Development of Software Tools and Experimental In Situ Electron Spin Resonance for Characterizing the Magnetic and Electrocatalytic Properties of Transition Metal Chalcogenide Crystals

Jose Armando Delgado
University of Texas at El Paso

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DEVELOPMENT OF SOFTWARE TOOLS AND EXPERIMENTAL IN SITU ELECTRON SPIN RESONANCE FOR CHARACTERIZING THE MAGNETIC AND ELECTROCATALYTIC PROPERTIES OF TRANSITION METAL CHALCOGENIDE CRYSTALS

JOSE ARMANDO DELGADO

Master’s Program in Physics

APPROVED:

______________________________
Srinivasa Rao Singamaneni, Ph.D., Chair

______________________________
Dino Villagrán, Ph.D.

______________________________
Jose L. Bañuelos, Ph.D.

______________________________
Stephen L. Crites, Jr., Ph.D.
Dean of the Graduate School
Dedication

To my parents,

for inspiring me to pursue higher education

and providing their support, love, and guidance along the way.
DEVELOPMENT OF SOFTWARE TOOLS AND EXPERIMENTAL IN SITU ELECTRON SPIN RESONANCE FOR CHARACTERIZING THE MAGNETIC AND ELECTROCATALYTIC PROPERTIES OF TRANSITION METAL CHALCOGENIDE CRYSTALS

By

JOSE ARMANDO DELGADO, B.Sc.

THESIS

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ABSTRACT

Studying the magnetic properties and crystal defects of transition metal chalcogenide crystals is of paramount importance for utilizing them for next generation spintronics devices and hydrogen evolution reaction catalysts. Hydrothermally grown transition metal chalcogenide nanocrystals (MoS$_2$, Ru$_2$S$_3$, Rh$_2$S$_3$, Co$_2$S$_8$) were chosen as catalysts for the hydrogen evolution reaction due to their low dimensionality and previous utilization as catalysts for hydrodesulfurization. The relationship between crystal defect sites and catalytic activity must be discerned to maximize the efficiency of hydrogen production during the hydrogen evolution reaction. ESR spectroscopy was utilized as a spin sensitive technique to study the defects and local changes to the composition and electronic structure of the crystals \textit{ex situ}, before and after the reaction. Additionally, an \textit{in situ} ESR cell was created to monitor the ESR response during the hydrogen evolution reaction. This new \textit{in situ} experimental set up allowed us to sensitively track voltage-dependent changes to MoS$_2$.

To further probe the magnetic properties of transition metal chalcogenide crystals, computational tools were developed to study the universality classes, spin dimensionality, spin correlations, and effective spatial dimensionality of magnetic interactions. Continuous phase transitions may be described in terms of critical exponents, critical amplitudes, and the critical transition temperature, which can lead to the determination of the magnetic properties mentioned above. Despite the intrinsic value, experimentally extracting the critical exponents and critical amplitudes from isothermal magnetization measurements is a time-consuming, monotonous task that is prone to error. These errors often result in the incorrect assignment of critical exponents, and contradictions in published literature often exist for the same compound. To address these issues, a program has been developed to automate and simplify the task of calculating the critical
parameters. The program calculates the critical exponents using self-consistent methods, including the modified and traditional asymptotic analyses, based on the Kouvel Fisher method, Modified Arrott Plot method, and generalized magnetic equation of state (scaling analysis). For the first time, a computational routine has been integrated to calculate explicit numerical solutions for the critical exponents with isotropic, long-range interactions, resulting in excellent agreement between theoretical and experimental calculations of the spin correlations. These tools can be applied to a broad range of magnetic material systems. Using these computational tools, the critical parameters and spin dimensionalities have been calculated for Mn$_3$Si$_2$Te$_6$ and Fe$_{2.64}$GeTe$_2$; our calculations were found to agree with previously published results. To further demonstrate the program’s abilities, the critical parameters of proton irradiated Mn$_3$Si$_2$Te$_6$ were calculated. Trends in the spin correlations of the irradiated samples allowed us to gain incredible insight on the nature of spin interactions as a function of proton irradiation.
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PART I: DEVELOPMENT OF IN SITU ELECTRON SPIN RESONANCE FOR THE HYDROGEN EVOLUTION REACTION

CHAPTER 1: MOTIVATION AND BACKGROUND

Hydrogen has been suggested as an alternative energy source to replace gasoline[1]. This is partially due to the fact that hydrogen possesses roughly 3 times the energy density of gasoline[2]. Despite this advantage, mass production of hydrogen is expensive. Hydrogen is commonly produced by methane gas reforming – a process which relies on fossil fuels and requires a high amount of thermal energy and pressure (900-1200 K with applied pressure of 5-25 bar [3]). Alternatively, hydrogen can be obtained by decomposing water into hydrogen and oxygen through an electrocatalytic process known as the hydrogen evolution reaction (HER). The theoretical electric potential required for splitting water is 1.23 V, but in reality, the required potential is higher due to solution resistance and other factors [4]. This voltage can be reduced with the use of a catalyst. Currently, the best catalyst for HER is platinum due to its favorable Gibbs free energy of approximately 0 eV and high conductivity[5]; however, due to the rarity and expensive nature of platinum, it is of paramount importance to find low-cost, Earth-abundant catalysts to replace platinum for hydrogen production.

The catalysts in this study are commonly used for the hydrodesulfurization reaction. Studies have shown that hydrodesulfurization (HDS) catalysts perform well as catalyst substitutes for platinum in the HER [6–9]. Their exceptional performance has been attributed to similarities between the reaction mechanisms of HDS and HER, since both reactions involve hydrogenation of the active catalyst. To quantify the intrinsic activity of HER catalysts, the Gibbs free energy of hydrogen adsorption (ΔG_H) is often used as a baseline for comparison, and should ideally be as

1
close to zero as possible ($\Delta G_H \approx 0$ eV). The desired adsorption energy of catalysts for HDS is higher since the energy of sulfhydryl adsorption ($\Delta E_{SH} \approx 0.1$ eV) determines the intrinsic activity for HDS catalysts. Despite the small difference in target adsorption energies, many HDS catalysts perform well for HER due to their relative proximity to $\Delta G_H$ [10,11].

To improve the intrinsic activity of catalysts towards HER, the catalytically active sites, i.e. active participants in the reaction, must be well understood. As a canonical example, transition metal dichalcogenides (TMDs) have been the subject of many experimental and theoretical studies for understanding active sites. These studies have revealed that semiconducting TMDs most actively participate in the HER along the edges of the TMD crystals [11–14]. It has also been shown that sulfur vacancies and molybdenum antisites perform well as active sites [15]. Such studies have resulted in efforts to engineer TMDs with an increased number of active sites for maximum reaction participation e.g. by increasing the number of edge sites, sulfur vacancies, and molybdenum antisites. Investigations are therefore required for other catalysts to further engineer them for optimum reaction participation.

During the aforementioned reactions, hydrogen and other reaction intermediates are adsorbed onto the surface of the catalytically active sites. This hydrogen adsorption has been shown to modify the local electronic structure[16], conductivity[17], and magnetic moment [16,18,19] of the active sites. Probing changes in these properties can accordingly be used to identify, understand, and ultimately engineer the active sites. However, empirically tracking these changes in situ can be challenging since these modifications are dynamic and localized to the nanoscale active sites. To solve this problem, the catalysts will be studied using in situ and ex situ electron spin resonance (ESR). ESR is a powerful tool for active monitoring of catalytic reactions. These reactions often yield intermediate paramagnetic species associated with unpaired electron
spins such as dangling bonds[20], metal complexes, sulfur vacancies [21–23], antisites [24], and free radicals [25,26]. Thus, these local changes can be sensitively tracked using ESR. Electron transfers can be directly observed as long as paramagnetic species are involved. Atomic scale identification of such defects is possible by performing frequency and temperature dependent measurements. Despite advances in analytical techniques over the last several decades such as scanning electrical probe microscopy and other in situ techniques [14,27,28], in situ ESR spectroscopy remains as one of the most versatile techniques to precisely monitor chemical modifications in electrochemical processes such as HER.
CHAPTER 2: EXPERIMENTAL METHODS

2.1 Synthesis and Crystallographic Characterization

The nanocrystalline transition metal chalcogenides in the present study were synthesized using a bottom-up hydrothermal method. The details of the synthesis methods are described in our previously published work [24]. Bright-field, high resolution electron microscopy (HREM) and selected area electron diffraction (SAED) studies were carried out using a JEOL JEM 2100 HR transmission electron microscope (TEM) operated at 200 kV. Energy dispersive x-ray spectroscopy (EDS) studies on the TEM were carried out using an Oxford Instruments X-MAX 80 TLE spectrometer. TEM specimens were prepared by dispersing the powder samples in isopropyl alcohol and drop casting on to a carbon coated TEM grid. Powder X-Ray Diffraction (P-XRD) was conducted using a PANalytical Empyrean Series 2 using a Cu k-alpha radiation source.

