Evolution Of The Magnetic Properties On Van Der Waals Layered Magnets Via Pressure And Proton Irradiation

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EVOLUTION OF THE MAGNETIC PROPERTIES ON VAN DER WAALS LAYERED MAGNETS VIA PRESSURE AND PROTON IRRADIATION

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Rubyann Olmos

2022
Dedication

To my beloved grandmother,

for inspiring me to pursue higher education

and for providing support, love, and prayers along the way.
EVOLUTION OF THE MAGNETIC PROPERTIES ON VAN DER WAALS LAYERED MAGNETS VIA PRESSURE

By

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THESIS

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ABSTRACT

Probing the magnetism in quasi two-dimensional materials has the potential in driving their properties towards future use in spin electronic based devices. Studying such layered magnets will enable the scientific community to uncover tunable exotic phases such as superconductivity, quantum paramagnetism, etc. This work examines the influence of two types of external perturbations, namely, the pressure and proton irradiation, on the magnetic properties of several compounds in the van der Waals crystal family.

Pressure has been found to induce structural and magnetic phase transitions in many of these materials. Using hydrostatic pressure as a disorderless approach to manipulate the interlayer coupling, we apply pressure to CrBr₃, Fe₂.₇GeTe₂, Mn₃Si₂Te₆, and CrSiTe₃ with a high-pressure piston cell up to ~1.3 GPa. Materials with weakly held layers allow relatively easy manipulation of the superexchange mechanism. Magnetic property measurements revealed that each material studied has shown the ability to have their corresponding Curie temperature (T_C) and the saturation magnetization tuned by pressure. The overall pressure effect on layer separation, bond angle, and exchange coupling are found to strongly influence the change in subsequent magnetic characteristics.

Proton irradiation was employed to manipulate the spin fluctuations on Mn₃Si₂Te₆ (MST) and being irradiated at 1 × 10¹⁵, 5 × 10¹⁵, 1 × 10¹⁶, and 1 × 10¹⁸ H⁺/cm². A critical behavior analysis was performed to examine the physical system at the critical point for each fluence rate. The analytical study of the critical phenomena has been used to discern the magnetic behavior of proton irradiated MST. In this work, we report the critical parameters related to magnetization, magnetic susceptibility, exchange distance, space and spin dimensionality to sort the universality class as a function of proton irradiance.
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CHAPTER 1: MOTIVATION AND BACKGROUND

In 2004, the two-dimensional (2D) material graphene was successfully isolated by researchers Andre K. Geim and Konstantin S. Novoselov, which generated exceptional quantum properties and a promising future for investigating 2D magnetism [1]. The discovery of graphene not only prompted the 2010 Nobel Prize award in Physics but sparked a revolution in van der Waals (vdW) layered materials for the search of the previously unattainable 2D magnet. The weak interlayer bonding present in vdW crystals have allowed scientists to fabricate these materials either through mechanical exfoliation of the layers or by synthesizing atom by atom through molecular beam epitaxy techniques. Many studies have shown that the vdW layered class of materials can retain long-range 2D ferromagnetism down to the monolayer limit [2-6]. Such a breakthrough ended up proving the limitations in the Mermin–Wagner theorem differently as uniaxial magnetic anisotropy in vdW materials stabilizes the magnetic ordering in the monolayer limit [7]. The opening of magnon excitation gaps due to the magnetocrystalline anisotropy in turn resist thermal fluctuations, therefore allowing isotropic Heisenberg systems to maintain long-range magnetic ordering in two dimensions. The bulk magnetoelectrical properties and structural characteristics on chromium trihalides and transition metal dichalcogenides have been amply studied since 2D magnetism was found in CrI$_3$ and Cr$_2$Ge$_2$Te$_6$ [5,8]. The chromium trihalide (CrX$_3$) and ternary transition metal chalcogenides have shown interesting properties making them potential candidates for applications in magnetoelectronics. For instance, bulk CrSiTe$_3$ exhibits ferromagnetic ordering at 32 K and is easily manipulated to exhibit ordering around 80 K by mechanically exfoliating to the monolayer [9]. In addition, CrI$_3$ in the bulk and monolayer have shown ferromagnetic behavior, whereas the bilayer displays antiferromagnetism [5]. However, the
main attraction to the family of vdW compounds is due to their susceptibility in responding to external stimuli such as temperature, stress, and environment.

There are many tactics used in the literature to perturb the magnetic states in 2D materials whether the methods are optical, mechanical, or chemical in nature such as through light, strain, pressure, electrostatic gating, and doping to name a few. This work focuses on separately employing hydrostatic pressure and proton irradiation on the CrX₃ family and ternary transition metal chalcogenides (Fe₂.₇GeTe₂, CrSiTe₃, Mn₃Si₂Te₆). Hydrostatic pressure can be used as a disorderless approach to tuning the magnetic properties as pressure on a system of weakly coupled layers affects bonding and interlayer coupling without destroying the crystal [6]. A remarkable tuning of the properties has recently been seen with the material CrGeTe₃ where ~ 9 GPa of pressure significantly increased the Curie temperature (T_C) to a value greater than 250 K, a jump of nearly 184 K from its ambient conditions [10]. Proton irradiation has recently been used as a mode in positively impacting the magnetic properties of materials [11, 50, 69-71]. There are several studies that have employed proton irradiation which have induced magnetism in non-magnetic materials such as MoS₂ and graphite [12-19].
CHAPTER 2: EXPERIMENTAL METHODS

2.1 Synthesis

Single crystal samples of CrBr$_3$ were prepared using chemical vapor transport by placing powders of Cr metal and TeBr$_4$ inside a quartz tube and maintaining the hot and cold zones at 700 and 600 °C for 5 days. The green plate-like crystals are a few millimeters across and 50 microns thick \[20,21\]. Bulk Fe$_{2.7}$GeTe$_2$, CrSiTe$_3$, and Mn$_3$Si$_2$Te$_6$ crystals were synthesized as outlined in previous reports by co-authors, Y. Liu and C. Petrovic, using a self-flux technique \[22-24\].

2.2 Magnetic Characterization

Magnetic measurements for Part I were performed using a Quantum Design MPMS (Magnetic Properties Measurement System) 3 with Superconducting Quantum Interface Device (SQUID) magnetometer. Isothermal magnetization measurements were taken at 2 K with a ± 7 T magnetic field. Zero-field cool (ZFC) temperature dependent magnetization was performed from 2–150 K with a measuring field of 500 Oe.

Magnetization measurements for Part II were performed using a Quantum Design PPMS VersaLab system with a temperature range of 50–400 K and magnetic field of ± 3 T. Magnetization measurements were performed with a vibrating sample magnetometer (VSM) with the magnetic field applied along the $ab$ plane for the pristine and irradiated samples.

2.3 Hydrostatic Pressure Application

2.3.1 Experiment

Hydrostatic pressure was applied using a BeCu Quantum Design piston cell. The pressure transmitting medium is Daphne (Silicon) oil and a Pb manometer was used to monitor the pressure in the cell. Compression of the cell length was increasingly applied and only depressurized after the data collection was completed. The pressure is determined by measuring the moment of Pb as
a function of temperature between 6.8–7.3 K with a 1 Gauss magnetic field. The derivative of the moment with temperature reveals a minimum, indicating the magnetic transition temperature of the Pb. It is already well-known how the Pb manometer behaves with pressure following the rate of 0.379 K/GPa. As the ambient transition temperature for Pb is lies between 7.185-7.19 K, calculating the change in transition temperature from the applied pressure to zero pressure will allow one to simply calculate the pressure inside the cell using the expression: \((7.19 \text{[K]} - T_C \text{[K]}) / 0.379 \text{[K/GPa]}\).

**Figure 2.1** Depiction of the center cylinder and pistons of the BeCu pressure cell. Inside the center cylinder is a Teflon tube with Teflon caps on each end.

