Heisenberg Models of 2D magnetic materials: The Importance of Quantum Corrections to the Exchange Coupling,” Dec. 2019, doi: 10.1088/1361-648X/ab8664.
- [7] B. Zhai, J. Du, X. Li, C. Xia, and Z. Wei, “Two-dimensional ferromagnetic materials and related van der Waals heterostructures: A first-principle study,” *Journal of Semiconductors*, vol. 40, no. 8. Institute of Physics Publishing, 2019. doi: 10.1088/1674-4926/40/8/081509.
- [8] K. S. Burch, D. Mandrus, and J. G. Park, “Magnetism in two-dimensional van der Waals materials,” *Nature*, vol. 563, no. 7729. Nature Publishing Group, pp. 47–52, Nov. 01, 2018. doi: 10.1038/s41586-018-0631-z.
- [9] N. Miao, B. Xu, L. Zhu, J. Zhou, and Z. Sun, “2D Intrinsic Ferromagnets from van der Waals Antiferromagnets,” *J Am Chem Soc*, vol. 140, no. 7, pp. 2417–2420, Feb. 2018, doi: 10.1021/jacs.7b12976.
- [10] K. E. Madsen, “Intrinsic Ferromagnetism in Two-Dimensional Materials,” 2018. <https://chemistry.illinois.edu/system/files/inline-files/Ken%20Madsen%20-%20Intrinsic%20Ferromagnetism%20in%20Two-Dimensional%20Materials.pdf>

- [11] W. Zhang, P. K. J. Wong, R. Chua, and A. T. S. Wee, "Growth and properties of magnetic two-dimensional transition-metal chalcogenides," in *Spintronic 2D Materials: Fundamentals and Applications*, Elsevier, 2019, pp. 227–251. doi: 10.1016/B978-0-08-102154-5.00007-2.
- [12] S. Liu *et al.*, "Wafer-scale two-dimensional ferromagnetic Fe₃GeTe₂ thin films grown by molecular beam epitaxy," *NPJ 2D Mater Appl*, vol. 1, no. 1, Dec. 2017, doi: 10.1038/s41699-017-0033-3.
- [13] H. Berry, B. Wang, and Q. Zhang, "The behavior of magnetic properties in the clusters of 4d transition Metals," *Molecules*, vol. 23, no. 8, p. 1DUMMY, 2018, doi: 10.3390/molecules23081896.
- [14] Y. Sugita, T. Miyake, and Y. Motome, "Electronic band structure of 4d and 5d transition metal trichalcogenides," *Physica B Condens Matter*, vol. 536, pp. 48–50, May 2018, doi: 10.1016/j.physb.2017.10.126.
- [15] C. M. Hurd, "Varieties of magnetic order in solids," *Contemp Phys*, vol. 23, no. 5, pp. 469–493, 1982, doi: 10.1080/00107518208237096.
- [16] Marcon, Petr, and K. Ostanina. "Overview of methods for magnetic susceptibility measurement." *PIERS Proceedings*. 2012.
- [17] "MSB-AUTO," "MAGNETIC SUSCEPTIBILITY BALANCE." 13094-3003 Printed in the UK 6th edition Sherwood Scientific Ltd 1 The Paddocks Cherry Hinton Road Cambridge, England CB1 8DH 700 91 001 Issue 6 December 2006 ECN 438.
- [18] "Magnetic susceptibility measurements of transition metal containing compounds Introduction." https://www.unf.edu/~michael.lufaso/chem3610L/instructions_magnetic_susceptibility.pdf
- [19] M. Dalal, "Gouy's Method for Determination of Magnetic Susceptibility." [Online] <https://www.dalalinstitute.com/wp-content/uploads/Books/A-Textbook-of-Inorganic-Chemistry-Volume-1/ATOICV1->
- [20] Anna, S. A. N. D. U. L. Y. A. K., et al. "Study of ferromagnetic dispersed samples and particles magnetic susceptibility by faraday method (magnetometer with polar hemispheres)." *WSEAS Transactions on Systems and Control* 12 (2017): 374-385.
- [21] Sandulyak, Alexander V., et al. "The working zone in the interpolar area of the Faraday balance: an approach to testing the magnetic force factor stability criterion." *MATEC Web of Conferences*. Vol. 108. EDP Sciences, 2017.