2.2 Electrochemical Characterizations

Eight catalysts were studied for the HER, including MoS$_2$, CoMoS$_2$, NiMoS$_2$, MnMoS$_2$, FeMoS$_2$, Rh$_2$S$_3$, RuS$_2$, and Co$_9$S$_8$. To characterize the electrocatalytic properties of Rh$_2$S$_3$, RuS$_2$, and Co$_9$S$_8$, a three-electrode cell was used with carbon paper, a saturated calomel electrode, and 0.25 mm platinum wire for the working, reference and counter electrodes respectively. For the catalysts to be deposited on the working electrode, 5 mg of each catalyst were suspended separately in 1 mL of isopropyl alcohol. The solutions were then sonicated for 10 minutes to form homogeneous inks. The ink was then drop cast onto the carbon paper with a surface area of 0.25 cm$^2$. Electrochemical measurements were then conducted with a CHI760D potentiostat. 0.5 M sulfuric acid in water was used as the electrolyte for hydrogen evolution, and potassium hydroxide was used as the electrolyte for the oxygen evolution reaction.
The working electrodes for MoS$_2$, NiMoS$_2$, MnMoS$_2$, FeMoS$_2$, and CoMoS$_2$ were prepared on fluorinated tin oxide, with 0.25 cm$^2$ silver paste used as a conducting substrate. Homogeneous inks composed of 0.5 mg catalyst and 1 mL ethanol were deposited on the silver paste and allowed to dry. A saturated calomel electrode (Hg/Hg$_2$Cl$_2$/KCl (saturated in water)) [29] was used as the reference electrode, platinum wire was used as the counter electrode, and 0.5 M H$_2$SO$_4$ was used as the electrolyte. Linear sweep voltammetry (LSV) was then used to determine the effect of transition metal doping on the catalytic activity.

### 2.3 Electron Spin Resonance Spectroscopy

In this method, the sample under study is exposed to a magnetic field and microwave radiation (9-10 GHz for X-band ESR [30]). The atoms in the sample experience changes to their spin Hamiltonian in accordance with the Zeeman effect, and the degenerate energy levels split. When the energy of the microwaves matches the energy of the split degenerate energy levels, a photon is absorbed, and the derivative of photon absorption with respect to field ($dP/dH$) is recorded. As seen in Figure 2.1, the difference in the energy levels is given by $\Delta E = g\mu_B B_o = \hbar \nu$, where $g$ is the Landé g-factor, $\mu_B$ is the Bohr magneton, and $B_o$ is the magnetic flux density at which the electron transition occurred. The “$in situ$” prefix is added to denote that these catalysts will be studied under HER reaction conditions.

Electron spin resonance is especially suited for studying these highly dynamic and localized reactions. The key to using this method for $in situ$ characterization lies in the Landé g-
factor, which depends sensitively upon the sample’s total angular momentum \((J)\) and magnetic moment \((\mu)\) according to the equation \(\mu = g \frac{\mu_B}{h} J\). Since the magnetic moment for MoS\(_2\) has been theoretically predicted to change following hydrogen adsorption \([16,18,19]\), and hydrogen adsorption would alter the total angular momentum of localized active sites, then the catalyst’s active sites can be identified and/or studied. Therefore, in this work, \textit{in situ} and \textit{ex situ} ESR will be used to study the preferential hydrogen adsorption sites of catalysts under HER reaction conditions.

\subsection*{2.3.1 \textit{Ex Situ} ESR Measurements}

All \textit{ex situ} ESR measurements were measured on a Bruker EMX Plus X-band (\(\sim 9.40\) GHz) ESR Spectrometer. The nanocrystalline powdered catalysts were measured before catalysis at 77 K. To study the effects of hydrogen adsorption, ESR spectra were obtained on the catalysts before and after participating in the HER. Fluorinated Tin Oxide (FTO), rather than carbon paper, was used as a substrate so that the catalysts could be easily removed following the reaction. The conductivity of the sample was reduced by crushing it into a powder and suspending the powder in paraffin wax. This procedure was to improve the resonance condition of the spectrometer’s cavity by reducing the electric dipole interactions between the sample and the electric field of the resonator. The effect of HER on the catalysts was then measured via ESR at 77 K using a cold finger dewar. For “perfect” comparison of the ESR spectra before and after the reaction, all samples were prepared using this procedure.
2.3.2 In Situ ESR Measurements

For the ESR spectra to be obtained during the HER reaction, a new electrochemical cell was set up inside a 4 mm quartz ESR tube using the potentiostat described previously. In this three-electrode cell set-up, 0.25 mm gold wire, 0.1 mm silver wire, and 0.25 mm platinum wire were used as the working, reference and counter electrodes respectively. 0.1 M H₂SO₄ was used as an electrolyte for the HER. A catalyst ink, composed of 20 mg MoS₂, 10 μL nafion, and 1 mL isopropyl alcohol, was sonicated for 10 minutes to ensure ink homogeneity. The gold wire was then covered in a thin layer of silver paste, and the catalyst ink was deposited on the silver layer. To ensure that the catalyst would not fall off after immersion into the electrolyte, the working electrode was heated at 80°C for 30 minutes. A simple illustration of the cell design and EPR set up is displayed in Figure 2.2. The working electrode was insulated with electrical tape to prevent short-circuiting between the three electrodes. To ensure that HER could be performed within the 4mm quartz tube, cyclic voltammetry (CV) was performed inside the tube. The CV curve was then

![Figure 2.2: Schematic of the in situ ESR set up.](image-url)
compared to CV measurements performed in a larger beaker (100 mL) using an SCE reference electrode, platinum counter electrode, and 0.25 mm Au/Ag paste/MoS2 working electrode. For the in situ ESR measurements, the tube was flash-frozen in liquid nitrogen at incrementing electrode potentials, and low temperature ESR measurements were conducted. Freezing the cell ensured that the cavity could be tuned without the problems associated with measuring conducting samples [31]. *In situ* ESR measurements then had to be obtained quickly to prevent significant drift in the temperature and accumulation of moisture on the quartz tube. To obtain the measurements quickly, a narrow magnetic field sweep (1000 G) was performed in the region of interest.
CHAPTER 3: PREVIOUS STUDY ON TRANSITION METAL DICHALCOGENIDES FOR THE HYDROGEN EVOLUTION REACTION

3.1 Electrochemical Characterization

Our interest in tracking the nature of defect sites in catalysts using ESR and other magnetic characterizations was first realized in a project completed by our group on the magnetic and electrocatalytic properties of transition metal doped MoS$_2$ nanocrystals. The contents of this chapter were published in the Journal of Applied Physics [24]. MoS$_2$ nanocrystals were doped with Co, Ni, Fe, and Mn following a bottom-up hydrothermal synthesis. After vigorous crystallographic and chemical characterizations, we determined that 10% doping had been achieved. The crystals were utilized as catalysts for the HER, and the magnetic and electrocatalytic properties were characterized.