For the materials FGT, CST, and CrBr\(_3\) we perform pressure measurements with the magnetic field applied parallel to the \(c\)-axis (H \(\parallel\) \(c\)), otherwise known as out-of-plane measurements. These samples are fixed flat using carbon tape on the Teflon cap which will be inserted first into the sample chamber. However, MST exhibits an easy axis of H \(\parallel\) \(ab\), therefore the sample must be fixed in a “vertical” fashion. For this case we align the sample using two pieces of carbon tape sandwiching the lower portion of the sample, still allowing for the Daphne oil to surround the sample to give a hydrostatic pressure effect. In this orientation, it is important to know the length of the sample so that the clearance is known so that the sample is not crushed as the length of the cell is increasingly compressed.
2.3.2 Theory

The optimization of the crystal structures of CrBr$_3$ were carried out with Vienna ab initio (VASP) code [25,26] within projector augmented-wave (PAW) method [27,28]. General gradient approximation (GGA) in the Perdew-Burke-Enzerhof (PBE) [29] method was used for the exchange correlation functional. The non-local vdW functional in form of optB88-vdW [30,31] is incorporated to account for the interlayer vdW force. The plane-wave cut-off energy is 500 eV, and an 8×8×3 k-point is used to sample the Brillouin zone [32]. For the magnetic property calculations, the on-site Coulomb interactions are taken into account using LDA+U [33] to improve the description of the interactions between localized d electrons of transition atoms. The hydrostatic pressure effect calculation was done by adding the PSTRESS [34] tag, which adds the stress to the stress tensor and an energy generated from the external pressure. All the lattice constants and ionic coordinates were relaxed until the maximum force on all ions is less than 5 × 10$^{-3}$ eV/Å.

The electronic structure calculations for the magnetic properties are carried out using the pseudo-atomic orbital based [35] OpenMX code [36]. The core electrons are replaced with norm-conserving pseudopotential [37,38] with energy cutoff 200 Ry. The 7×7×3 k-point mesh was used for BZ integration. On-site Coulomb interactions are particularly strong for the localized d electrons in the CrBr$_3$ system. To remedy this shortcoming in this correlated system, the Hubbard-U method pioneered by Anisimov et al. is applied [39,40]. In treating the localized d-electron states from Cr, we use parameters U = 2.7 eV and J = 0.7 eV taken from Ref. [41] which have also been used in previous studies [42-44]. The Green’s function method [45] implemented in OpenMX 3.9 [56] was used to calculate exchange coupling constants J$_i$ for up to the 3rd nearest neighbor (NN).
This approach allows the direct calculation of exchange coupling parameter between any pair of magnetic sites for any inter-pair distance.

For MAE, the charge and spin densities were obtained using a self-consistent calculation without spin-orbit coupling (SOC) and kept fixed in subsequent MAE calculations. The MAE was determined as the difference in the total band energy for the configurations with the magnetization aligned in-plane and out-of-plane, with SOC included [547].

2.4 Proton Irradiation

MST samples were irradiated with protons at Texas A&M University. A 2 MeV proton beam and a 1.7 MV Tandetron accelerator was utilized at $1 \times 10^{15}$, $5 \times 10^{15}$, $1 \times 10^{16}$, and $1 \times 10^{18}$ H$^+/\text{cm}^2$. The proton beam spot size is 6mm x 6mm, with a beam current of ~1 μA. The beam is filtered with multiple magnet bending devices to remove carbon contamination. During the irradiation process, the vacuum maintains a pressure of $6 \times 10^{-8}$ Torr or lower. Liquid nitrogen trapping is applied during irradiation in order to improve the vacuum. The projected range of 2 MeV H$^+$ ions is about 30 microns. The damage profile has a relative flat distribution from the surface up to ~30 microns. Further details on the proton irradiation process are described in previous reports [48,49].
PART I: TUNING MAGNETIC PROPERTIES BY APPLICATION OF PRESSURE

CHAPTER 3: THE PRESSURE EFFECT ON TRANSITION METAL CHALCOGENIDES

3.1 Experimental Characterization on Fe$_{2.7}$GeTe$_2$ with Pressure

The itinerant Fe$_{3-x}$GeTe$_2$ (FGT) compound is of particular interest as it is strongly ferromagnetic between 152-230 K depending on the iron content [50-53]. May et al. observed that $T_C$ tends to decrease by an increasing number of Fe vacancies introduced into the lattice where the in-plane lattice parameter decreases [54]. FGT consists of Fe$_{2.7}$Ge slabs which contain two inequivalent Fe Wyckoff sites, Fe1 and Fe2, which are seen in Figure 3.1.

There have been a few studies which employ pressure on the Fe$_{3-x}$GeTe$_2$ compound with the common finding of observing decrease in $T_C$ with increase in pressure. In Fe$_3$GeTe$_2$, the structural stability is found to be stable up to 25.9 GPa, however, $T_C$ is found to decrease at a rate of 9.2 K/GPa ($T_C = 195$ K at 13.4 GPa). Further compression prominently suppresses the magnetic moment and decreases the anomalous Hall effect [55]. Another study on Fe$_3$GeTe$_2$, performs in situ magnetic circular dichroism (MCD) [56] measurements. As pressure is increased, the coercive field ($H_c$) and $T_C$ decrease. This implies that there is a decrease in the exchange interaction and the magneto-crystalline anisotropy with pressure. Calculations from the same study show a weak structural transition occurring at ~6 GPa. The structural change is in line with the significant change they observe in the Fe1–Fe1 bond length, which strongly influences the magnetic interactions in FGT. An additional study on Fe$_3$GeTe$_2$ confirms the same trend in decreasing $T_C$ which decreases by 15 K as the pressure increases up to 1.44 GPa [57]. They also find that magnetization is suppressed by pressure and confirm that the Fe-Fe bond lengths tend to decrease as well. This in
turn causes the Fe-Ge(Te)-Fe bond angles to deviate away from 90° under hydrostatic pressure, indicating a modification of the exchange interactions as also explained in Ref. [56]. Direct-exchange ends up becoming stronger at a higher pressures leading to increased antiferromagnetic components causing decreased $T_C$. In another work, magneto-transport measurements are performed on Fe$_{2.75}$GeTe$_2$ which ultimately show a decrease in $T_C$ and magnetic moment up to 13.9 GPa [58]. A metallic to nonmetallic behavior is observed when pressure is increased. X-ray diffraction shows compression of the unit cell and a reduction of volume by $\sim$25% with no evidence of structural phase changes up to 29.4(4) GPa. They confirm that the decrease in $T_C$ due to pressure is from increased intralayer coupling and delocalization changing the mechanism behind the exchange interaction.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.1.png}
\caption{The crystal structure of Fe$_{3.4}$GeTe$_2$ compound [22].}
\end{figure}
In this work, we investigated the magnetization of Fe$_{2.7}$GeTe$_2$ in the low-pressure regime up to 1.22 GPa to confirm the trends that are seen in the literature. Figure 3.2(a) displays the isothermal magnetization at 2 K (± 7 T) for FGT up to 1.22 GPa of pressure. These measurements were conducted along the easy axis direction for FGT (H || c) which is clear from the square shape of the hysteresis loop. Magnetization is manipulated from 36 emu/g to 32.5 emu/g at 1.22 GPa, a 9.7% decrease. These results are in line with the literature where a suppression of the magnetic moment is seen in Ref.’s [55,57-58]. The magnetization vs. temperature data can be seen in Figure 3.2(b) where the curves shift to the left as pressure is increasing. This shifting is indicative of a decrease in T$_C$, where the derivative of magnetization with temperature minimum(s) are seen in Figure 3.2(c) for all pressures. A decrease of about 13 K in the T$_C$ is seen at 1.22 GPa, comparable to the decrease of 15 K at 1.44 GPa previously reported in Ref. [56]. Figure 3.2(d) shows the magnetization at 7 T and T$_C$ plotted as a function pressure. In the present work, we correlate the decrease in T$_C$ to the decrease in magnetic moment as there is linear relationship between the two. It is gathered that pressure is most likely influencing the superexchange mechanism in FGT, by affecting the Fe-Ge(Te)-Fe bonding angle. In the literature, it has been seen that Fe-Fe bond length is decreasing as a function of increasing pressure, therefore affecting the super exchange interaction that is mediated by the ligands Ge and Te.