- [22] B. L. Morris and A. Wold, "Faraday balance for measuring magnetic susceptibility," *Review of Scientific Instruments*, vol. 39, no. 12, pp. 1937–1941, 1968, doi: 10.1063/1.1683276.
- [23] Vannette, Matthew Dano. Dynamic magnetic susceptibility of systems with long-range magnetic order. Iowa State University, 2009.
- [24] Martien, Dinesh. "Introduction to AC susceptibility." *Quantum design* (1994): 1-4.
- [25] M. Bałanda, "AC susceptibility studies of phase transitions and magnetic relaxation: Conventional, molecular and low-dimensional magnets," in *Acta Physica Polonica A*, Dec. 2013, pp. 964–976. doi: 10.12693/APhysPolA.124.964.
- [26] Nikolo, Martin. "Superconductivity: A guide to alternating current susceptibility measurements and alternating current susceptometer design." *American Journal of Physics* 63.1 (1995): 57-65.
- [27] A. A. Zatsiupa *et al.*, "Magnetization, magnetic susceptibility, effective magnetic moment of Fe^{3+} ions in $\text{Bi}_{25}\text{FeO}_{39}$ ferrite," *J Solid State Chem*, vol. 212, pp. 147–150, Apr. 2014, doi: 10.1016/j.jssc.2014.01.019.
- [28] K. J. Little, "Magnetic Properties of One-, Two-, and Three-dimensional Crystal Structures built of Manganese (III) Cluster-based Coordination Polymers," 2006. <http://www.phys.ufl.edu/REU/2006/reports/little.pdf>
- [29] P. T. Phong *et al.*, "Griffiths-like phase, critical behavior near the paramagnetic-ferromagnetic phase transition and magnetic entropy change of nanocrystalline $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$," *J Magn Magn Mater*, vol. 449, pp. 558–566, Mar. 2018, doi: 10.1016/j.jmmm.2017.10.103.
- [30] Yang, J., and Y. P. Lee. "Structural and magnetic properties of $\text{Pr}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$." *Journal of the Korean Physical Society* 51.9 (2007): 1560-1563.
- [31] G. Theses and D. David Belyea, "Scholar Commons Analysis of Critical Behavior in Magnetic Materials." [Online]. Available: <https://scholarcommons.usf.edu/etd>
- [32] A. Gschneidner, V. K. Pecharsky, and A. O. Tsokol, "Recent developments in magnetocaloric materials," *Reports on Progress in Physics*, vol. 68, no. 6. pp. 1479–1539, Jun. 01, 2005. doi: 10.1088/0034-4885/68/6/R04.
- [33] Gschneidner Jr, K. A., and Vitalij K. Pecharsky. "Magnetocaloric materials." *Annual review of materials science* 30.1 (2000): 387-429.

- [34] Heitler, W., and Edward Teller. "Time effects in the magnetic cooling method—I." *Proceedings of the Royal Society of London. Series A-Mathematical and Physical Sciences* 155.886 (1936): 629-639.
- [35] J. Evanovich and L. King, *Hardcore twenty-four : a Stephanie Plum novel*.
- [36] Q. Y. Dong, B. G. Shen, J. Chen, J. Shen, H. W. Zhang, and J. R. Sun, "Magnetic entropy change and refrigerant capacity in GdFeAl compound," *J Appl Phys*, vol. 105, no. 7, 2009, doi: 10.1063/1.3059372.
- [37] X. Wang, Q. Wang, B. Tang, P. Yu, L. Xia, and D. Ding, "Large magnetic entropy change and adiabatic temperature rise of a ternary Gd₃₄Ni₃₃Al₃₃ metallic glass," *Journal of Rare Earths*, vol. 39, no. 8, pp. 998–1002, Aug. 2021, doi: 10.1016/j.jre.2020.04.011.
- [38] M. Hamisi, M. Supervisor, : Prof, M. Bertin, and T. Tchokonte, "Giant Magnetocaloric effect and Magnetic Properties of selected Rare-Earth compounds," 2021. [Online]. Available: <https://etd.uwc.ac.za/>
- [39] M. H. Phan, T. L. Phan, S. C. Yu, N. D. Tho, and N. Chau, "Large magnetocaloric effect in La_{0.845}Sr_{0.155}Mn_{1-x}MxO₃ (M = Mn, Cu, Co) perovskites," in *Physica Status Solidi (B) Basic Research*, Jun. 2004, pp. 1744–1747. doi: 10.1002/pssb.200304587.
- [40] L. W. Li, "Review of magnetic properties and magnetocaloric effect in the intermetallic compounds of rare earth with low boiling point metals," *Chinese Physics B*, vol. 25, no. 3. Institute of Physics Publishing, Jan. 18, 2016. doi: 10.1088/1674-1056/25/3/037502.
- [41] Foldeaki, M., et al. "Comparison of magnetocaloric properties from magnetic and thermal measurements." *Journal of applied physics* 82.1 (1997): 309-316.
- [42] Nguyen, Thành Trung. "First-order phase transitions and giant magnetocaloric effect." (2010).
- [43] A. A. O. Imaddin, M. D. Al-Mamari, and D. J. Sellmyer, "Tuning the giant Magnetocaloric Effect and refrigerant capacity in Gd_{1-x}Y_xCrO₃ (0.0 < x < 0.9) perovskites nanoparticles," *AIMS Mater Sci*, vol. 9, no. 2, pp. 297–310, 2022, doi: 10.3934/matricsci.2022018.
- [44] Guo, Z. B., et al. "Large magnetic entropy change in perovskite-type manganese oxides." *Physical review letters* 78.6 (1997): 1142.