Figure 3.1: Electrochemical characterizations of transition metal doped MoS$_2$. (a) LSV curves; (b) $\frac{dJ}{dV}$ vs. $V$ (c) Tafel plot
To study the reaction kinetics of the catalysts for the HER, the current densities obtained from LSV were compared at a potential of -300 mV, as indicated by the vertical dotted line in Figure 3.1(a). This was done for comparison with a previous study in which MoS$_2$ was doped with Fe, Co, Ni, and Cu [32]. Listed from greatest to least for comparison, the reaction kinetics revealed the following trend: FeMoS$_2$ > CoMoS$_2$ > MoS$_2$ > NiMoS$_2$ > MnMoS$_2$. This was observed to be true for $372.8 \text{ mV} \leq V \leq 169.6 \text{ mV}$. This progression is the exact same order of activity that was previously found by theoretical calculations of the Gibbs free energy of hydrogen adsorption ($\Delta G_H$) for MoS$_2$, FeMoS$_2$, CoMoS$_2$, and NiMoS$_2$, where the compounds with $\Delta G_H$ closest to 0 eV were theoretically predicted to possess the highest electrocatalytic activity towards the HER [32]. Additionally, previous electrochemical characterizations on transition metal doped MoS$_2$ show comparable current densities with the data collected in our study [32,33]. As another benchmark for studying the catalytic activity, the onset overpotential was obtained. Lower onset overpotentials are associated with faster reaction kinetics [34,35]. A consistent benchmark for the onset overpotential is not well established in the literature [5], but for our study, this potential was studied by taking the derivative of the current density with respect to V (Figure 3.1(b)). The onset overpotential was then obtained by finding the potential at which the current density initially

![Figure 3.2](image_url)

Figure 3.2: (a) EIS plots for Co, Ni, Fe doped MoS$_2$, and pristine MoS$_2$; (b) EIS plot for Mn doped MoS$_2$; V vs. RHE = 0.5 V.
exhibits an exponential dependence on the potential. A zero-phase digital filter was used to smooth the data for easier comparison. The onset potential showed the following trend: FeMoS₂ > CoMoS₂ > NiMoS₂ > MoS₂ > MnMoS₂, which was the same trend observed for the reaction kinetics from the LSV curves. To study the reaction kinetics further from equilibrium, the logarithm of the current density was plotted versus potential, known as the Tafel plot. The data was then fitted using the Tafel equation $\eta = b \times \log(J) + a$, where $J$ is the current density and $b$ is the Tafel slope. The Tafel slopes obtained for each sample are plotted in Figure 3.1(c). Lower Tafel slopes are associated with higher reaction kinetics; thus, the following trend was observed in the reaction kinetics further from equilibrium: CoMoS₂ > MoS₂ > NiMoS₂ > FeMoS₂ > MnMoS₂. Doping with different transition metals showed a slight change in the Tafel slope, which is consistent with other literature reports [36,37].

Electrochemical Impedance Spectroscopy (EIS) was performed on the samples at overpotentials of 0.445, 0.5, 0.545, and 0.645 V. Figure 3.2 shows the EIS measurements taken at $\eta = 0.5$ V. Smaller semicircle diameters correspond to higher charge transfer, higher conductivity, and thus lower charge transfer resistance ($R_{ct}$) [38]. The samples can be ranked in the order from least to greatest $R_{ct}$ in the following order: FeMoS₂, CoMoS₂, pristine MoS₂, NiMoS₂, MnMoS₂. Fe doped MoS₂ had the greatest conductivity and charge transfer ability, while Mn doped MoS₂ possessed the least $R_{ct}$. Another literature report performed a similar electrocatalytic study of transition metal doped MoS₂ and found the exact same trend in $R_{ct}$ [32], with $R_{ct}$ increasing from Fe to Ni doping in the same order.

3.2 Characterization of Active Sites Using ESR and VSM

As discussed in Chapter 1, characterizing the defect sites of these crystals, including sulfur vacancies and transition metal antisites, are of special interest for studying the catalytic activity.
These catalytically active sites may be sensitively studied using ESR spectroscopy due to the presence of unpaired electrons at dangling bonds and uncoordinated transition metal sites. We utilized ESR and vibrating sample magnetometry (VSM) measurements to study the magnetic properties of the crystals in an attempt to correlate the magnetic properties to the number of catalytically active sites. Magnetization measurements on these samples were carried out using a Quantum Design Physical Property Measurement System (PPMS) (5–300 K, ±5 T). The VSM measurements revealed short-range room temperature ferromagnetism in CoMoS$_2$, FeMoS$_2$, NiMoS$_2$, and pristine MoS$_2$, while MnMoS$_2$ exhibited paramagnetism even at a temperature of 10 K. Anhysteretic behavior of the magnetization versus temperature was also observed for CoMoS$_2$, FeMoS$_2$, NiMoS$_2$, and pristine MoS$_2$ as the temperature was lowered to 10 K. Additional resistivity versus magnetic field measurements reveal a very small dependence of the resistivity on magnetic field. From this information, it was deduced that the samples also contain a canted antiferromagnetic ground state [24].

To further our understanding of the relationship between catalytically active sites and magnetic properties, ESR spectra for the nanocrystalline catalysts before HER was collected at room temperature (Figure 3.3). The ESR spectra for MnMoS$_2$ showed a single signal corresponding to Mn$^{2+}$. The absence of other signals from crystal defects such as sulfur vacancies indicated that MnMoS$_2$ would likely exhibit reduced catalytic activity. In contrast, the MoS$_2$ catalysts that were doped with Co, Fe, and Ni showed several sharp, narrow signals. The interaction between these spin centers is thought to be responsible for the room temperature ferromagnetism observed. The paramagnetic and ferromagnetic sites observed in FeMoS$_2$, CoMoS$_2$, and pristine MoS$_2$ corresponded to higher catalytic activity, likely indicating that the signals from ESR were from catalytically active crystal defects.
ESR and VSM measurements were thus used to study the catalytically active sites of transition metal doped MoS$_2$ nanocrystals. MnMoS$_2$ exhibited room temperature paramagnetism, and unpaired electrons from crystal defects were not detected by ESR. As a result, MnMoS$_2$ was estimated to contain few active sites. Fe, Co, and Ni doped MoS$_2$ showed room temperature ferromagnetism along with several narrow ESR signals from crystal defect sites, corresponding to increased catalytic activity. The relative catalytic activity of these materials could be estimated by correlating our VSM and ESR measurements with the electrocatalytic characterizations. These methods proved to be useful for gaining a relative understanding of the catalytic activity. Following our study of transition metal doped MoS$_2$, we decided to shift our attention to the development of methods for tracking local changes to the catalysts following hydrogen adsorption.

![Room temperature ESR measurements](image)

**Figure 3.3:** Room temperature ESR measurements on MoS$_2$, NiMoS$_2$, MnMoS$_2$, FeMoS$_2$, and CoMoS$_2$
CHAPTER 4: PRELIMINARY CHARACTERIZATIONS OF
NANOCRYSTALLINE CATALYSTS

4.1 Crystallographic Characterization

Before performing ESR measurements and characterizing the electrochemical properties
of Co9S8, MoS2, Rh2S3 and RuS3, the crystallographic nature and morphologies were
characterized. X-ray Diffraction was performed on the RuS2 nanoparticles, and the Miller indices
were identified (Figure 4.1). The diffraction pattern agrees well with previous studies [39]. Figure
4.2 depicts the results of the TEM studies. Figures 4.2 (a-d) show the bright-field images and
Figures 4.2 (e-h) show the corresponding lattice images of Co9S8, MoS2, Rh2S3 and RuS3
respectively. Overall, the TEM studies revealed the different compositions to have distinctly
different microstructures. Co9S8 (Figure 4.2(a)) exhibited a flowery morphology with individual
flakes made up of a few atomic layers as seen in the lattice image (Figure 4.2(e)). Figure 4.2(b)
shows a bright-field image of MoS2 exhibiting a sheet-like microstructure containing large sheets
of MoS2 lying flat on the TEM grid as well as some rod-shaped grains. The image on the right
(Figure 4.2(f)) shows the lattice image recorded from one of these rod-shaped grains exhibiting
an interlayer spacing of 0.65 nm which corresponds to the (002) planes of MoS$_2$. Fig 4.2(c) & (g)

**Figure 4.2:** Transmission Electron Microscopy (TEM) bright field images of (a) Co$_9$S$_8$, (b) MoS$_2$, (c) Rh$_2$S$_3$, (d) RuS$_2$, and (e-h) shows the lattice images for samples following the same order. The inset graphs in figures (a-d) include the Selected Area Electron Diffraction (SAED) images for each crystal.
how respectively the bright field and lattice images recorded from Rh$_2$S$_3$. The bright field image shows that this sample is made of “donut” shaped grains. The lattice image on the right shows that each of these donuts contain numerous nanocrystals of varied sizes. The presence of Moire fringes further confirms the presence of either overlapping of multiple grains or misorientation between the layers of Rh$_2$S$_3$. Moire fringes also make it difficult to measure the size of the individual nanocrystals as well as the spacing between the fringes. **Fig 4.2(d)** shows the bright-field image of RuS$_2$ and the corresponding lattice image is shown in **Figure 4.2(h)**. This sample is made up of nearly monodispersed nanoparticles of about 5 nm in size. In addition to bright field and lattice images, Selected Area Electron Diffraction (SAED) studies were carried out on these samples and the diffraction patterns are shown as insets to the bright-field images. The SAED pattern for all the samples showed the presence of rings of uniform intensity indicating the polycrystalline nature of these samples.