In the future, density functional theory (DFT) calculations will be employed to further understand the impact of pressure on the magnetic properties of FGT. In addition, to first principles calculations, a proposal has been accepted at Argonne National Laboratory (ANL) to perform high pressure x-ray magnetic circular dichroism (XMCD) measurements as well as high pressure resistance and x-ray diffraction measurements at the Air Force Research Laboratory (AFRL) in Dayton, Ohio for pressure well above 1.3 GPa.
Figure 3.2 Experimental data collection on Fe$_{2.7}$GeTe$_2$ with application of pressure. (a) The isothermal magnetization for the easy axis direction taken at 2 K with $\pm 7$ T. INSET: Close up of the magnetization in the 1$^\text{st}$ quadrant. (b) Zero field cool temperature dependent magnetization with a 500 Oe magnetic field in the easy axis ($H \parallel c$). (c) Derivative of the magnetization with respect to temperature shown for all applied pressures. (d) Magnetization (left y-axis) and $T_c$ (right y-axis) plotted as a function of increasing pressure up to 1.22 GPa.

3.2 Experimental Characterization on CrSiTe$_3$ with Pressure

The semiconducting material, CrSiTe$_3$ (CST), exhibits a $T_c$ of 32 K and has a large spin orbit coupling resulting in a large magnetocrystalline anisotropy [59-62] CST crystallizes with rhombohedral symmetry in a honeycomb network with space group R-3 [61]. The Cr ions are arranged in hexagonal planes stacking along the $c$-axis with one-third of layers being composed of Si$_2$Te$_6$. Each Cr$^{3+}$ atom (S = 3/2) is octahedrally coordinated with Te that are edge sharing [63],
see Figure 3.3 CST has recently shown interesting effects under the application of pressure. A study that employed pressures up to 15 GPa saw structure and property transformations in CST. In the low-pressure regime, a metallization and spin reorientation transition are seen. Pressures reaching 15 GPa revealed transformation from a 2D-like phase of layers to a quasi-three-dimensional phase where vdW gaps disappear. This was followed by an amorphization process occurring at 25 GPa via rotation of Si-Si dimer [63]. Another study employs pressures up to 47.1 GPa finding a structural transition at approximately 7.5 GPa joined by a ferromagnetic to paramagnetic transition where superconductivity began to emerge [64]. At the maximum applied pressure, the magnetoresistance shows an evidence of sign reversal along with an abrupt change in the Hall coefficient. The most recent work on CST with pressure saw a dramatic increase in the $T_C$ coming to around 138 K at 7.8 GPa as well as seeing an increase in the coercivity (0.17 T) [65]. Between 4-5 GPa a soft to hard ferromagnetic state is observed, along with the onslaught in increased $T_C$ (~36 K) and coercive field ($H_c$) (0.02 T).

![Schematic of the crystal structure of CrXTe$_3$ where X = Si from reference [23]](image)

**Figure 3.3** Schematic of the crystal structure of CrXTe$_3$ where X = Si from reference [23].
The experimental results in this study obtained for CST go up to 0.686 GPa with measurements conducted in the easy axis which is for H || c. Figure 3.4(a) shows that pressure effects the magnetization decreasing to the range of 34.16-34.11 emu/g for pressures between 0.158 to 0.686 GPa. This is small decrease from the ambient conditions, which give the magnetization value of 34.95 emu/g at + 7 T. The temperature dependent measurements seen in Figure 3.4(b) shows similar decrease in the magnetization in the ferromagnetic region along with a small shift of the curves to the left, indicating a decrease in the magnetic phase transition temperature as pressure is increasing. Figure 3.4(c) displays the derivative of the magnetization with respect to temperature. It is observed at the maximum applied pressure that $T_c$ decreases from 33.71 K to 28.43 K, in addition to a drastic decrease in the magnitude of the minimums at the largest pressure. This shrinking of the derivative curve, along with the suppression of $T_c$ and magnetization indicate a decrease in the overall magnetic ordering as similarly seen in Ref. [58] for pressure up to 16 GPa on Fe$_3$GeTe$_2$. However, completion of this experimental work supplemented with DFT calculations with pressure will help reveal the low-pressure effect in CST. Moreover, it will be important to observe the coercivity and the interplanar distance to corroborate the results from previous high-pressure studies. It also seems that the literature will benefit from a comprehensive magnetization study in the high-pressure regime to bring together the results of pressure enhanced ferromagnetism in Ref. [65] up to 7.8 GPa and a structural transition causing a ferromagnetic to paramagnetic transition leading to superconductivity at 7.5 GPa [64], to a spin reorientation at ~ 6 GPa inducing metallization [63].
Figure 3.4 Experimental data collection on CrSiTe$_3$ with application of pressure. (a) The isothermal magnetization for the easy axis direction taken at 2 K with $\pm 7$ T. INSET: Close up of the magnetization in the 1$^{st}$ quadrant. (b) Zero field cool temperature dependent magnetization with a 500 Oe magnetic field in the easy axis ($H \parallel c$). (c) Derivative of the magnetization with respect to temperature shown for all applied pressures.

3.3 Experimental Characterization on Mn$_3$Si$_2$Te$_6$ with Pressure

The insulating compound, Mn$_3$Si$_2$Te$_6$, (MST), is a ferrimagnet whose antiferromagnetic contribution stems from frustration between the three nearest neighbor interactions between Mn1 (multiplicity of two) and Mn2 sites (see Figure 3.5). MST is often referred to as the sister compound to CrSiTe$_3$ as layers are composed of MnTe$_6$ octahedra sharing an edge with the $ab$
plane at the Mn1 site and with Si-Si dimers. However, MST differs in that one-third of the Mn atoms link the layers together by filling the octahedral holes at the Mn2 site as shown in Figure 3.5 [66]. MST has a trigonal crystal structure with space group no. 163 [67,68] where the $T_C$ for MST has been found to be between 73 to 78 K [69-71]. Although CST has been vastly studied in the literature, MST has remained relatively untouched when it comes to inducing changes in its properties through external means. This report is one of the first on pressure dependent magnetic properties on MST which shows distinct pressure induced increase in the moment and $T_C$ in comparison to our experimental results on FGT and CST with pressure.

Figure 3.5 Schematic of the Mn sites in MST displaying a triangular frustration and the crystal structure from the work of May et. al. [66].

In this experimental study on MST, we apply hydrostatic pressure up to 1.06 GPa with magnetic fields applied along the easy axis ($H \parallel ab$). The sample is carefully fixed in the easy axis direction with carbon tape securing the edge to the Teflon cap. The scenario in which MST is fixed is different than those materials whose easy axis is for $H \parallel c$. Crystals with out-of-plane moments can easily be fixed flat against the Teflon cap, however, in the case of MST the sample will need be fixed on its side in order to have magnetic fields parallel to the $ab$-plane ($H \parallel ab$). Therefore, it is important to note the length of the sample so one does not crush the material upon compression.
of the pressure cell. Figure 3.6(a) displays the isothermal magnetization at 2 K for ± 7 T. It is observed that the magnetization can be tuned by pressure where the general trend shows a decrease in magnetization from the 0 GPa state up until reaching the maximum pressure at 1.06 GPa. At the largest pressure magnetization at + 7 T is 30.43 emu/g, less than one degree Kelvin difference from the pristine conditions at 0 GPa (29.69 emu/g). However, when comparing the largest magnetization at 1.06 GPa to the minimum at 0.9 GPa, we observe a about a 3 K difference.