- [45] Pecharsky, Vitalij K., and Karl A. Gschneidner Jr. "Magnetocaloric effect and magnetic refrigeration." *Journal of magnetism and magnetic materials* 200.1-3 (1999): 44-56.
- [46] M. Jeddi, H. Gharsallah, M. Bekri, E. Dhahri, and E. K. Hlil, "Structural, magnetic, critical behavior and phenomenological investigation of magnetocaloric properties of $\text{La}_{0.6}\text{Ca}_{0.4-x}\text{Sr}_x\text{MnO}_3$ perovskite," *Journal of Materials Science: Materials in Electronics*, vol. 30, no. 15, pp. 14430–14444, Aug. 2019, doi: 10.1007/s10854-019-01813-z.
- [47] Kohama, Yoshimitsu, et al. "AC Heat capacity and magnetocaloric effect measurements for pulsed magnetic fields." arXiv preprint arXiv:1003.3184 (2010).
- [48] Brec, Raymond. "Review on structural and chemical properties of transition metal phosphorous trisulfides MPS_3 ." *Solid State Ionics* 22.1 (1986): 3-30.
- [49] B. L. Chittari *et al.*, "Electronic and magnetic properties of single-layer M PX_3 metal phosphorous trichalcogenides," *Phys Rev B*, vol. 94, no. 18, Nov. 2016, doi: 10.1103/PhysRevB.94.184428.
- [50] B. L. Chittari, D. Lee, A. H. MacDonald, E. Hwang, and J. Jung, "Carrier and strain tunable intrinsic magnetism in two-dimensional MAX_3 transition metal chalcogenides," Sep. 2017, doi: 10.1103/PhysRevB.101.085415.
- [51] V. V. Volkov *et al.*, "HREM Image Analysis up to Structure Determination of SbCrSe_3 : A New 1D Ferromagnet," *J Solid State Chem*, vol. 132, no. 2, pp. 257–266, Sep. 1997, doi: 10.1006/jssc.1997.7438.
- [52] B. L. Chittari *et al.*, "Electronic and magnetic properties of single-layer M PX_3 metal phosphorous trichalcogenides," *Phys Rev B*, vol. 94, no. 18, Nov. 2016, doi: 10.1103/PhysRevB.94.184428.
- [53] W. Zhang, P. K. J. Wong, R. Zhu, and A. T. S. Wee, "Van der Waals magnets: Wonder building blocks for two-dimensional spintronics?," *InfoMat*, vol. 1, no. 4, pp. 479–495, Dec. 2019, doi: 10.1002/inf2.12048.
- [54] L. Webster and J. A. Yan, "Strain-tunable magnetic anisotropy in monolayer CrCl_3 , CrBr_3 , and CrI_3 ," *Phys Rev B*, vol. 98, no. 14, Oct. 2018, doi: 10.1103/PhysRevB.98.144411.
- [55] M. D. Watson *et al.*, "Direct observation of the energy gain underpinning ferromagnetic superexchange in the electronic structure of CrGeTe_3 ," Dec. 2019, doi: 10.1103/PhysRevB.101.205125.

- [56] Y. Sun and X. Luo, "Magnetic Entropy Scaling in Ferromagnetic Semiconductor CrGeTe₃," *Phys Status Solidi B Basic Res*, vol. 256, no. 11, Nov. 2019, doi: 10.1002/pssb.201900052.
- [57] Zhuang, Houlong L., et al. "Computational discovery of ferromagnetic semiconducting single-layer CrSnTe₃." *Physical Review B* 92.3 (2015): 035407.
- [58] Lin, Zhisheng. *Charge and Spin Transport in Graphene Heterostructures and Cr₂Ge₂T₆*. University of California, Riverside, 2017.
- [59] Y. F. Li *et al.*, "Electronic structure of ferromagnetic semiconductor CrGeTe₃ by angle-resolved photoemission spectroscopy," *Phys Rev B*, vol. 98, no. 12, Sep. 2018, doi: 10.1103/PhysRevB.98.125127.
- [60] H. Yang *et al.*, "Solution Synthesis of Layered van der Waals (vdW) Ferromagnetic CrGeTe₃Nanosheets from a Non-vdW Cr₂Te₃Template," *J Am Chem Soc*, vol. 142, no. 9, pp. 4438–4444, Mar. 2020, doi: 10.1021/jacs.9b13492.
- [61] J. Zhang *et al.*, "Unveiling Electronic Correlation and the Ferromagnetic Superexchange Mechanism in the van der Waals Crystal CrSiTe₃," *Phys Rev Lett*, vol. 123, no. 4, Jul. 2019, doi: 10.1103/PhysRevLett.123.047203.
- [62] Suo, Peng, et al. "Terahertz Emission on the Surface of a van der Waals Magnet CrSiTe₃." *Laser & Photonics Reviews* 14.7 (2020): 2000025.
- [63] Z. Yu *et al.*, "Pressure-Induced Structural Phase Transition and a Special Amorphization Phase of Two-Dimensional Ferromagnetic Semiconductor Cr₂Ge₂Te₆," *Journal of Physical Chemistry C*, vol. 123, no. 22, pp. 13885–13891, Jun. 2019, doi: 10.1021/acs.jpcc.9b02415.
- [64] S. Wu *et al.*, "The direct observation of ferromagnetic domain of single crystal CrSiTe₃," *AIP Adv*, vol. 8, no. 5, May 2018, doi: 10.1063/1.5024576.
- [65] Q. Pei, X. Wang, J. Zou, and W. Mi, "Efficient band structure modulations in two-dimensional MnPSe₃/CrSiTe₃ van der Waals heterostructures," *Nanotechnology*, vol. 29, no. 21, Mar. 2018, doi: 10.1088/1361-6528/aab5ab.
- [66] L. D. Casto *et al.*, "Strong spin-lattice coupling in CrSiTe₃," *APL Mater*, vol. 3, no. 4, Apr. 2015, doi: 10.1063/1.4914134.
- [67] G. T. Lin *et al.*, "Tricritical behavior of two-dimensional intrinsic ferromagnetic semiconducting CrGeTe₃," Jun. 2017, doi: 10.1103/PhysRevB.95.245212.