### 4.2 Electrochemical Characterization

![Linear Sweep Voltammetry Curves for the Hydrogen Evolution Reaction.](image)

**Figure 4.3:** Linear Sweep Voltammetry Curves for the Hydrogen Evolution Reaction.

Electrochemical linear sweep voltammetry was conducted on Rh$_2$S$_3$, MoS$_2$, RuS$_2$, and Co$_9$S$_8$ using the methods described in §3.3.1. Higher current densities at lower overpotentials are
associated with faster reaction kinetics. Co$_9$S$_8$ possessed the anodic highest current density at a potential of 2 V, while, carbon paper (the substrate for the catalysts) had the lowest current density. Therefore, the relative reaction kinetics of each catalyst towards the Oxygen Evolution Reaction displayed the following order of performance for potentials greater than 1.8 V: carbon paper < MoS$_2$ < RuS$_2$ < Rh$_2$S$_3$ < Co$_9$S$_8$. Likewise, by comparing the potentials at which the highest current density was achieved, the reaction kinetics of the catalysts towards the hydrogen evolution reaction (Figure 4.3) were found to display the following trend in reaction performance: MoS$_2$ < RuS$_2$ < Rh$_2$S$_3$ < Co$_9$S$_8$ < Pt. In a separate experiment, platinum wire was used as a working electrode in the HER for comparison with the other catalysts. The onset overpotentials in Figure X(b) showed the following trend: Co$_9$S$_8$ < MoS$_2$ < RuS$_2$ < Rh$_2$S$_3$ < Pt.

The ability to perform HER within the EPR tube was demonstrated by performing cyclic voltammetry inside and outside the EPR tube, as seen in Figure 4.4. NiMoS$_2$ was used as the catalyst, with a saturated calomel electrode for the set up outside the EPR tube, and a silver reference electrode used inside the tube. The uniform increase in current density as a function of potential in Figure 4.4 indicates that the reaction was successful in both set ups.
4.3 *Ex Situ* ESR Measurements

*Ex situ* ESR measurements were performed to the catalysts before and after HER. In order to ensure that the ESR spectra before and after HER were comparable, the samples measured before and after HER were prepared and measured using identical methods. The ESR measurements performed at 77 K were obtained using a cold finger dewar. More experimental details are included in §3.3.1. Significant nitrogen boil-off within the cold finger dewar caused disruptions to the resonance condition of the cavity while recording the spectra; thus, many random

![Figure 4.5](image)

**Figure 4.5:** Low temperature *ex situ* ESR measurements on MoS$_2$. (a) and (b) show MoS$_2$ before and after HER respectively, with Lorentzian fits and spectral parameters. (c) shows several measurements obtained on MoS$_2$ after HER using a cold finger dewar.
jumps in the dispersion spectra were observed, as seen in Figure 4.5(c). To overcome this limitation, many measurements had to be obtained for each sample to distinguish the sample signal from nitrogen boil-off.

The low temperature ESR spectra for MoS$_2$ before HER is shown in Figure 4.5(a). The ESR signals were fitted with two asymmetric Lorentzian line-shapes. The $g$ factors and peak-to-peak linewidths are shown within Figure 4.5(a). The signals observed at $g \approx 1.97$ and $g \approx 1.93$ are attributed to Mo$^{5+}$ paramagnetic defects[20]. After HER (Figure 4.5(b)), the signal at $g \approx 1.97$ was preserved, and has been previously attributed to Mo$^{5+}$ defects that likely involve the adsorption of oxygen or OH moieties on the basal plane of MoS$_2$ [20,40]. Additionally, a new asymmetric signal with $g \approx 2.07$ appeared following HER. As will be shown in the in situ ESR measurements, this anisotropic signal will exhibit a voltage-dependent behavior. A previous in situ ESR study of MoS$_2$ transistors showed a signal centered at $g \approx 2.055$, which they attributed to the accumulation of electrons at sulfur vacancies [22]. The increased $g$ value observed in our signal is likely due to the adsorption of hydrogen, but computational studies are needed to support this hypothesis. By plotting the ESR spectra for MoS$_2$ before and after HER together in Figure 4.6, it seems clear that one of the signals are shared between the spectra collected before and after HER (at $g = 1.97$); however, a slight increase in the $g$-value following HER was observed. Further studies are needed to understand the $g$-value shift.

**Figure 4.6**: Low temperature ex situ ESR measurements on MoS$_2$ before and after HER.
CHAPTER 5: IN SITU ELECTRON SPIN RESONANCE

To prove that in situ ESR measurements would be possible without spectral components from the electrodes and electrolyte interfering with the sample signal, ESR measurements were performed on all the constituent parts of the in situ ESR cell using a low sensitivity cavity (Figure 5.1). The low sensitivity cavity was chosen because previous attempts to conduct in situ measurements resulted in a poor resonance condition due to the conductivity of the electrolyte. These measurements included individual measurements of the Au wire (Figure 5.1 (c)), Rh₂S₃ deposited on Au with silver paste (Figure 5.1 (b)), Rh₂S₃ deposited on Au with nafion (Figure 5.1 (d)), and the electrolyte by itself (Figure 5.1 (a)). The primary signal observed from all four graphs of Figure 5.1 comes from the cavity, without any signals originating from the components of in situ ESR measurements.

Figure 5.1: Room temperature background ESR measurements of different components of the in situ ESR cell: (a) The electrolyte versus empty cavity; (b) Rh₂S₃ deposited with silver paste on the Au working electrode; (c) The Au versus empty ESR tube; (d) Rh₂S₃ deposited on the Au wire only using a nafion binder.
To deposit the Rh$_2$S$_3$, a homogenous ink of 20 mg Rh$_2$S$_3$ and 1 mL isopropyl alcohol was created. Without the use of silver paste, an additional 20 μL was added to the catalyst solution. The ink was then dropcasted onto the wire.

In spite of the perceived success, in situ ESR measurements could not detect signals from the Rh$_2$S$_3$ nanocrystalline at room temperature. In order to perform sensitive *in situ* measurements, ESR signals from the catalyst must also be visible. As seen in Figure 5.2, room temperature measurements of ~10 mg Rh$_2$S$_3$ powder alone yielded a visible signal; therefore, it is clear that our experimental set up needed to be altered in order to track *in situ* changes of the catalyst. Our previous attempts to use an ESR cavity with higher sensitivity resulted in a poor resonance condition due to the dipolar interactions between the electrolyte, conducting wires, and electrical component of the incident EM field within the cavity.

In response, we decided to try an *in situ* method discussed by Yury Kutin et al [31], in which the cell is flash frozen during the electrochemical reaction and ESR spectra are subsequently obtained. Using this method, the cavity could be properly tuned since the interaction between the electrolyte and electric field component of the microwaves was minimized. ESR measurements

**Figure 5.2:** Room temperature ESR spectra of the Rh$_2$S$_3$ nanocrystalline powder (~10 mg) versus ESR spectra of the empty ESR tube.
Figure 5.3: Low temperature ($T \approx 77 \, K$) in situ ESR spectra of MoS$_2$ taken at different potentials across the electrodes. The inset graph shows the normalized intensity (calculated by double integration) of the signals as a function potential.

were quickly made following exposure to the liquid nitrogen ($T \approx 77 \, K$). The magnetic field scans were made as quickly as possible to obtain the spectra before the cell temperature changed significantly. Performing these measurements quickly was challenging because the position of the working electrode was not perfectly fixed to the center of the tube. Care had to be taken to ensure that the tube was inserted consistently in the same orientation into the ESR cavity so that overloading of the diode current was minimized to secure a strong resonance condition.

The in situ ESR measurements were successfully carried out at incrementing applied potentials to determine the potential-dependent behavior of the paramagnetic centers. As evident from Figure 5.3, the signals collected at all three potentials appeared at approximately the same resonance field. These signals seem to match the ex situ signal obtained for MoS$_2$ after HER at $g \approx 2.07$. As the cathodic potential increased, it became clear that the line shape possessed axial asymmetry, rather than a simple Dysonian shape. To quantify the relative number of spins, the
intensity of the signals was obtained by double integration [41]. The intensities were normalized by the intensity of the ESR signal measured at 0 V ($I_o$). The spins were observed to increase nonlinearly as the potential was increased, as seen in the inset of Figure 5.3. Hyperfine splitting of the $g_z$ component of the $g$ tensor is apparent on the low-field portion of the yellow curve in Figure 5.3. The hyperfine splitting and rhombic asymmetry was more pronounced as the potential increased. More measurements at a wider field sweep are needed to determine the origin of this signal, along with the hyperfine splitting parameters. Further in situ measurements could not be made due to limitations related to the Covid-19 pandemic.