Figure 3.6(b) shows the ZFC magnetization for each pressure as a function of temperature (2-150 K) using a 500 Oe magnetic field. Not only do we see pressure affecting the magnetization, but also, we see an apparent shifting of the curves to the right as pressure is steadily increased. The $T_C$ is estimated in Figure 3.6(c), which shows an increase up to 87.41 K at 1.06 GPa, a 14 K jump from the 0 GPa state. This increase in $T_C$ is a great indicator that MST should be studied at even higher pressures, although the relationship between magnetization and $T_C$ as a function of pressure is not very clear with the current experimental results (Figure 3.6(d)). In the future, first principles calculations will elucidate this complex relationship on $T_C$ and magnetization, and a high-pressure study conducted at ANL using XMCD complemented with Raman and resistivity measurements at AFRL will provide a complete story on the pressure induced magnetic properties on the ferrimagnetic MST at pressures greater than the current work.
Figure 3.6 Experimental data collection on \( \text{Mn}_3\text{Si}_2\text{Te}_6 \) with application of pressure. (a) The isothermal magnetization for the easy axis direction taken at 2 K with \( \pm 7 \) T. INSET: A close up of the magnetization in the 1st quadrant. (b) Zero field cool (ZFC) temperature dependent magnetization with a 500 Oe magnetic field in the easy axis \( (H \parallel ab) \). (c) Derivative of the magnetization with respect to temperature shown for all applied pressures. (d) Magnetization and \( T_C \) plotted as a function of increasing pressure up to 1.06 GPa.

CHAPTER 4: THE PRESSURE EFFECT ON THE CHROMIUM TRIHALIDE FAMILY

4.1 Experimental Characterization

The CrX\(_3\) family are a class of exfoliable semiconductors with strong magnetic properties originating from their crystalline structure. In particular, the source of magnetic anisotropy arises from an increase in spin orbit coupling associated with the halogen atom as one moves down the
periodic table. Therefore, the magneto-crystalline anisotropy energy (MAE) in the CrX₃ family serves as a form of counteracting thermal fluctuations. In the CrX₃ family, magnetic ordering temperatures and Cr-Cr distance increase with the size of halogen atom from Cl to Br to I, which allows for direct exchange to weaken. Furthermore, the Cr-X bond becomes more covalent as electronegativity decreases from Cl to Br to I, leading to a strengthening of the superexchange interactions, in this order. CrBr₃ is ferromagnetic in the bulk exhibiting a phase transition from a monoclinic C2/m phase at high temperatures to a rhombohedral-trigonal R3 phase at very low temperatures.

In Figure 4.1(a), we present the isothermal magnetization at 2 K collected at various pressures up to 0.844 GPa. A ferromagnetic magnetization signal is observed for all pressures for magnetic fields applied out-of-plane. The saturation magnetization (Mₘ) transitions from 58.89 (0 GPa) to 57.84 emu/g at 0.844 GPa where the inset of Figure 4.1(a) shows an amplified view of the Mₘ. Figure 4.1(b) displays the temperature dependence of magnetization with applied pressure up to 0.844 GPa. The same trend is followed where magnetization is decreasing as the cell is increasingly compressed. Curie temperature (T_C) is extracted from the derivative (dM/dT) of the temperature dependent magnetization data, as seen in Figure 4.1(c). The variation of T_C as a function of pressure is also plotted in Figure 4.1(d), which shows a monotonic decrease of about 2.6 K at the largest applied pressure. Moreover, if pressure causes the bond angle to deviate away from a 90° for the Cr-X-Cr bond angle, T_C is expected to decrease—weakening the superexchange interaction [72,73]. We do note that after the pressure was released, a zero-pressure measurement showed a larger saturation magnetization (~62 emu/g) than before (~ 59 emu/g) the application of pressure, whereas the T_C does not show any change at all.
Figure 4.1 (a) Isothermal magnetization for pressure up to 0.844 GPa at 2 K with ± 7 T magnetic field. (b) Zero field cool temperature dependent magnetization measurements from 2 - 150 K. (c) Derivative(s) of magnetization with respect to temperature for all pressures. (d) Saturation magnetization, $M_s$, (left, orange) and Curie temperature, $T_C$, (right, blue) plotted as a function of pressure where green indicates values at zero pressure upon decompressing the pressure cell from 0.844 GPa.

4.2 Theoretical Calculations

To gain further insights on the pressure effect within the 1 GPa range, we performed first-principles calculations examining the structure of CrBr$_3$ and its magnetic properties. In treating the localized d-electron states from Cr, we use parameters $U = 2.7$ eV and $J = 0.7$ eV. Figure 4.2(a) shows the pressure dependence of the lattice ratio c/a as a function of pressure showing a
monotonic decrease up to 1 GPa. Similarly, the volume of the crystal is decreasing with increasing pressure, as seen in Figure 4.2(b). This suggests that the pressure is compressing the interatomic layer separation of the lattice. It is not surprising that the reduction of c is more significant due to weak interlayer coupling. A similar trend is also observed in several other vdW layered systems such as \( \text{Cr}_2\text{Si}_2\text{Te}_6 \) [74].

![Figure 4.2](image)

**Figure 4.2** Theoretical calculations performed as a function of pressure for the (a) lattice parameter ratio \( c/a \) and (b) volume.

To understand how the magnetic properties vary with pressure the exchange coupling \( J \) and MAE are considered. As discussed in the previous section, the external pressure changes the lattice constants, which influence the inter-site electron hopping process. Two of the main mechanisms that contribute to exchange coupling between the localized moments are direct and super-exchange interactions. It is often the result of the competition between the two that dictates the response of the applied pressure. We employed Green’s Function based method to obtain exchange interaction constant \( J_i \) \((i = 1\text{-}3 \text{ and out})\) that correspond to up to 3rd NN and the nearest interlayer interaction. This method requires only the ground state and allows a direct calculation of the exchange coupling constant between any given pair of magnetic sites of any distance, which has proven to be more advantageous for large systems with localized moments [75]. The results of \( J_1 \) is plotted in Figure
4.3(a) and $J_2$ and $J_{out}$ due to their energy scale are plotted in Figure 4.3(b). $J_3$ is omitted due to the minuscule contribution. As one can see, in the given pressure range, the only dominant component is the 1st NN interaction $J_1$ and the interaction strength decreases rapidly as the distance between the pair increases. This is similar to what is suggested by previous studies [76] where both the $J_{out}$ and $J_2$ are much weaker compared to $J_1$, particularly under such ambient pressures. Therefore, as our data suggest, they are unlikely to have significant effects on $T_C$ under mean-field consideration.

**Table 1** Calculated lattice parameters, volume, and Cr-Cr distance with pressure on.

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$ (Å)</th>
<th>$V$ (Å)</th>
<th>Cr-Cr (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>6.347</td>
<td>18.236</td>
<td>2.873</td>
<td>636.308</td>
<td>3.668</td>
</tr>
<tr>
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<td>2.860</td>
<td>629.442</td>
<td>3.658</td>
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<td>0.50</td>
<td>6.317</td>
<td>17.994</td>
<td>2.849</td>
<td>621.759</td>
<td>3.651</td>
</tr>
<tr>
<td>0.75</td>
<td>6.308</td>
<td>17.928</td>
<td>2.842</td>
<td>617.721</td>
<td>3.642</td>
</tr>
<tr>
<td>1.00</td>
<td>6.289</td>
<td>17.821</td>
<td>2.833</td>
<td>610.497</td>
<td>3.634</td>
</tr>
</tbody>
</table>

In our model, we consider the (intra-plane) nearest neighbor exchange interaction $J_1$. This interaction originates due to the virtual hopping of electrons between the two NN Cr-ions via the Br ion. The super-exchange interaction, due to the presence of the non-magnetic Br atom in between the Cr ions, increases with applied pressure and subsequently, $J_1$ increases with isothermal compression, see Figure 4.3(a). A small but noticeable change due to the applied pressure is seen where $J_1$ increases almost linearly up to 1 GPa of pressure.
Figure 4.3 (a) Calculated first nearest neighbor exchange coupling parameter $J_1$ up to 1 GPa. (b) Second nearest neighbor, $J_2$, and $J_{\text{out}}$ as a function of increasing pressure. (c) Calculated magnetocrystalline anisotropy energy as a function of hydrostatic pressure. (d) Reduction of the Cr-Br-Cr bond angle as pressure is increasing.