- [68] M. W. Lin *et al.*, “Ultrathin nanosheets of CrSiTe₃: A semiconducting two-dimensional ferromagnetic material,” *J Mater Chem C Mater*, vol. 4, no. 2, pp. 315–322, 2016, doi: 10.1039/c5tc03463a.
- [69] J. ming Zhang, Y. zhuang Nie, Q. lin Xia, R. Xiong, and G. hua Guo, “Electronic structures and magnetic properties of CrSiTe₃ single-layer nanoribbons,” *Physics Letters, Section A: General, Atomic and Solid State Physics*, vol. 383, no. 19, pp. 2346–2351, Jul. 2019, doi: 10.1016/j.physleta.2019.04.049.
- [70] K. H. Lee, H. S. Yu, S. il Kim, S. P. Moon, J. Y. Hwang, and S. W. Kim, “Correlation between thermoelectric transport properties and crystal structure in two-dimensional CrSiTe₃,” *J Alloys Compd*, vol. 790, pp. 93–98, Jun. 2019, doi: 10.1016/j.jallcom.2019.03.198.
- [71] Z. Zhang, Z. Wang, and Z. Zhang, “Magneto-transport and weak anti-localization in ferromagnetic semiconductor CrSiTe₃ single crystal,” *Appl Phys Lett*, vol. 113, no. 14, Oct. 2018, doi: 10.1063/1.5048208.
- [72] V. Carteauxts, D. Brunet\$, G. Ouvrardt:, and G. Andrdt, “Crystallographic, magnetic and electronic structures of a new layered ferromagnetic compound Cr₂Ge₂Te₆ Crystallographic, magnetic and electronic structures of a new layered ferromagnetic compound crzGezTe6,” 1995. [Online]. Available: <http://iopscience.iop.org/0953-8984/7/1/008>
- [73] G. T. Lin *et al.*, “Tricritical behavior of the two-dimensional intrinsically ferromagnetic semiconductor CrGeTe₃,” *Phys Rev B*, vol. 95, no. 24, Jun. 2017, doi: 10.1103/PhysRevB.95.245212.
- [74] Bhoi, Dilip, et al. "Pressure dependent electronic phase diagram of the 2D Ferromagnetic insulator CrGeTe₃." (2020).
- [75] B. Liu *et al.*, “Critical behavior of the quasi-two-dimensional semiconducting ferromagnet CrSiTe₃,” *Sci Rep*, vol. 6, Sep. 2016, doi: 10.1038/srep33873.
- [76] A. Milosavljević *et al.*, “Evidence of spin-phonon coupling in CrSiTe₃,” *Phys Rev B*, vol. 98, no. 10, Sep. 2018, doi: 10.1103/PhysRevB.98.104306.
- [77] Martinez, L. M., et al. "Enhanced Magnetization from Proton Irradiated Bulk van der Waals Magnet CrSiTe₃." arXiv preprint arXiv:1907.07222 (2019).
- [78] V. Carteaux, F. Moussa, and M. Spiesser, “2D Ising-Like Ferromagnetic Behaviour for the Lamellar Cr₂Si₂Te₆ Compound: A Neutron Scattering Investigation 2D Ising-like Ferromagnetic Behaviour for the Lamellar Cr₂Si₂Te₆

Compound: a Neutron Scattering Investigation,” 1995. [Online]. Available: <http://iopscience.iop.org/0295-5075/29/3/011>

- [79] Carteaux, V., et al. "Magnetic structure of the new layered ferromagnetic chromium hexatellurosilicate $\text{Cr}_2\text{Si}_2\text{Te}_6$." *Journal of magnetism and magnetic materials* 94.1-2 (1991): 127-133.
- [80] N. Sethulakshmi *et al.*, “Magnetism in two-dimensional materials beyond graphene,” *Materials Today*, vol. 27. Elsevier B.V., pp. 107–122, Jul. 01, 2019. doi: 10.1016/j.mattod.2019.03.015.
- [81] N. Ito, T. Kikkawa, J. Barker, D. Hirobe, Y. Shiomi, and E. Saitoh, “Spin Seebeck effect in the layered ferromagnetic insulators CrSiTe_3 and CrGeTe_3 ,” *Phys Rev B*, vol. 100, no. 6, Aug. 2019, doi: 10.1103/PhysRevB.100.060402.
- [82] Y. Liu *et al.*, “The environmental stability characterization of exfoliated few-layer CrXTe_3 (X = Si, Ge) nanosheets,” *Appl Surf Sci*, vol. 511, May 2020, doi: 10.1016/j.apsusc.2020.145452.
- [83] Q. Xie *et al.*, “Two stage magnetization in van der Waals layered CrXTe_3 (X = Si, Ge) single crystals,” *Mater Lett*, vol. 246, pp. 60–62, Jul. 2019, doi: 10.1016/j.matlet.2019.03.017.
- [84] N. Sivadas, M. W. Daniels, R. H. Swendsen, S. Okamoto, and D. Xiao, “Magnetic ground state of semiconducting transition-metal trichalcogenide monolayers,” *Phys Rev B Condens Matter Mater Phys*, vol. 91, no. 23, Jun. 2015, doi: 10.1103/PhysRevB.91.235425.
- [85] S. Kang, S. Kang, and J. Yu, “Effect of Coulomb Interactions on the Electronic and Magnetic Properties of Two-Dimensional CrSiTe_3 and CrGeTe_3 Materials,” *J Electron Mater*, vol. 48, no. 3, pp. 1441–1445, Mar. 2019, doi: 10.1007/s11664-018-6601-2.
- [86] X. Li and J. Yang, “ CrXTe_3 (X = Si, Ge) nanosheets: Two dimensional intrinsic ferromagnetic semiconductors,” *J Mater Chem C Mater*, vol. 2, no. 34, pp. 7071–7076, Sep. 2014, doi: 10.1039/c4tc01193g.
- [87] M. S. Baranava, D. C. Hvezdouski, V. A. Skachkova, V. R. Stempitsky, and A. L. Danilyuk, “Magnetic interactions in $\text{Cr}_2\text{Ge}_2\text{Te}_6$ and $\text{Cr}_2\text{Si}_2\text{Te}_6$ monolayers: ab initio study,” 2018. [Online]. Available: www.sciencedirect.com
- [88] B. Siberchicot, S. Jobic, V. Carteaux, P. Gressier, and G. Ouvrard, “Band Structure Calculations of Ferromagnetic Chromium Tellurides CrSiTe_3 and CrGeTe_3 ,” 1996. [Online]. Available: <https://pubs.acs.org/sharingguidelines>