Despite all the challenges, in situ potential dependent ESR spectra was successfully obtained for MoS$_2$. Several characterizations of MoS$_2$ have been performed in an attempt to understand the defect-reactivity relationships between active sites and catalytic activity. To the best of our knowledge, this is the first time that MoS$_2$ is characterized under reaction conditions for the hydrogen evolution reaction using a spin-sensitive technique. Future work should be done to obtain wider field sweeps and the hyperfine splitting parameters.
PART II: DEVELOPMENT OF GRAPHICAL USER INTERFACE FOR ANALYSIS OF MAGNETIC CRITICAL PHENOMENA

CHAPTER 6: INTRODUCTION – EXPERIMENTAL CHARACTERIZATION OF CONTINUOUS MAGNETIC PHASE TRANSITIONS

6.1 Motivation and Background

The determination of an equation of state for continuous phase transitions around a critical point has been the subject of great interest in the scientific community for over a century. Despite the collective interest, an equation of state for magnetic phase transitions was not developed beyond classical considerations until half-way through the 20th century [42–45]. Physical variables changing near a continuous phase transition may be described by power-law distributions of the form \( f(x) = ax^k \), where \( k \) is a constant known as the critical exponent. A wide range of phase transitions in physics, chemistry and biology have been observed to obey these laws near a continuous transition point. Surprisingly, the critical exponents governing these interactions are often identical across vastly different systems. For example, the critical exponents governing the liquid-gas phase transition, and the exponents describing the ferromagnetic-paramagnetic phase transition in Ising ferromagnets have been observed to match perfectly [46]. The correlation in critical exponents across these systems has been attributed to similarities in the dimensionality of interactions, spatial dimensionality, and correlation length. As a result, systems undergoing a phase transition are placed into groups of identical behavior near the critical region, known as universality classes. Studying these universality classes and categorizing physical systems has been the subject of significant theoretical, computational, and experimental interest.

Proper characterization of the critical exponents for magnetic phase transitions can lead to the determination of several important physical quantities, including the effective spatial
dimensionality, spin degrees of freedom, and the magnetic exchange distance. Therefore, the reliable determination of critical exponents is a necessary process for the proper characterization of novel magnetic materials. However, as many practitioners of these methods have pointed out, the methods employed in studying the critical phenomena of magnetic materials is time-consuming and tedious [47–50]. These methods involve iterative self-consistent calculations between the modified Arrott plot method and Kouvel Fisher method, which involve many fits for each iteration. Several iterations are often needed to obtain the correct critical parameters; as a result, these approaches are often very time consuming. To add to these difficulties, it is easy to mischaracterize or incorrectly assign the critical exponents, even while using well-established procedures such as scaling analyses and self-consistent asymptotic analyses [51]. Contradictory critical exponents are often obtained for the same compound by different researchers (See CrI₃ for example [52,53]). As with any iterative method, small successive deviations in the user’s method from one iteration to the next can have drastic consequences for the results. Errors are also propagated if analyses are performed outside the critical region – especially for the Kouvel Fisher analysis and scaling analysis [51].

Despite the difficulty and intrinsically repetitive nature of these procedures for experimentally determining the critical behavior for these systems, to the best of our knowledge, computational tools have not been created to simplify or automate these methods. Completing these tasks “by hand” using software such as Microsoft Excel, OriginLab, or the Curve-fitting toolbox in MATLAB is extremely tedious and time consuming, due to the sheer number of fits that need to be performed for each iteration. For reasons that will be outlined in the Methodology, if 10 isotherms were measured in the critical region, and 3-15 iterations were performed to deduce the correct exponents, then these methods may require anywhere from 33-165 fits. With the help
of our program, these tasks have been reduced to a few clicks in the graphical user interface (GUI). The use of this program ensures that every fit is performed with the same domain and fit parameters across every iteration of the asymptotic analyses. Thus, systematic error due to inconsistent treatment of the isotherms is eliminated. The temperature range of the analyses can also be easily tuned in the GUI to ensure that isotherms measured outside the critical region are excluded. To demonstrate the program’s capabilities, the critical exponents, critical amplitudes, and magnetic correlation decay rates were calculated for Mn$_3$Si$_2$Te$_6$, Fe$_{2.64}$GeTe$_2$, and CrI$_3$. These calculations will then be compared to the findings obtained in previous studies [47,52–54].

6.2 Methodology

Continuous phase transitions that exist around a critical transition point can be mathematically described by the critical point, critical exponents, and the corresponding critical amplitudes. In particular, for a ferromagnetic – paramagnetic phase transition, these parameters are related by the following equations [46]:

\[ M_{sp}(T) = M_0(-\epsilon)^\beta, \quad T < T_C, \quad \epsilon < 0 \]  
\[ \chi_0^{-1}(T) = (h_0/m_0)^\gamma, \quad T > T_C, \quad \epsilon > 0 \]  
\[ M = D H^{1/\delta}, \quad T = T_C, \quad \epsilon = 0 \]

where \( \beta, \gamma, \delta \) are the critical exponents, \( M_0, h_0/m_0, D \) are the critical amplitudes, \( T_C \) is the critical temperature, and \( \epsilon = (T - T_C)/T_C \) is the reduced temperature. To study the critical behavior using experimental means, isothermal magnetization measurements in the critical region are conducted on the material of interest using a magnetometer such as a superconducting quantum interference device (SQUID), vibrating sample magnetometer, or optical magnetometer.

The modified Arrott plot method is a common tool for studying critical behavior, and is based on the Arrott Noakes equation of state,
\[(H/M)^{1/\gamma} = a\epsilon + bM^{1/\beta}\]  \hspace{1cm} (4)

in which \(a\) and \(b\) are constants [43]. From this relationship, the magnetization versus field is plotted as \(M^{1/\beta}\) versus \((H/M)^{1/\gamma}\) to create what is known as the modified Arrott plot, where \(\beta\) and \(\gamma\) are initially chosen from standard universality classes such as the Heisenberg, Ising, Landau mean-field, XY, or tricritical mean-field model. A sufficiently correct choice of \(\beta\) and \(\gamma\) will produce a series of straight isotherms that are parallel, especially near the critical temperature. The intercepts of the isotherms at high field can be linearly extrapolated along the \(M^{1/\beta}\) and \((H/M)^{1/\gamma}\) axis to obtain the \(M_{sp}(T)\) and \(\chi_0^{-1}(T)\) respectively. The correct critical parameters are then obtained using a method known as Asymptotic Analysis, in which the \(M_{sp}(T)\) and \(\chi_0^{-1}(T)\) are fitted using Equations (1) and (2) to produce a new pair of critical exponents \(\beta'\) and \(\gamma'\). These new exponents are then used to construct a new modified Arrott plot with \(M^{1/\beta'}\) versus \((H/M)^{1/\gamma'}\). For self-consistency, this process is repeated until \(\beta', \gamma',\) and \(T_C\) become relatively stable. Once the critical parameters are stable, the \(M_{sp}(T)\) and \(\chi_0^{-1}(T)\) from the final modified Arrott plot are used as independent variables in the Kouvel-Fisher equations:

\[M_s \left(\frac{dM_s}{dT}\right)^{-1} = \frac{T-T_C}{\beta}\]  \hspace{1cm} (4)

\[\chi_0^{-1} \left(\frac{d\chi_0^{-1}}{dT}\right)^{-1} = \frac{T-T_C}{\gamma}\]  \hspace{1cm} (5)

Plotting \(M_s(dM_s/dT)^{-1}\) vs. \(T\), and \(\chi_0^{-1}(d\chi_0^{-1}/dT)^{-1}\) vs. \(T\) near the critical region results in a set of linear functions with intercepts at \(T_C\) and slopes of \(1/\beta\) and \(1/\gamma\) [55]. Therefore, as a final check for self-consistency, the final \(\beta\) and \(\gamma\) obtained from this plot, known as the Kouvel-Fisher plot, should be very close to the final exponents obtained from the modified Arrott plot.

A similar iterative method for calculating the critical exponents and critical temperature, known as the modified asymptotic analysis [56], has also been employed in this work. This method
was developed with the aim of obtaining the most accurate critical exponents [50]. As before, a modified Arrott plot is first constructed by choosing the beta and gamma from a standard universality class. The $M_s$ and $\chi_o^{-1}$ obtained from this plot are then treated using the Kouvel-Fisher method from equations 4 and 5 to obtain a new set of $\beta'$ and $\gamma'$. These critical exponents obtained from the Kouvel Fisher method are then used to create a new modified Arrott plot. The method should be repeated in this order until the isotherms in the modified Arrott plot are straight and parallel.