Experimentally [77], a previous report on CrBr$_3$ showed that the $T_c$ decreases from 35.2 K (0 GPa) to approximately 33 K (~1.1 GPa). Such is represented in its negative pressure coefficient ($dT_c/dP$) = -0.2 K/kbar, implying a negative dependence of $J_1$ with pressure. From the theoretical perspective, the FM in-plane super-exchange interaction between the Cr$_{3+}$ in bulk CrBr$_3$ appears to be more dominant than the direct exchange (AFM) interaction, which leads to the increase of $J_1$.  

with pressure in our calculation. In the experiment in Ref. [77], H. Yoshida claims that the exchange interaction becomes stronger with decreasing atomic distance as there are stronger orbital overlaps. For example, Br has a smaller atomic radius (114 pm) than that of its neighbor I (133 pm), which can contribute to the dominant Cr-Cr direct exchange interaction. Combining all these effects, the competition between the direct exchange and the indirect super-exchange interaction determines the nature of the $J_1$ dependence with pressure for CrBr$_3$. The competition between AFM direct exchange through Cr–Cr bonding, and FM super-exchange through Cr–Br–Cr bonding, are what determine the nature of the $J_1$ dependence with pressure for CrBr$_3$.

The pressure dependence of MAE is shown in Figure 4.3(c). At $P = 0$, MAE is about 200 μeV/Cr, similar to that of single layer CrBr$_3$ from a previous theoretical study [78,79]. The overall result also shows a similar pressure dependent trend to monolayer CrBr$_3$ under strain in terms of in-plane distance where the MAE decreases as bond length reduces due to increasing pressure. When comparing CrBr$_3$ to CrI$_3$, for example, the Cr-Cr separation increases with expanding halogen size from Br to I, as a result direct exchange (overlap between neighboring Cr orbitals) weakens successively enhancing the covalent nature of the Cr-X bond [80]. It is important to note that the change in bond angle, Figure 4.3(d), and the increase in interlayer coupling, Figure 4.3(a), could give rise to larger $T_C$ if the system goes to higher pressures. An interesting case has recently been seen for CrGeTe$_3$ where $T_C$ initially decreases with increasing pressure, then significantly increases above 250 K at pressures above 9.1 GPa [81]. Therefore, the relationship of MAE and $T_C$ might not be consistent with the general trend observed in CrBr$_3$ warranting further investigations into the magnetic behavior at pressures greater than 1 GPa.

It is important to point out that the theoretical explanation of pressure dependence of exchange coupling on chromium halides is still controversial and debatable [80]. It is known that
such type of systems possesses localized $d$-electrons, which are strongly correlated, and pure DFT is inadequate. As a result, an additional correction $U$ to onsite Coulomb interaction is necessary [82,83]. However, the popular LDA+U method, which has been widely adopted in many previous studies, is only able to produce correct pressure dependent trend for exchange coupling of certain systems in the chromium (i.e. CrI$_3$) halide family and fail at the others. For example, $T_C$ for CrI$_3$ and CrBr$_3$ are experimentally observed to have the opposite pressure dependency. However, theoretically, DFT+U approach predicts both to have similar trend as $T_C$ increases with pressure in both cases. This is possibly due to the limit of the empirical nature of the method.
PART I CONCLUSIONS AND FUTURE WORK

In Part I of this work, we used pressure as the tuning parameter to explore the magnetic characteristics of ternary transition chalcogenides and the less studied chromium trihalide, CrBr$_3$. We reveal the tunability of the magnetization and $T_C$ through experiment with the application of pressures below 1.3 GPa, particularly seeing an enhancement in ferromagnetism in the ferrimagnet MST. We confirm the decrease in $T_C$ with literature for FGT, explore the tunability of pressure in the low-pressure regime in CST, and reveal a 14 K jump in $T_C$ for MST. Moreover, computations on CrBr$_3$ realize that the role of pressure on J values is very complicated and gives rise to further questioning, especially considering that there are a very few pressure-induced calculations and experiments performed on the bulk CrBr$_3$ system. Many works on pressure that were discussed in this work show the importance of carrying out pressure dependent studies at significantly higher pressures. Thus, it is important to fully characterize the pressure dependent magnetic properties of FGT, CST, MST, and CrBr$_3$ at pressures well above 1 GPa in the future — as well as performing calculations to support the findings of FGT and CST and to reveal the complex relationship between moment and $T_C$ in MST. DFT calculations are underway for these compounds and additional experiments at ANL and the AFRL are in the works to further gauge the structural and magnetic characteristics of ternary chalcogenides as a function of pressure.
PART II: AN ANALYSIS OF THE CRITICAL BEHAVIOR ON MST
UPON PROTON IRRADIATION AS A FUNCTION OF FLUENCE

CHAPTER 5: CRITICAL BEHAVIOR ON PROTON IRRADIATED MN3SI2TE6

5.1 Motivation and Background

Proton irradiation has served as a means of inducing magnetism in non-magnetic layered materials [11-19] and has recently shown modification to the magnetic properties in MST [69-71]. In our previous work [71], we reported that the magnetization was significantly enhanced by 53% and 37% in the ferrimagnetic phase (at 50 K) when MST was irradiated with protons at the fluence of $5 \times 10^{15} \text{H}^+ / \text{cm}^2$ along $ab$ and $c$ planes, respectively. Essentially proton irradiation serves as a mode to creating vacancies in crystals structures, an effect expected from radiation damage. However, inducing vacancies can cause the overall entropy of a material to increase, therefore increasing the thermodynamical stability in the crystalline material. In the case of MST enhanced magnetization coincides with the maximum entropy for a particular fluence of protons at $5 \times 10^{15} \text{H}^+ / \text{cm}^2$ in Ref. [71].

Analytically studying the critical phenomena can be used to discern the behavior of a materials physical system at its critical point. The importance of critical behavior analysis has recently been demonstrated on the vDW material Cr$_2$X$_2$Te$_6$ (X = Si, Ge), where 2D-Ising systems were identified and coupled with long-range interactions [23,84]. Upon studying the anisotropic critical behavior of these materials, it was found that the potential proponent for sustaining long-range interactions was magnetocrystalline anisotropy [66]. Interestingly, it was recently revealed that colossal magnetoresistance occurs along the magnetic hard axis ($H \parallel c$) of MST by way of avoiding a fully a polarized magnetization [85]. This finding further proves MST to be a vDW
material of substantial interest whose anisotropic magnetism and electrical properties should be thoroughly explored.

In this study, the critical phenomena of proton irradiated MST are analyzed to investigate how the magnetic properties of MST evolve as a function of proton irradiance for measurements in the easy axis (H \parallel ab). Measurements were conducted on five samples: a non-irradiated pristine crystal and four crystals irradiated at the following proton fluence rates: \(1 \times 10^{15}, 5 \times 10^{15}, 1 \times 10^{16},\) and \(1 \times 10^{18}\) \(\text{H}^+/\text{cm}^2\). A modified asymptotic analysis method developed by S. N. Kaul [86] was employed to conduct the critical exponent analysis and is often used as a tool to characterize the magnetic properties of novel materials. Critical exponents for pristine and proton irradiated MST were found to exhibit an increasingly mean field-like behavior as a function of proton fluence. The reliability of these critical exponents is confirmed by performing a scaling analysis.

Analysis on the pair correlation function revealed a possible spin transition where spin dimensionality goes from \(n = 3, 2,\) and \(1\) for pristine, \(1 \times 10^{15},\) and \(5 \times 10^{15}\) \(\text{H}^+/\text{cm}^2\), respectively. The change in magnetic entropy revealed a maximum for the fluence of \(5 \times 10^{15}\) \(\text{H}^+/\text{cm}^2\), corresponding to the largest increase in magnetization as reported earlier [71].