- [89] K. Zollner, M. Gmitra, and J. Fabian, “Electrically tunable exchange splitting in bilayer graphene on monolayer $\text{Cr}_2\text{X}_2\text{Te}_6$ with $\text{X}=\text{Ge}$, Si , and Sn ,” Oct. 2017, doi: 10.1088/1367-2630/aace51.
- [90] Z. Shen *et al.*, “First-principles study the single-layer transition metal trihalide CrXSe_3 ($\text{X} = \text{Sn}$, Ge , Si) as monolayer ferromagnetic semiconductor,” *Journal of Physics Condensed Matter*, vol. 32, no. 8, 2020, doi: 10.1088/1361-648X/ab462a.
- [91] Bodénan, F., et al. "Spin-glass-like behavior in the selenide $\text{Cr}_2\text{Sn}_3\text{Se}_7$." *Journal of Solid State Chemistry* 137.2 (1998): 249-254.
- [92] Jobic, S., et al. "Structural determination and magnetic properties of a new mixed valence tin chromium selenide: $\text{Cr}_2\text{Sn}_3\text{Se}_7$." *Journal of alloys and compounds* 205.1-2 (1994): 139-145.
- [93] Y. Ren, Y. Ge, W. Wan, Q. Li, and Y. Liu, “Two dimensional ferromagnetic semiconductor: Monolayer CrGeS_3 ,” *Journal of Physics Condensed Matter*, vol. 32, no. 1, 2020, doi: 10.1088/1361-648X/ab4395.
- [94] Y. Liu and C. Petrovic, “Three-dimensional magnetic critical behavior in CrI_3 ,” *Phys Rev B*, vol. 97, no. 1, Jan. 2018, doi: 10.1103/PhysRevB.97.014420.
- [95] G. T. Lin *et al.*, “Tricritical behavior of the two-dimensional intrinsically ferromagnetic semiconductor CrGeTe_3 ,” *Phys Rev B*, vol. 95, no. 24, Jun. 2017, doi: 10.1103/PhysRevB.95.245212.
- [96] B. Liu *et al.*, “Critical behavior of the quasi-two-dimensional semiconducting ferromagnet CrSiTe_3 ,” *Sci Rep*, vol. 6, Sep. 2016, doi: 10.1038/srep33873.
- [97] M. K. Hamad and K. A. Ziq, “Critical behavior of $\text{CrTe}_{1-x}\text{Sb}_x$ ferromagnet,” *AIP Adv*, vol. 8, no. 10, Oct. 2018, doi: 10.1063/1.5042550.
- [98] K. Riahi *et al.*, “Adiabatic temperature change, magnetic entropy change and critical behavior near the ferromagnetic–paramagnetic phase transition in $\text{La}_{0.7}(\text{Ca},\text{Sr})_{0.3}\text{MnO}_3$ perovskite,” *Phase Transitions*, vol. 91, no. 7, pp. 691–702, Jul. 2018, doi: 10.1080/01411594.2018.1474356.
- [99] E. Zarai, F. Issaoui, A. Tozri, M. Hussein, and E. Dhahri, “Critical Behavior Near the Paramagnetic to Ferromagnetic Phase Transition Temperature in $\text{Sr}_{1.5}\text{Nd}_{0.5}\text{MnO}_4$ Compound,” *Journal of Superconductivity and Novel Magnetism*, vol. 29, no. 4. Springer New York LLC, pp. 869–877, Apr. 01, 2016. doi: 10.1007/s10948-015-3367-0.
- [100] Kundu, S., and T. K. Nath. "Critical behavior and magnetic relaxation dynamics of $\text{Nd}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$ nanoparticles." *Philosophical Magazine* 93.19 (2013): 2527-2548.