As a final way of verifying the validity of the obtained critical exponents and $T_C$, the magnetization and field may be scaled using $m \equiv \epsilon^{-\beta} H$ and $h \equiv \epsilon^{\beta+\gamma} M(H, \epsilon)$ to satisfy the generalized magnetic or Scaling Equation of State (SES) [42,44,45]:

$$m = f_{\pm}(h)$$

If the critical exponents and critical temperature have been correctly chosen, this scaling relation dictates that the scaled $m$ and $h$ should fall on two curves: $f_{\pm}(h)$ for $T > T_C$, and $f_{\pm}(h)$ for $T < T_C$. This method is susceptible to error since the scaling functions may appear to fall on two individual curves for data collected outside the critical region. Such an occurrence would invalidate the results, since the SES should only apply for $T \sim T_c$. Consequently, care must be taken to limit the analysis to isotherms measured within the critical region. To avoid any ambiguity in the determined exponents, the critical exponents are verified with an alternate form of the SES [47],

$$\frac{H}{M^6} = k\left(\frac{\epsilon}{H^{1/\beta}}\right)$$

where $k(\epsilon, H)$ is the scaling function. Using this equation of state, the magnetization and field are renormalized and plotted such that $h = \epsilon H^{-1/(\beta \delta)}$, and $m = MH^{-1/\delta}$. The rescaled isotherms in this case should fall onto a single curve, where isotherms above and below $T_C$ fall on the positive and negative $h$ axis respectively:
\[ \begin{aligned}
\left\{ eH^{-1/(\beta \delta)} > 0, & \quad T > T_C \\
\left\{ eH^{-1/(\beta \delta)} < 0, & \quad T < T_C. \right. \end{aligned} \tag{8} \]

Once the correct critical exponents have been obtained, the exchange distance for isotropic long-range interactions can be deduced using the following procedure. First, the spatial dimensionality \( d \) and spin dimensionality \( n \) are assumed to take on integer values from 1 to 3. The assumed value for \( d, n, \) and experimentally obtained \( \gamma \) are then substituted in Equation (9) \[57\],

\[
\gamma = 1 + \frac{4}{d} \left( \frac{n+2}{n+8} \right) \Delta \sigma + \frac{8(n+2)(n-4)}{d^2(n+8)^2} \times \left[ 1 + \frac{2G \left( \frac{d}{2} \right)(7n+20)}{(n-4)(n+8)} \right] \Delta \sigma^2 \tag{9}
\]

where \( \Delta \sigma = \left( \sigma - \frac{d}{2} \right) \) and \( G \left( \frac{d}{2} \right) = 3 - \frac{1}{4} \left( \frac{d}{2} \right)^2 \). By convention, the parameter \( \sigma \) is adjusted until a solution for the equation has been reached \[57\]. This processing of “guessing” solutions to Eq. (9) has been common practice for the last 48 years. Consequently, this has led to disagreement in the literature between the experimentally determined \( \gamma \) and the theoretically obtained \( \gamma \) from Eq. (9). This discrepancy is understandable, due to the large number of variables involved in Eq. (9). To address this issue, we have integrated a simple program into our GUI to calculate explicit numerical solutions to Eq. (9). After \( \sigma \) has been obtained using all possible combinations of \( n \) and \( s \), the critical exponents \( \beta, \gamma, \alpha, \nu, \) and \( \delta \) are obtained again using common scaling relations (\( \nu = \gamma/\sigma, \alpha = 2 - \nu d, \beta = (2 - \alpha - \gamma)/2, \) and \( \delta = 1 + \gamma/\beta \)) \[58\]. A match is then sought between the theoretically and experimentally obtained exponents to determine the true value of \( n, d \) and \( \sigma \). Finally, the magnetic exchange distance may be estimated for isotropic long-range interactions \[59\] using

\[ J(r) \approx r^{-(3+\sigma)}. \tag{10} \]

The methods discussed herein for studying the ferromagnetic-paramagnetic phase transition, including the modified Arrott plot, the Kouvel-Fisher plot, traditional asymptotic analysis, modified asymptotic analysis, and the generalized magnetic equation of state (AKA
scaling analysis) will now be discussed in terms of the software, which is the main result of this work.
CHAPTER 7: SOFTWARE OVERVIEW

7.1 Design Principles

The GUI was designed in the MATLAB 2020a App Designer, and the code was generated in the App Designer’s integrated MATLAB editor. The program was then compiled using the MATLAB compiler on a Windows and Linux operating system; thus, the app is available for download for Windows and Linux-based operating systems. The flexibility of MATLAB’s App Designer ensures that changes and modifications to the GUI can easily be made whenever the need arises. The GUI is dependent on the MATLAB Curve Fitting Toolbox, which is used for systematically fitting the data with full control over the fit parameters and fitting methods. The Curve Fitting Toolbox functions are equipped with the ability to track statistics relating to the goodness of fit and the optimized fit coefficients. The program was designed so that these fit statistics are tracked for every iteration of the traditional and modified asymptotic analysis.

7.2 Program Features

In order to equip the user with multiple, independent ways of verifying the authenticity of obtained critical exponents and transition temperatures, the GUI can be toggled between multiple analysis methods. These methods include the traditional self-consistent asymptotic analysis (based on the Kouvel Fisher [55] and modified Arrott plot method [43]), the modified asymptotic analysis designed by S. N. Kaul (referred to by S. N. Kaul as Asymptotic Analysis-II [50]), and the generalized magnetic equation of state, also known as scaling analysis [42,44,45]. The program iterates through the asymptotic analyses while tracking all fit parameters and critical exponents for each iteration. The critical exponents, transition temperature, and critical amplitudes are simultaneously plotted as a function of the iteration number within the user-interface while the
program runs. In this way, the convergence/divergence of these self-consistent methods can be intuitively determined by the user.

![Program interface with graphs and data tables]

**Figure 7.1: Main window of the graphical user interface.**

The program is capable of automatically determining the convergence and optimal critical parameters of the asymptotic analyses by toggling the “Automatic Convergence Detection” in the method options. This automatic detection is performed by simply taking the absolute value of the difference between each successive critical exponent $\beta$ and $\gamma$. Given $n$ iterations of an asymptotic analysis, the program will continue iterating as long as $|\beta_n - \beta_{n-1}| > \tau$, and $|\gamma_n - \gamma_{n-1}| > \tau$, where $\tau$ is a user-defined tolerance. Usually $0.001 \leq \tau \leq 0.0001$ is acceptable. If the user decides not to use this feature, the number of iterations for the asymptotic analyses can be manually specified in the set-up panel. Once the user has obtained a set of critical exponents and the critical temperature, the critical exponents and $T_C$ can be entered in the scaling analysis tab. Here, the exponents can be used to construct the renormalized magnetization and field plots using the
generalized magnetic equations of state (Eqs. 6 and 7). Of course, the user may also use this feature to test the applicability of other universality classes.

The primary window of the GUI is pictured in Figure 7.1. The main window of the GUI is comprised of three panels. The first panel, located on the right side of the GUI in Figure 7.1, is the method set-up panel. On this panel, the user can upload raw data and specify fit parameters for the asymptotic analysis. These fit parameters include the critical exponents, critical amplitudes, and critical temperature. The user can also limit the number of isotherms for the modified Arrott plot and Kouvel Fisher methods on the set-up panel. The ability to easily tune the number of isotherms was added due to the inclusion of the modified asymptotic analysis, which relies heavily on the Kouvel-Fisher method. The Kouvel-Fisher plots are linear near the critical region, but tend to deviate non-linearly for T further away from $T_C$. Therefore, including too many isotherms away from the critical region may drastically alter the obtained critical exponents from the Kouvel-Fisher analysis. To circumvent this issue, the user can easily tune the temperature range of the isotherms included in this analysis by selecting the “Limit Isotherms” option in the set-up panel.