5.2 Critical Exponent Analysis

To evaluate the critical parameters of MST as a function of proton fluence, a modified asymptotic analysis approach is employed. In a review by S. N. Kaul [86], the modified asymptotic analysis method employed in this work was developed with the goal of arriving at the most accurate critical parameters. In the modified asymptotic analysis method, an appropriate spin model is used to construct a modified Arrott plot (MAP) \((M^{1/\beta} \text{ vs. } (H/M)^{1/\gamma})\). From the MAP, spontaneous magnetization, \(M_S(T)\), and inverse initial susceptibility, \(\chi_0^{-1}(T)\), are obtained from the intercepts of the \(M^{1/\beta}\) and \((H/M)^{1/\gamma}\) axes, respectively. Fitting of equations (1) and (2) reveal
the $T_C$ associated with $\beta$ and $\gamma$. With the intercepts $(M_5(T), \chi_0^{-1}(T))$, the Kouvel-Fisher (KF) plot is generated and the critical exponents $\beta$ and $\gamma$ are extracted and used to construct a new MAP. This process is then repeated iteratively until the exponents converge or remain unchanged. An automated program described in Ref. [87] is used to perform self-consistent calculations as outlined above. Throughout the iterative process the MAP isotherms in the critical regime should become increasingly parallel and straight. Although there are inherent difficulties extrapolating the values of critical exponents and $T_C$, the values extracted using the modified asymptotic analysis are more reliable and converge more quickly compared to other asymptotic analysis methods [86].

A second order phase transition from a paramagnetic (PM) to ferromagnetic (FM) state can be characterized by the critical exponents $\beta$, $\gamma$, $\delta$, $\eta$, $\nu$. The exponents are determined in terms of the dimensionless variable, $\varepsilon = (T - T_C)/T_C$, known as the reduced temperature, and the critical amplitudes $M_0$ and $(h_0/m_0)$ [88]. The magnetization exponents $\beta$, $\gamma$, and $\delta$, are characterized by the scaling hypothesis and are obtained using the following power law equations:

$$M_5(T) = M_0(-\varepsilon)\beta, \quad \varepsilon < 0, T < T_C, \quad (1)$$

$$\chi_0^{-1}(T) = \left(\frac{h_0}{m_0}\right)\varepsilon\gamma, \quad \varepsilon > 0, T > T_C, \quad (2)$$

$$M = DH^{1/\delta}, \quad T = T_C, \quad (3)$$

To determine the critical exponents associated with the previous equations, the KF plot and Arrott plot techniques are employed to extract $\beta$ and $\gamma$ from $M_5(T)$ and $\chi_0^{-1}(T)$, respectively. The critical isotherm (Eq. (3)) can be fit to extract an effective value for $\delta$. The scaling hypothesis also gives the magnetic equation of state in the critical region, and can be expressed as:

$$M(H, \varepsilon) = \varepsilon\beta f_{\pm}\left(\frac{H}{\varepsilon\beta+\gamma}\right), \quad (4)$$
where the regular functions $f_+$ and $f_-$ correspond to $T > T_C$ and $T < T_C$, respectively. Defining renormalized magnetization, $m$, and field, $h$, as $m \equiv \epsilon^{-\beta} M(H, \epsilon)$ and $h \equiv \epsilon^{-(\beta+\gamma)} H$, the equation of state transforms to $m = f_\pm(h)$. This implies that for true scaling relations and proper selection of $\beta$, $\gamma$, and $\delta$, that scaled $m$ and $h$ will fall onto two universal curves, one below and one above $T_C$. This critical behavior analysis was carried out using a MATLAB program developed in our lab by Jose Delgado [87], enabling a faster and efficient means to analyzing the data collected for all five samples.

### 5.3 Critical behavior of proton irradiated Mn$_3$Si$_2$Te$_6$

In a previous work, the magnetization of MST decreased as a function of proton irradiation except at $5 \times 10^{15}$ H$^+/cm^2$ where the magnetization was significantly enhanced by 53% for the magnetic easy axis ($H \parallel ab$) [71]. Figure 5.1(a) shows isothermal magnetization for this fluence with temperature isotherms in the vicinity of the $T_C$ between 60 to 80 K. The easy axis is initially confirmed through isothermal magnetization for the control measurements carried out on the pristine MST sample [71].

An Arrott plot ($M^2$ vs. $H/M$) is constructed using mean field critical exponents ($\beta = 0.5$ and $\gamma = 1.0$) producing a set of straight parallel lines with the isotherm at $T_C$ passing through the origin [89]. Pristine isothermal curves in the Arrott plot exhibit a nonlinear behavior with downward curvature from low to high fields. Therefore, the mean field model does not entirely apply to MST for the pristine crystal where parallel lines were obtained for $\beta = 0.41$ and $\gamma = 1.21$, as implicated in Ref. [24]. Furthermore, the order of the magnetic transition can be estimated through the criterion established by Banerjee by examining the slope of the straight lines in the Arrott plot [90]. A negative slope corresponds to a first-order transition and a positive slope to a
second order transition, with the latter recently confirmed for pristine in Ref. [24] and in this work, similarly for the irradiated set MST samples.

To further characterize proton irradiated MST, we adopt the MAP technique which is constructed using the Arrott-Noakes equation of state:

\[
\left( \frac{H}{M} \right)^{1/\gamma} = a \varepsilon + b M^{1/\beta},
\]

where \(a\) and \(b\) are constants and \(\varepsilon\) is the reduced temperature, which has been previously defined in Ref. [91]. The MAP as seen in Figure 5.1(b) for \(5 \times 10^{15}\) H\(^+\)/cm\(^2\) MST shows a clear set of parallel isotherms in the high field region. Figure 5.1(c) shows the spontaneous magnetization and initial inverse susceptibility plots from Eq(s). (1) and (2) for the fluence \(5 \times 10^{15}\) H\(^+\)/cm\(^2\). From these final power law plots the \(T_C\) associated with the critical exponent \(\beta\) and \(\gamma\) are extracted and listed in Table 2 for all samples.

**Table 2** Critical exponents for pristine and proton irradiated \(\text{Mn}_3\text{Si}_2\text{Te}_6\) for different techniques such as Kouvel-Fisher (KF), neutron diffraction, and theory. \(T_C\) as seen in fourth column of this table is extracted from the power law dependence of \(M_S\) and \(\chi_0^{-1}\) exponents, relating to beta and gamma, respectively. This is following the asymptotic analysis method as spelled out in S. N. Kaul [86]. The experimental critical isotherm exponent delta is calculated through the Widom scaling law relation [40].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Reference</th>
<th>Technique</th>
<th>(T_C) (K)</th>
<th>(B)</th>
<th>(\gamma)</th>
<th>(\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine (\text{Mn}_3\text{Si}_2\text{Te}_6)</td>
<td>This work</td>
<td>KF</td>
<td>73.46, 73.36</td>
<td>0.41(9)</td>
<td>1.11(0)</td>
<td>3.65(2)</td>
</tr>
<tr>
<td>(1 \times 10^{15}) (H(^+)/cm(^2))</td>
<td>This work</td>
<td>KF</td>
<td>73.20, 73.22</td>
<td>0.45(2)</td>
<td>1.06(9)</td>
<td>3.36(3)</td>
</tr>
<tr>
<td>(\text{Mn}_3\text{Si}_2\text{Te}_6)</td>
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<td>KF</td>
<td>72.77, 72.75</td>
<td>0.42(9)</td>
<td>1.18(5)</td>
<td>3.75(9)</td>
</tr>
<tr>
<td>(5 \times 10^{15}) (H(^+)/cm(^2))</td>
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<td>KF</td>
<td>73.29, 73.24</td>
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<td>1.05(7)</td>
<td>3.41(1)</td>
</tr>
<tr>
<td>(\text{Mn}_3\text{Si}_2\text{Te}_6)</td>
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<td>KF</td>
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<td>3.38(9)</td>
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<tr>
<td>(1 \times 10^{16}) (H(^+)/cm(^2))</td>
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<td>KF</td>
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<td>0.41(1)</td>
<td>1.21(2)</td>
<td>3.75(3)</td>
</tr>
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<td>(\text{Mn}_3\text{Si}_2\text{Te}_6)</td>
<td>[24]</td>
<td>KF</td>
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</tr>
<tr>
<td>Mn₃Si₂Te₆</td>
<td>[66]</td>
<td>Neutron</td>
<td>78</td>
<td>0.25</td>
<td></td>
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</tr>
<tr>
<td>Mean Field Model</td>
<td>[86, 88]</td>
<td>Theory</td>
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<td>1.0</td>
<td>3.0</td>
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<tr>
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<td>3D XY Model</td>
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<td>0.345</td>
<td>1.316</td>
<td>4.81</td>
<td></td>
</tr>
</tbody>
</table>