- [101] M. Jeddi, H. Gharsallah, M. Bekri, E. Dhahri, and E. K. Hlil, “Structural, magnetic, critical behavior and phenomenological investigation of magnetocaloric properties of $\text{La}_{0.6}\text{Ca}_{0.4-x}\text{Sr}_x\text{MnO}_3$ perovskite,” *Journal of Materials Science: Materials in Electronics*, vol. 30, no. 15, pp. 14430–14444, Aug. 2019, doi: 10.1007/s10854-019-01813-z.
- [102] D. Ginting *et al.*, “Second order magnetic phase transition and scaling analysis in iron doped manganite $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ compounds,” *J Magn Magn Mater*, vol. 395, pp. 41–47, Jul. 2015, doi: 10.1016/j.jmmm.2015.07.033.
- [103] A. Oleaga, A. Salazar, M. Ciomaga Hatnean, and G. Balakrishnan, “Three-dimensional Ising critical behavior in $\text{R}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (R=Pr, Nd) manganites,” *Phys Rev B Condens Matter Mater Phys*, vol. 92, no. 2, Jul. 2015, doi: 10.1103/PhysRevB.92.024409.
- [104] Thaljaoui, R., et al. "Critical analysis of the paramagnetic to ferromagnetic phase transition in $\text{Pr}_{0.55}\text{K}_{0.05}\text{Sr}_{0.4}\text{MnO}_3$." *Physica B: Condensed Matter* 482 (2016): 8-13.
- [105] Beving, Lucas Paul. "Magnetic behavior of bulk and nanostructured Mn_xTaS_2 ." (2017).
- [106] G. R. Haripriya, R. Pradheesh, K. Sethupathi, and V. Sankaranarayanan, “The order of magnetic phase transitions in disordered double perovskite oxides $\text{Sm}_2\text{FeCoO}_6$ and $\text{Dy}_2\text{FeCoO}_6$ ARTICLES YOU MAY BE INTERESTED IN Calculating the spontaneous magnetization and defining the Curie temperature using a positive-feedback model The order of magnetic phase transitions in disordered double perovskite oxides $\text{Sm}_2\text{FeCoO}_6$ and $\text{Dy}_2\text{FeCoO}_6$,” *J Appl Phys*, vol. 8, p. 101340, 2018, doi: 10.1063/1.5042757@adv.2018.ICM2018.issue-1.
- [107] P. T. Phong *et al.*, “Griffiths-like phase, critical behavior near the paramagnetic-ferromagnetic phase transition and magnetic entropy change of nanocrystalline $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$,” *J Magn Magn Mater*, vol. 449, pp. 558–566, Mar. 2018, doi: 10.1016/j.jmmm.2017.10.103.
- [108] A. Dhahri, M. Jemmali, M. Hussein, E. Dhahri, A. Koumina, and E. K. Hlil, “Critical behavior near the ferromagnetic to paramagnetic phase transition temperature in polycrystalline $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.15$ and 0.2),” *J Alloys Compd*, vol. 618, pp. 788–794, Jan. 2015, doi: 10.1016/j.jallcom.2014.08.128.
- [109] M. Tadout *et al.*, “Magnetic Properties and Magnetocaloric Effect in $\text{Gd}_{100-x}\text{Co}_x$ Thin Films,” *Crystals (Basel)*, vol. 9, no. 6, 2019, doi: 10.3390/cryst9060278i.

- [110] Z. Sniadecki, J. Marcin, and B. Idzikowski, "Critical behavior near the ferromagnetic to paramagnetic phase transition in $\text{Y}_8\text{Co}_{62}\text{B}_{30}$ amorphous alloy," in *Acta Physica Polonica A*, Polish Academy of Sciences, Apr. 2017, pp. 967–969. doi: 10.12693/APhysPolA.131.967.
- [111] L. Zhang *et al.*, "Critical behavior of spinel MnV_2O_4 investigated by dc-magnetization," *J Appl Phys*, vol. 115, no. 23, Jun. 2014, doi: 10.1063/1.4884339.
- [112] Z. R. Zhao, G. F. Wang, and X. F. Zhang, "Critical behavior of $\text{Gd}_5\text{Si}_2\text{Ge}_{1.9}\text{Ga}_{0.1}$ near the ferromagnetic-paramagnetic phase transition," in *Advanced Materials Research*, 2014, pp. 855–860. doi: 10.4028/www.scientific.net/AMR.873.855.
- [113] B. Liu *et al.*, "Critical behavior of the van der Waals bonded high TC ferromagnet Fe_3GeTe_2 ," *Sci Rep*, vol. 7, no. 1, Dec. 2017, doi: 10.1038/s41598-017-06671-5.
- [114] B. Sahu, J. J. Mboukam, and A. M. Strydom, "Critical behavior of $\text{Gd}_2\text{Rh}_3\text{Ge}$ intermetallic compound," *J Magn Magn Mater*, vol. 498, Mar. 2020, doi: 10.1016/j.jmmm.2019.166081.
- [115] A. K. Pramanik and A. Banerjee, "Critical behavior at paramagnetic to ferromagnetic phase transition in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$: A bulk magnetization study," *Phys Rev B Condens Matter Mater Phys*, vol. 79, no. 21, Jun. 2009, doi: 10.1103/PhysRevB.79.214426.
- [116] Kouvel, James S., and Michael E. Fisher. "Detailed magnetic behavior of nickel near its Curie point." *Physical Review* 136.6A (1964): A1626.
- [117] X. C. Zhong *et al.*, "Table-like magnetocaloric effect and large refrigerant capacity in $\text{Gd}_{65}\text{Mn}_{25}\text{Si}_{10}$ -Gd composite materials for near room temperature refrigeration," *Mater Today Commun*, vol. 14, pp. 22–26, Mar. 2018, doi: 10.1016/j.mtcomm.2017.12.005.
- [118] Shirane, Takashi, Teruo Bitoh, and Susumu Chikazawa. "Critical behavior of magnetic losses in nickel near the Curie temperature: Separation of magnetic losses by analyzing linear and nonlinear susceptibilities." *Journal of the Korean Physical Society* 46.3 (2005): 694.
- [119] J. Fan, L. Ling, B. Hong, L. Zhang, L. Pi, and Y. Zhang, "Critical properties of the perovskite manganite $\text{La}_{0.1}\text{Nd}_{0.6}\text{Sr}_{0.3}\text{MnO}_3$," *Phys Rev B Condens Matter Mater Phys*, vol. 81, no. 14, Apr. 2010, doi: 10.1103/PhysRevB.81.144426.
- [120] Mukherjee, Goutam Dev, et al. "Critical exponents of NiFeV alloys for the ferromagnetic–paramagnetic phase transition." *Journal of Magnetism and Magnetic Materials* 214.3 (2000): 185-194.