Another feature worth discussing is the ability to specify the fit domain used in the modified Arrott plot method. In order to obtain the spontaneous magnetization and inverse susceptibility, the isotherms in this plot are fitted in the linear region of the isotherms, and the intercepts of the linear fits are extrapolated to obtain $M_s$ and $\chi^{-1}$. The main issue with performing these fits by hand is that the “linear region” of the isotherms is left to the user to interpret. The user may unknowingly use different criteria for finding this linear region between each iteration. As with any iterative method, small successive deviations in the user’s method from one iteration to the next can have drastic consequences for the final results. Thus, it is important that the method is performed consistently for every iteration. To remediate this issue, the GUI is equipped with the
isotherm fit-domain slider, which allows the user to specify the percentage of the isotherm domains that will be considered for these linear fits. Given a chosen percentage $p$, the linear fits are performed for $\chi_{\text{max}}^{-1} * p/100 < \chi^{-1} \leq \chi_{\text{max}}^{-1}$ across every iteration of the modified Arrott plot method. In this way, the method is consistent for every iteration, and the results are completely reproducible.

The plots and MATLAB workspace variables from the asymptotic analyses and scaling analysis can be exported upon completion of the analyses in a number of ways. Once the user has specified an output directory path, the plots will be automatically saved as .png and .fig format. The .fig MATLAB figure files have been included in the outputs so that the user can open the figure files and customize the colors, linewidths, text size, etc. in MATLAB. If the user prefers to plot the data outside of MATLAB using other software, the processed data can be obtained from the .mat MATLAB workspace file output.

**Figure 7.2: Set-up panel in the GUI: customized for Mn$_3$Si$_2$Te$_6.$**
CHAPTER 8: EXAMPLE CALCULATIONS – EXPERIMENTAL

DETERMINATION OF CRITICAL BEHAVIOR

To demonstrate the ability of this program to analyze the critical phenomena of magnetic materials, the critical exponents and critical temperatures for Mn₃Si₂Te₆ and Fe₂.₆₄GeTe₂ have been calculated using the GUI. These bulk crystals, along with other van der Waals materials, have recently gained tremendous research interest due to the discovery of retained/improved magnetic properties upon reduction of the crystal dimensionality to a few layers or monolayers [16,60–62]. Isothermal bulk magnetization measurements near the critical region were performed in our laboratory on Mn₃Si₂Te₆ and Fe₂.₆₄GeTe₂ using a Quantum Design Versalab magnetometer with the field parallel to the easy axis for each crystal [63–65]. Magnetization measurements were performed by Yu Liu and C. Petrovic on CrI₃ with H//ab using a Quantum Design MPMS-XL5 system [52]. Proton irradiation on Mn₃Si₂Te₆ was conducted with an energy of 2 MeV using a 1.7 MV Tandetron accelerator at fluences of 1 × 10¹⁵, 5 × 10¹⁵, 1 × 10¹⁶, and 1 × 10¹⁸ H⁺/cm² [63]. Further experimental details concerning the proton irradiation may be found in ref. [66]. Proton irradiation at each respective irradiance was carried out on separate crystals so that the critical behavior as a function of proton irradiance could be studied.

The input file loaded into the GUI is formatted in three columns: temperature, magnetization, and applied field. Common delimiters such as commas, spaces and tabs are acceptable. Once the data has been loaded, the program automatically separates the magnetization and field into individual isotherms by temperature association; thus, there is no need to format the data prior to loading.
8.1 Modified asymptotic analysis and scaling analysis on Mn$_3$Si$_2$Te$_6$

![Graphs showing modified asymptotic analysis and scaling analysis on Mn$_3$Si$_2$Te$_6$.](image)

The critical behavior of Mn$_3$Si$_2$Te$_6$ was first studied using the modified asymptotic analysis described above. The isothermal magnetization measurements were carried out between 66 K and 80 K, but during our analysis the temperature range was purposefully limited from 67 to 79 K. The mean field critical exponents were chosen as the starting exponents for the Modified Arrott Plot, and the isotherm fit domain was set to 20% of $\chi_{mmax}^{-1}$. These parameters were easily entered into the set-up panel of the GUI, as seen in Figure 8.2. The modified asymptotic analysis was allowed to run for 8 iterations, and the critical exponents and $T_C$ were observed to converge at the fifth iteration. From our experience, the modified asymptotic analysis converges much more quickly than the traditional asymptotic analysis. The Modified Arrott Plot, Kouvel-Fisher Plot, and
temperature dependence of spontaneous magnetization and inverse susceptibility for the final exponents are displayed in Figure 8.3.

The final critical exponents obtained from the modified asymptotic analysis were $\beta = 0.419 \pm 0.001$, and $\gamma = 1.110 \pm 0.001$. Using these exponents, the isotherms in the Modified Arrott Plot in Figure 8.3(a) were observed to be straight and parallel, especially near $T_C$, thus supporting the validity of the exponents. In the traditional asymptotic analysis, the critical temperature is obtained from both the Kouvel-Fisher plot and modified Arrott plot; however, in the modified asymptotic analysis, the $T_C$ is obtained from the power law fits on the spontaneous magnetization and inverse susceptibility [50]. We suspect this is done because the modified asymptotic analysis converges much more quickly than the traditional method, so discrepancies in the $T_C$ obtained from the Kouvel Fisher plot and modified Arrott plot are likely to exist. The critical temperature was therefore found to be $T_C = 73.41$ K. The critical exponent $\delta$ can be easily obtained from the Widom Scaling Relation [46]: $\delta = 1 + \gamma/\beta$. Using this relationship, we obtained $\delta = 3.65$. The critical exponent $\delta$ was also found by taking the isotherms closest to $T_C$, and fitting them according to the power law equation $M(H, T) = DH^{1/\delta}$ (Eq. 3), where $T = T_C$, and $D$ is the

![Figure 8.4: Scaled plots of magnetization and field for Mn$_3$Si$_2$Te$_6$ using the generalized magnetic equations of state. (a) follows Eq. 6, while the inset graph in (b) follows Eq. 7.](image-url)
critical amplitude. Since $T_C$ lies between the isotherms at 73 and 74 K, both isotherms were fitted. Using this method, $\delta(T = 73K) = 3.817$ and $\delta(T = 74K) = 3.420$ was found. The $\delta$ from the Widom Scaling Relation ($\delta = 3.65$) lies between these two values, which indicates that $T_C$ is between 73 and 74 K, in agreement with our determined experimentally determined $T_C$.

The critical exponents $\beta$ and $\gamma$ were then confirmed by scaling the field and magnetization using Equations (6) and (7). As evident from Figure 8.4(a) and (b), the scaled curves fall on two curves: one above $T_C$ (in red) and the other below $T_C$ (in blue). This behavior is characteristic for critical exponents and $T_C$ that have been chosen correctly[47]. The inset graph of Figure 8.4(b) is also observed to follow the criteria described in section 1.2, which says that the scaled data should collapse onto a single curve, with isothermal above $T_C$ in the positive domain, and isothermal data below $T_C$ in the negative domain of the scaled $eH$ axis. The few points located at $eH = 0$, $MH^{1/8} = 0$ are present for magnetization data collected very close to $T_C$. The finally obtained critical exponents $\beta = 0.419 \pm 0.001$, $\gamma = 1.110 \pm 0.001$, and $T_C = 73.41$ K were thus confirmed using the scaling analysis. These values are in close agreement with a previous study on the critical behavior of Mn$_3$Si$_2$Te$_6$ ($\beta = 0.41 \pm 0.01$, $\gamma = 1.21 \pm 0.02$) [54].

Since the critical exponents $\beta$ and $\gamma$ lie close to the mean field critical exponents ($\gamma = 1$, $\beta = 0.5$), the presence of long-range interactions can be safely assumed. Eq. 9 could therefore be
used to determine the spin dimensionality $n$, spatial dimensionality $d$, and $\sigma$. Table 1 shows the numerical solutions to Eq. 9 obtained for different values of $n$ and $d$ after substituting the experimentally determined $\gamma$. Unlike previous methods where values for $\Delta \sigma$ were guessed until a solution was reached, our solutions are explicit numerical solutions. The reader should find that all the columns of Table 1 correspond to one exact solution of Eq. 9 by substituting the values for $\Delta \sigma$, $n$, $d$, and $\gamma$. As described in section 1.2, scaling relations are then used to calculate the remaining critical exponents $\beta$, $\delta$, $\alpha$, and $\nu$. The correct $n$ and $d$ are determined by comparing the theoretical $\beta$, $\gamma$ and $\delta$ to the experimentally obtained values. Remarkably, the theoretical values in Table 1 for $\beta$, $\gamma$ and $\delta$ matched the experimentally obtained values within 3 significant figures of accuracy, with $d = 3$ and $n = 1$. The isotropic long-range exchange distance was found to decay as $J(r) \approx r^{-4.71}$, which is reasonably close to the value previously reported ($J(r) \approx r^{-4.79}$) [54]. The Ising spin dimensionality ($n = 1$) found from our calculations is likely an indication of anisotropic magnetic interactions [67]. This hypothesis is supported by the fact that the critical exponents do not seem to match a universality class. As several researchers have pointed out, frustration or spatial anisotropy in Heisenberg spins can cause crossover to XY or Ising behavior [67]. It is safe to assume that the cause of this crossover is magnetic frustration since ferromagnetic superexchange interactions between Mn-Te-Mn and competing anisotropic direct exchange interactions between Mn sites were previously confirmed to cause magnetic frustration in Mn$_3$Si$_2$Te$_6$ [68].