Critical exponents can be determined by the KF method following [92],

\[
\frac{M_S(T)}{dM_S(T)/dT} = \frac{T - T_c}{\beta} \quad \text{(6)}
\]

\[
\frac{\chi^{-1}_0(T)}{d\chi^{-1}_0(T)/dT} = \frac{T - T_c}{\gamma} \quad \text{(7)}
\]

Figure 2(d) shows the KF plot represented with linear fits following Eq(s). (6) and (7). The Widom scaling law, \( \delta = 1 + \gamma / \beta \) [93], is used to calculate \( \delta \) with the critical exponents obtained from the KF method. Table 2 shows the values for the critical parameters for all fluences in this work with reference to other critical exponent analyses and theoretical quantities. MST roughly exhibits an increasingly mean field-like behavior as a function of proton irradiation where \( \beta \) increased and \( \gamma \) decreased from their pristine counterpart. However, an anomaly appears at \( 5 \times 10^{15} \text{ H}^+/\text{cm}^2 \) in which a sharp increase in \( \gamma \) and slight decrease in \( \beta \) was observed in comparison to pristine and other fluences, respectively. Moreover, long-range interactions are presumed to exist in each sample of MST as the critical exponents \( \beta \) and \( \gamma \) lay closer to mean field critical exponents relative to the other universality classes presented in Table 2.
Figure 5.1 (a) 1st quadrant isothermal magnetization curves from 60 to 80 K for $H \parallel ab$ $5 \times 10^{15}$ H$^+/\text{cm}^2$ MST. (b) MAP for $5 \times 10^{15}$ H$^+/\text{cm}^2$ MST with a linear fit on isotherms with KF critical exponents. (c) Spontaneous magnetization and initial inverse susceptibility analysis displaying corresponding $T_C$’s. (d) Kouvel-Fisher plot for $5 \times 10^{15}$ H$^+/\text{cm}^2$ with critical exponents beta, gamma, and delta using the Widom scaling relation.

The reliability of the critical exponents and $T_C$ obtained from KF and MAP methods are confirmed by following Eq. (4) plotted as scaled $m$ vs $h$. Figure 5.2(a) shows the data collapsing into two branches, one above and below $T_C$ for the sample irradiated at $5 \times 10^{15}$ H$^+/\text{cm}^2$. The two branched curves were present in all pristine and irradiated samples indicating that the correct critical regime was used for obtaining the critical exponents. The inset of Figure 5.2(a) shows the log-log scale of scaled $m$ and $h$ for $5 \times 10^{15}$ H$^+/\text{cm}^2$. A more rigorous confirmation of the critical exponents was done by plotting scaled $m^2$ vs $h/m$ where two independent branches of data further
confirm the reliability of the obtained exponents. This is shown in Figure 5.2(b) for $5 \times 10^{15}$ H$^+/\text{cm}^2$. The scaling equation of state can take on another form where all the curves should collapse into a single curve:

$$\frac{H}{M^\delta} = k \left( \frac{\varepsilon}{H^{1/\beta}} \right), \quad (8)$$

where $k(\varepsilon, H)$ is the scaling function. The inset of Figure 5.2(b) shows $MH^{-1/\delta}$ vs $H^{-(\delta \beta)}$ with a single curve and the zero point of the horizontal axis locates the $T_C$, confirming the $T_C$ and critical exponents found for all proton irradiated samples of MST. The scaling equation of state is clearly satisfied in the critical regime indicating that the interactions have been properly renormalized.

**Figure 5.2** (a) Scaling of renormalized magnetization, $m$, and renormalized field, $h$, with isotherms falling into two branches, below and above $T_C$ for $5 \times 10^{15}$ H$^+/\text{cm}^2$ MST. Inset: The log-log scale of the renormalized $m$ and $h$ for the pristine case. (b) Data from $5 \times 10^{15}$ H$^+/\text{cm}^2$ MST where isotherms collapse into two separate branches, one below and one above $T_C$, further confirming the reliability of the exponents in the critical regime. Inset: Experimental data for $5 \times 10^{15}$ H$^+/\text{cm}^2$ MST collapsing into one single curve where $T_C$ is located at the zero point of the horizontal axis.

It is important to determine the range of interaction in proton irradiated MST to understand how it is affected by proton bombardment. The universality class of the magnetic phase transition
for a homogeneous magnet with isotropic long-range interactions depends on the exchange distance \( J(r) = r^{-(d+\sigma)} \), where \( r \) is the distance and \( \sigma \) is the range of interaction [94]. It is worth noting that competing exchange and superexchange interactions disqualify MST from being categorized as an “isotropic magnet”. However, as will be shown in the results, the long-range nature of the magnetic interactions makes this model a fair approximation to suitably study trends in the spin correlations. From this model, the spin interaction can either be long or short depending on whether \( \sigma < 2 \) or \( \sigma > 2 \), respectively. According to renormalization group theory, the susceptibility exponent \( \gamma \) can be calculated as,

\[
\gamma = 1 + \frac{4}{d} \left( \frac{n + 2}{n + 8} \right) \Delta \sigma + \frac{8(n + 2)(n - 4)}{d^2(n + 8)^2} \times \left[ 1 + \frac{2G \left( \frac{d}{2} \right)}{(n - 4)(n + 8)} \right] \Delta \sigma^2,
\]

where \( \Delta \sigma = \sigma - \frac{d}{2} \) and \( G \left( \frac{d}{2} \right) = 3 - \frac{1}{4} \left( \frac{d}{2} \right)^2 \), \( d \) is the effective spatial dimensionality and \( n \) is the spin dimensionality [95]. This method is carried out by inserting experimentally gained \( \gamma \) into Eq. (9) for different values of \( d \) and \( n \). Values of \( d \) and \( n \) are confirmed by using additional critical exponent expressions that should match well with experimentally found exponents. These remaining exponents are obtained from the following expressions: \( \eta = 2 - \sigma \), \( \nu = \gamma / \sigma \), and the following scaling relations: \( \alpha = 2 - \nu d \), \( \beta = (2 - \alpha - \gamma) / 2 \).

For pristine MST, we find that the \( J(r) \) decreases as \( r^{-4.71} \). This result is close to the previously reported exchange distance for pristine MST, as seen in Table 3 [24]. For pristine MST, we obtain \( d = 3 \) and \( n = 1 \) with a \( \sigma = 1.71 \). Moreover, the effective spatial dimensionality remains
as \( d = 3 \) for all samples (see Table 2). The Ising spin dimensionality \((n = 1)\) indicates anisotropic magnetic interactions and is present for the pristine case, along with the samples irradiated with \(1 \times 10^{16}\) and \(1 \times 10^{18}\) H\(^+\)/cm\(^2\) [96]. Interestingly, the spin dimensionality increases to \(n = 2\) and \(n = 3\) for \(1 \times 10^{15}\) and \(5 \times 10^{15}\) H\(^+\)/cm\(^2\), indicating an \(XY\) and a Heisenberg interaction, respectively. This observation of the change in spin dimensionality at \(1 \times 10^{15}\) and \(5 \times 10^{15}\) H\(^+\)/cm\(^2\) is intriguing as a change of this type would indicate a crossover in the spin model and a change in the magnetic exchange interaction strength. As suggested by Fisher in Ref. [96], frustration or spatial anisotropy in Heisenberg spins can induce a crossover to \(XY\) or Ising spins. It is known that MST exhibits magnetic frustrations which arise from competing ferromagnetic superexchange interactions between Mn-Te-Mn bonds and the anisotropic direct exchange interactions between Mn sites [66]. Therefore, one may safely assume that the origin of this crossover behavior is due to magnetic frustrations present in the MST compound. The root of this variation should be investigated further to quantitatively understand the effects proton irradiation has on the spin dimensionality and the magnetic state of MST. Employing an anisotropic critical behavior study should also reveal significant changes in the magnetic anisotropy for magnetization measurements performed for in plane and out of plane magnetic fields. In addition, spin-polarized density functional theory calculations can reveal the mechanism in which proton irradiation is influencing the magnetic interactions [97].