- [121] Mohan, Ch V., et al. "Critical behaviour near the ferromagnetic–paramagnetic phase transition in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$." *Journal of magnetism and magnetic materials* 183.3 (1998): 348-355.
- [122] Y. Zhang *et al.*, "Arrott plots, M 4 plots and the critical temperature of the weak ferromagnet $\text{FeGa}_{3-y}\text{Ge}_y$," *AIP Adv*, vol. 8, no. 10, Oct. 2018, doi: 10.1063/1.5043119.
- [123] B. EMRE, "La_{1-x}Ce_xMn₂Si₂ (x=0.35 ve 0.45) kritik davranışının manyetik entropi değişim bağılılığına göre araştırılması," *Balıkesir Üniversitesi Fen Bilimleri Enstitüsü Dergisi*, pp. 1–12, Oct. 2017, doi: 10.25092/baunfbed.344783.
- [124] Z. G. Zheng, X. C. Zhong, Z. W. Liu, D. C. Zeng, V. Franco, and J. L. Zhang, "Magnetocaloric effect and critical behavior of amorphous $(\text{Gd}_4\text{Co}_3)_{1-x}\text{Si}_x$ alloys," *J Magn Magn Mater*, vol. 343, pp. 184–188, 2013, doi: 10.1016/j.jmmm.2013.04.087.
- [125] Mira, J., et al. "Critical exponents of the ferromagnetic-paramagnetic phase transition of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0.20 < x < 0.30$)." *Physical Review B* 59.1 (1999): 123.
- [126] Perumal, A. "Critical behavior of electrical resistivity in amorphous Fe-Zr alloys." *Pramana* 56 (2001): 569-577.
- [127] Rocker, Werner, and Rudolf Kohlhaas. "Über das magnetische Verhalten des Kobalts in der Umgebung des Curie-Punktes." *Zeitschrift für Naturforschung A* 22.2 (1967): 291-294.
- [128] Potter, Harold H. "The magneto-caloric effect and other magnetic phenomena in iron." *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* 146.857 (1934): 362-387.
- [129] Hashimoto, T., et al. "Magnetic refrigeration in the temperature range from 10 K to room temperature: the ferromagnetic refrigerants." *Cryogenics* 21.11 (1981): 647-653.
- [130] Zimm, C., et al. "Description and performance of a near-room temperature magnetic refrigerator." *Advances in cryogenic engineering* (1998): 1759-1766.
- [131] Kuhrt, Ch, Th Schittny, and K. Bärner. "Magnetic B–T phase diagram of anion substituted MnAs. magnetocaloric experiments." *physica status solidi (a)* 91.1 (1985): 105-113.

- [132] J. F. Herbst, C. D. Fuerst, and R. D. McMichael, “Structural, magnetic, and magnetocaloric properties of $(\text{Hf}_{0.83}\text{Ta}_{0.17})\text{Fe}_{2+x}$ materials,” *J Appl Phys*, vol. 79, no. 8 PART 2B, pp. 5998–6000, Apr. 1996, doi: 10.1063/1.362133.
- [133] M. P. Annaorazov, S. A. Nikitin, A. L. Tyurin, K. A. Asatryan, and A. K. Dovletov, “Anomalous high entropy change in FeRh alloy,” *J Appl Phys*, vol. 79, no. 3, pp. 1689–1695, Feb. 1996, doi: 10.1063/1.360955.
- [134] S. A. Nikitin, G. Myalikgulyev, A. M. Tishin, M. P. Annaorazov, K. A. Asatryan, and A. L. Tyurin, “The magnetocaloric effect in $\text{Fe}_{49}\text{Rh}_{51}$ compound,” 1990.
- [135] D. T. Morelli, A. M. Mance, J. v. Mantese, and A. L. Micheli, “Magnetocaloric properties of doped lanthanum manganite films,” *J Appl Phys*, vol. 79, no. 1, pp. 373–375, Jan. 1996, doi: 10.1063/1.360840.
- [136] Y. Liu, Z. Hu, and C. Petrovic, “Anisotropic magnetocaloric effect and critical behavior in CrSbSe_3 ,” Jul. 2020, doi: 10.1103/PhysRevB.102.014425.
- [137] Y. Liu and C. Petrovic, “Anisotropic magnetic entropy change in $\text{Cr}_2\text{X}_2\text{Te}_6$ (X=Si and Ge),” *Phys Rev Mater*, vol. 3, no. 1, Jan. 2019, doi: 10.1103/PhysRevMaterials.3.014001.
- [138] Y. Sun, Z. Song, Q. Tang, and X. Luo, “Origin of Anisotropic Magnetic Properties in the Ferromagnetic Semiconductor CrSbSe_3 with a Pseudo-One-Dimensional Structure,” *Journal of Physical Chemistry C*, vol. 124, no. 20, pp. 11110–11116, May 2020, doi: 10.1021/acs.jpcc.0c02101.
- [139] Y. Liu, M. Abeykoon, and C. Petrovic, “Critical behavior and magnetocaloric effect in VI_3 ,” *Phys Rev Res*, vol. 2, no. 1, Jan. 2020, doi: 10.1103/PhysRevResearch.2.013013.
- [140] X. Yang *et al.*, “Critical behavior and anisotropic magnetocaloric effect of the quasi-one-dimensional hexagonal ferromagnet PrCrGe_3 ,” *Phys Rev B*, vol. 103, no. 10, Mar. 2021, doi: 10.1103/PhysRevB.103.104405.
- [141] Y. Liu and C. Petrovic, “Anisotropic magnetocaloric effect and critical behavior in CrCl_3 ,” *Phys Rev B*, vol. 102, no. 1, Jul. 2020, doi: 10.1103/PhysRevB.102.014424.
- [142] X. Yu *et al.*, “Large magnetocaloric effect in van der Waals crystal CrBr_3 ,” *Frontiers of Physics*, vol. 14, no. 4. Higher Education Press, Aug. 01, 2019. doi: 10.1007/s11467-019-0883-6.
- [143] Y. Liu and C. Petrovic, “Anisotropic magnetocaloric effect in single crystals of CrI_3 ,” *Phys Rev B*, vol. 97, no. 17, May 2018, doi: 10.1103/PhysRevB.97.174418.