8.2 Modified asymptotic analysis and scaling analysis on Fe$_{2.64}$GeTe$_2$

As another example, the critical behavior of Fe$_{2.64}$GeTe$_2$ was investigated using the traditional asymptotic analysis. Figure 8.5 includes the modified Arrott plot, Kouvel Fisher plot, and the fits following Equations (1) and (2). Additionally, the convergence of the traditional
asymptotic analysis is shown in Figure 8.5(d). This figure of the convergence was automatically generated by the GUI. Table 2 was provided with the critical exponents and $T_c$ obtained for comparison with the critical parameters previously obtained by Y. Liu and C. Petrovic for Fe$_{2.64}$GeTe$_2$. As seen in the table, reasonable agreement exists between all the critical parameters.

![Figure 8.5](image)

**Figure 8.5:** Modified Arrott plot (a), Kouvel Fisher plot (b), modified Arrott plot fits following Eqs. (1) and (2) (c), and demonstration of the convergence of the asymptotic analysis (d) for Fe$_{2.64}$GeTe$_2$. 


In this section the magnetic critical behavior of Mn₃Si₂Te₆ with varying proton irradiance (H⁺/cm²) was studied using the GUI. The critical parameters as a function of proton irradiance can be found in Table 3. These experimental values were obtained following the modified asymptotic analysis discussed in §1.2. The task of performing this analysis “by hand” would have required an enormous effort since twelve isotherms of magnetization versus field were used to analyze each sample. Using the modified asymptotic analysis, the total number of fits performed easily exceeded 400 fits for the full analysis of Mn₃Si₂Te₆ as a function of proton irradiation. The critical exponents as a function of proton irradiance are plotted in Figure 8.6 (a) and (b) for better visualization. These plots are characterized by an increase in β towards 0.5, and a decrease in γ towards 1.0, as indicated by the dashed lines within the figures. The critical exponents for the mean field universality class have been theoretically shown to be γ = 1.0 and β = 0.5 [69]; therefore, it is evident that the Mn₃Si₂Te₆ exhibited an increasingly mean field-like behavior as a function of proton fluence. Despite this trend, an anomaly is observed at irradiance of 5x10¹⁵ H⁺/cm² in which a sharp increase in β and γ was observed.
To further examine the physical meaning of this these changes in critical behavior, the critical exponent $\eta$ was calculated using:

$$\eta = 2 - \frac{\gamma d}{2\beta + \gamma}$$  \hspace{1cm} (11)

which was derived from the scaling relations in §1.2. The effective spatial dimensionality $d = 3$ was observed to remain the same for all the samples after applying Eq. (9). The two-point correlation function, $G(r) = 1/r^{-d+2-\eta}$, was then used to study the spin correlations. The spin

<table>
<thead>
<tr>
<th>Fluence ($H^+$/cm$^2$)</th>
<th>Technique</th>
<th>$T_C (K)$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Kouvel-Fisher Plot</td>
<td>73.41</td>
<td>0.41(9)</td>
<td>1.11(0)</td>
<td>3.65</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>Kouvel-Fisher Plot</td>
<td>74.44(8)</td>
<td>0.45(2)</td>
<td>1.06(9)</td>
<td>3.36(3)</td>
</tr>
<tr>
<td>$5 \times 10^{15}$</td>
<td>Kouvel-Fisher Plot</td>
<td>73.41(1)</td>
<td>0.42(9)</td>
<td>1.18(5)</td>
<td>3.75(9)</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>Kouvel-Fisher Plot</td>
<td>74.60(8)</td>
<td>0.43(8)</td>
<td>1.05(7)</td>
<td>3.41(1)</td>
</tr>
<tr>
<td>$1 \times 10^{18}$</td>
<td>Kouvel-Fisher Plot</td>
<td>73.62(2)</td>
<td>0.44(6)</td>
<td>1.06(5)</td>
<td>3.38(9)</td>
</tr>
</tbody>
</table>

Table 3: Experimentally obtained Curie temperature and critical exponents for proton irradiated Mn$_3$Si$_2$Te$_6$ using the modified asymptotic analysis.

To further examine the physical meaning of this these changes in critical behavior, the critical exponent $\eta$ was calculated using:

$$\eta = 2 - \frac{\gamma d}{2\beta + \gamma}$$  \hspace{1cm} (11)

which was derived from the scaling relations in §1.2. The effective spatial dimensionality $d = 3$ was observed to remain the same for all the samples after applying Eq. (9). The two-point correlation function, $G(r) = 1/r^{-d+2-\eta}$, was then used to study the spin correlations. The spin

![Graphs](image.png)

Figure 8.6: The critical parameters $\beta$ (a) and $\gamma$ (b) as a function of proton irradiance. Additionally, the two-point correlation function decay as a function of proton irradiance is plotted in (c).
correlation function decay is plotted as a function of proton fluence in Figure 3(c). In this plot, a decrease in the spin correlation decay rate following proton irradiation was observed, indicating a decrease in the magnetic order. The sole exception to this trend was observed for the sample irradiated at $5 \times 10^{15}$ H$^+/\text{cm}^2$, in which the spin correlation decay rate was observed to sharply decrease, indicating an increase in magnetic interactions. Interestingly, these trends observed in the spin correlation decay rate perfectly match a previous study published by our group in which Mn$_3$Si$_2$Te$_6$ irradiated at a fluence of $5 \times 10^{15}$ H$^+/\text{cm}^2$ demonstrated a significant increase in magnetization compared to pristine Mn$_3$Si$_2$Te$_6$ [63]. This study also showed that the magnetization was decreased for the samples at $1 \times 10^{15}$, $1 \times 10^{16}$, and $1 \times 10^{18}$ H$^+/\text{cm}^2$ relative to the pristine sample, which is in perfect agreement with the trends observed in the spin correlation decay rate from the present study.
PART II CONCLUSION

The automation and simplification of current methods for experimentally determining the critical phenomena of magnetic materials was discussed herein. Importantly, this computational tool has automated a formidably tedious and time-consuming iterative process. The accuracy and precision of this tool is unprecedented – both for its reproducibility and immunity to systematic user errors caused by deviations in the fit domains. The capability of easily switch between several self-consistent methods with ease will assist users to determine the most accurate critical exponents. The critical exponents, critical amplitudes, the transition temperature, and magnetic exchange distance were successfully calculated and demonstrated for two compounds, namely, Mn$_3$Si$_2$Te$_6$ and Fe$_{2.64}$GeTe$_2$. The tool developed here has the potential to immensely benefit other scientists and engineers by reducing the time needed to characterize magnetic materials and by minimizing the possibility for analysis error.
REFERENCES


VITA

My name is Jose Armando Delgado. My parents inspired me with a passion for teaching and science from an early age. I gained my first teaching experience as a supplemental instructor at El Paso Community College, where I taught pre-calculus workshops and tutored students in mathematics subjects ranging from pre-calculus to differential equations and calculus III. I earned my Bachelor of Science degree in Physics from the University of Texas at El Paso (UTEP) in May, 2018.

My journey in academic research began in May 2017 after I joined Dr. Srinivasa Rao Singamaneni’s laboratory group. During my time in research, I’ve had the privilege of presenting our work at seven conferences, including COURI symposiums at UTEP, The Minerals, Metals & Materials Society conference, and Materials Research Society conferences. I obtained my first publication and co-authorship in 2018 concerning the “Magnetic and electrocatalytic properties of transition metal doped MoS₂ nanocrystals” (Ref. [24]). Since then, I have co-authored three other manuscripts, two of which are under preparation. The last paper, concerning the “Angular dependence and 2D correlations in the van der Waals ferromagnet CrBr₃ using high frequency electron spin resonance spectroscopy” (Ref. [70]) is currently under review.

Contact Information: jdelga3225@gmail.com