**Table 3** Exchange distance decay function \(J(r)\) and critical exponents for each MST fluence. Here, \(\sigma\) is the range of interaction and the spatial dimensionality is expressed as \(d\). Additionally, spin dimensionality is expressed as \(n\), and \(\nu\) as the correlation length. \(\eta\) describes the variation of the spin-spin correlation function with distance at \(T_C\). These critical exponents are calculated using our experimentally found \(\gamma\) from our KF method analysis.

<table>
<thead>
<tr>
<th>Fluence (H(^+)/cm(^2))</th>
<th>(J(r))</th>
<th>(\sigma)</th>
<th>(d)</th>
<th>(n)</th>
<th>(\nu)</th>
<th>(\eta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>(r^{-4.71})</td>
<td>1.71</td>
<td>3</td>
<td>1</td>
<td>0.649</td>
<td>0.29</td>
</tr>
<tr>
<td>Fluence (H(^+)/cm(^2))</td>
<td>r(^d) Exponent</td>
<td>G(r)</td>
<td>k</td>
<td>(\eta)</td>
<td>M(_{\text{sat}})</td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
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<td></td>
</tr>
<tr>
<td>1 \times 10^{15}</td>
<td>r(^{-4.62})</td>
<td>1.616</td>
<td>3</td>
<td>2</td>
<td>0.661</td>
<td></td>
</tr>
<tr>
<td>5 \times 10^{15}</td>
<td>r(^{-4.74})</td>
<td>1.743</td>
<td>3</td>
<td>3</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>1 \times 10^{16}</td>
<td>r(^{-4.62})</td>
<td>1.617</td>
<td>3</td>
<td>1</td>
<td>0.654</td>
<td></td>
</tr>
<tr>
<td>1 \times 10^{18}</td>
<td>r(^{-4.63})</td>
<td>1.632</td>
<td>3</td>
<td>1</td>
<td>0.653</td>
<td></td>
</tr>
<tr>
<td>Pristine [24]</td>
<td>r(^{-4.79})</td>
<td>1.79</td>
<td></td>
<td></td>
<td>0.676</td>
<td></td>
</tr>
</tbody>
</table>

To gain a better understanding of the spin correlations and the critical phenomena, the critical exponent \(\eta\) is calculated using \(\eta = 2 - \frac{\gamma d}{2\beta + \gamma}\). The critical exponent is used to calculate the two-point correlation function \(G(r) = 1/r^{-d+2-\eta}\), which describes how spins are related in a system. A decrease in the spin correlation decay as the proton irradiance is increased is observed. This indicates a decrease in magnetic ordering, except at the fluence of 5 \times 10^{15} H\(^+\)/cm\(^2\). The sample irradiated with 5 \times 10^{15} H\(^+\)/cm\(^2\) displayed the smallest correlation function decay rate, overall indicating a larger correlation of the spins. Interestingly, this trend observed for the correlation function decay rate (Figure 5.3) was found to match our previous magnetic characterization study of proton irradiated Mn\(_3\)Si\(_2\)Te\(_6\), where the sample irradiated with 5 \times 10^{15} H\(^+\)/cm\(^2\) possesses the largest magnetization [71]. Additionally, Ref. [71] also shows magnetization decreasing for the samples at 1 \times 10^{15}, 1 \times 10^{16}, and 1 \times 10^{18} H\(^+\)/cm\(^2\) relative to the pristine sample, in perfect agreement with the trends observed in the spin correlation decay rate in the present study (see Fig. 4). Therefore, the two-point correlation function, combined with our analysis of critical behavior, was found to be a valuable tool for characterizing the magnetic properties of MST following proton irradiation.
Figure 5.3 Correlation function (left, blue) and 50 K magnetization taken at 3 T (right, orange) plotted as a function of proton irradiation. A maximum peak at $5 \times 10^{15}$ H$^+$/cm$^2$ is observed for both plots. Magnetization data is taken from our previously published work as seen in reference 14.
We have identified the critical exponents for proton irradiated Mn$_3$Si$_2$Te$_6$ while examining the spin and spatial dimensionality, spin correlations, and magnetic entropy. We found that increasing the proton fluence leads to an increasingly mean field-like behavior, however the samples ultimately did not fall into one specific universality class. Exchange distance analysis showed that the decay rate of magnetic interaction is the smallest for $5 \times 10^{15}$ H$^+$/cm$^2$ compared to pristine and other irradiated samples. The spin correlations indicate an increase in magnetic interactions for $5 \times 10^{15}$ H$^+$/cm$^2$, in line with the increase in magnetization as seen in Martinez et al. [71]. It has been previously established that frustration in MST is caused by the short-range interactions of the AFM coupled Mn atoms [66]. Therefore, the in-plane frustration in MST is thought to be the cause of the crossover in critical phenomena. This crossover behavior is manifested differently for each sample, as observed in this study where $n = 1$ for pristine MST transitioning to $n = 2$ and $n = 3$ for $1 \times 10^{15}$ and $5 \times 10^{15}$ H$^+$/cm$^2$, respectively. Additionally, the fact that AFM coupling is not suppressed even above $T_c$ is worth investigating further to explore the possibility of an AFM transition at higher temperatures where spin fluctuations could be expected to diminish. In short, examination of the critical phenomena can be extended to other systems that involve external perturbations of vdW materials and/or their few to mono-layer counterparts. In regard to MST, critical phenomena studies in the fluence range spanning $10^{15}$ H$^+$/cm$^2$ can further illuminate the magnetic behavior in this region as well as the overall anisotropic properties and spin fluctuations present in MST.
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Rubyann Olmos was born in September 1997 in El Paso, Texas to parents Ruben and Norma Olmos. Rubyann attended Horizon High School graduating in 2016 where she soon began her undergraduate studies at The University of Texas at El Paso. Following her Bachelor of Science in Physics in 2020 she was admitted to the master’s program in physics at UTEP.

In 2018, Rubyann began working in the Nanomagnetic Materials Laboratory of Dr. Srinivasa Rao Singamaneni, supported by the Nuclear Regulatory Commission Scholarship. Her main project was to study the effect of proton irradiation on the van der Waals class of materials. As an undergraduate she contributed to five publications, first author on two, and presented her work(s) at the Materials Research Society (MRS) conference(s). She participated in two research internships at Ames Laboratory in 2019 and 2020.

In 2020, she continued her masters research in the lab of Dr. Singamaneni taking up a leadership role managing the laboratory and becoming president of the UTEP Materials Research Society Chapter. In these positions she facilitated important purchases and maintenance, trained users and students on instrumentation, and organized community outreach events. Rubyann published two more works during the course of her master’s and continued to present her work at MRS Meetings. She also participated in a remote internship with Ames Laboratory and will be participating in the U.S. Air Force Research Lab Summer Faculty Fellowship Program alongside Dr. Singamaneni in Dayton, Ohio, summer 2022.

In 2021, Rubyann was awarded the prestigious National Science Foundation Graduate Research Fellowship which will enable to her to pursue her doctoral physics studies at William Marsh Rice University, beginning fall 2022.

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