- [144] Pecharsky, Vitalij K., and Karl A. Gschneidner Jr. "Giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$." *Physical review letters* 78.23 (1997): 4494.
- [145] L. R. B. Elton and D. F. Jackson, "X-Ray Diffraction and the Bragg Law," *Am J Phys*, vol. 34, no. 11, pp. 1036–1038, Nov. 1966, doi: 10.1119/1.1972439.
- [146] C. W. Looney, "Resistivity and Susceptibility Measurements in a Helium-Gas System," 2014. https://web.physics.wustl.edu/jss/HeGas_2014_August.pdf
- [147] S. Yonezawa, T. Higuchi, Y. Sugimoto, C. Sow, and Y. Maeno, "Compact AC susceptometer for fast sample characterization down to 0.1 K," *Review of Scientific Instruments*, vol. 86, no. 9, Sep. 2015, doi: 10.1063/1.4929871.
- [148] Cevey, Laurent. Miniature AC susceptometer. No. STUDENT. 2008. [Online]. Available: <http://www.stoner.leeds.ac.uk/techniques/ACsuscept.htm>,
- [149] D. L. Duong, S. J. Yun, and Y. H. Lee, "Van der Waals Layered Materials: Opportunities and Challenges," *ACS Nano*, vol. 11, no. 12. American Chemical Society, pp. 11803–11830, Dec. 26, 2017. doi: 10.1021/acsnano.7b07436.
- [150] Shabbir, Babar, et al. "Long range intrinsic ferromagnetism in two dimensional materials and dissipationless future technologies." *Applied Physics Reviews* 5.4 (2018).
- [151] D. A. Odink, V. Carteaux, C. Payen, and G. Ouvrard, "Synthesis and Structure of CrSbSe_3 : A Pseudo-One-Dimensional Ferromagnet," 1993. [Online]. Available: <https://pubs.acs.org/sharingguidelines>
- [152] V. v. Volkov *et al.*, "HREM Image Analysis up to Structure Determination of SbCrSe_3 : A New 1D Ferromagnet," *J Solid State Chem*, vol. 132, no. 2, pp. 257–266, Sep. 1997, doi: 10.1006/jssc.1997.7438.
- [153] T. Kong, K. Stolze, N. Danrui, S. K. Kushwaha, and R. J. Cava, "Anisotropic magnetic properties of the ferromagnetic semiconductor CrSbSe_3 ," Nov. 2017, doi: 10.1103/PhysRevMaterials.2.014410.
- [154] Lin, G. T., et al. "Critical behavior of two-dimensional intrinsically ferromagnetic semiconductor CrI_3 ." *Applied Physics Letters* 112.7 (2018): 072405.
- [155] D. Soundararajan, D. Mangalaraj, D. Nataraj, L. Dorosinskii, and J. Santoyo-Salazar, "Observation of room temperature ferromagnetism in $\text{ZnTe}:\text{Cr}$ films grown onto glass substrate by thermal evaporation method," *J Phys Conf Ser*, vol. 153, 2009, doi: 10.1088/1742-6596/153/1/012048.

- [156] Q. Feng, X. Li, X. Li, and J. Yang, “CrSbS₃monolayer: A potential phase transition ferromagnetic semiconductor,” *Nanoscale*, vol. 13, no. 33, pp. 14067–14072, Sep. 2021, doi: 10.1039/d1nr03640h.
- [157] Pohle, Rico, and Ludovic DC Jaubert. "Curie-law crossover in spin liquids." arXiv preprint arXiv:2304.11031 (2023).

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| 6- How teaching in the lab | Sep. 2020 |
| 7- Introduction to quantum computing | Jan. 2023 |

Published Papers:

❑ New vdW Materials CrSnS₃

- 1- Obad, F., and Kh A. Ziq. "Magnetic properties of CrSnS₃ : A new Van der Waals ferromagnet." arXiv preprint arXiv:2207.14129 (2022).
- 2- F Obad and Kh. A. Ziq, "On the Magnetic States in CrSbS₃ Van der Waals Ferromagnetic Materials
- 3- M. O. Bolarinwa, F. Obed, K.A. Ziq, "Disorder Effects on the Paramagnetic Phase in [HoCo]₂System" Draft
- 4- J. Abiola, F. Obad and Kh. Ziq "Effects of Mn substitution in Cr_{1-x}Mn_xSbSe₃ van der Waals Ferromagnetic Material", IOP- Journal of Physics conference series". the 7th International Conference Advance Material For Better Future, October 17-18th, 2022; Solo, Indonesia