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A STRUCTURAL STUDY OF CORRELATED MATERIALS: INCIPIENT
MOTT INSULATORS AND LOW-DIMENSIONAL SYSTEMS

By
Alaa Alfaiakawi
M.Sc. in Physics, 2015

A Dissertation
Submitted to the Faculty of the
College of Arts and Sciences of the University of Louisville
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy in Physics

Department of Physics and Astronomy
University of Louisville
Louisville, Kentucky

August 2020

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Dissertation approved on

May 19, 2020

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Dr. Ming Yu

Dr. Farshid Ramezanipour

DEDICATION

To My family.

My parents Mahmoud and Aisha.

My sisters Mryam. Esraa and Asmaa and brother Abdualrahman.

My kids Khaled, Ahmad, Sarah, Shaikha, Moothy, Saleh and Dalal.

My husband Sabah for his continuous love and support.

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ABSTRACT

A STRUCTURAL STUDY OF CORRELATED MATERIALS: INCIPIENT MOTT INSULATORS AND LOW-DIMENSIONAL SYSTEMS

Alaa Mahmoud Alfailakawi

May 19, 2020

Current theories of high-temperature superconductivity suggest that electrons must organize into Cooper pairs in order for a material to exhibit a superconducting phase. Electrons in insulators experience significant repulsive interactions that tend to keep electrons localized at atomic positions. In contrast, electrons in metals are delocalized, interact weakly, and are free to conduct electricity. Therefore, the formation of Cooper pairs should have different mechanisms for metals compared to insulators. This contrast raises the debate about the origin of high-temperature superconductivity in iron-based material, whether it depends on the strong or weak coupling. Many iron-based materials are metallic in the normal phase; however, before entering the superconducting phase, iron-based superconductors are believed to harbor insulating characteristics in close proximity to a Mott insulator. Furthermore, because superconductivity in iron-based materials occurs the border of correlation-induced electronic order, it is crucial to understand the nature of the ordered states. The newly reported iron oxychalcogenide $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ is an antiferromagnetic (AFM) insulator at room temperature. Oxychalcogenides are structurally similar to the iron-based superconductors and it is possible to tune the Fe-Fe ion distance to drive the material from an insulating to a metallic phase. It is unexpected that a decrease in

the Fe-Fe ion distance for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ results in enhanced insulating properties instead of making the material more metallic. This violates the predictions of the well-established electron band theory.

The first aim in this work was to examine the novel Mott insulator $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$, crystal structure, and the effect of selenium doping on the material. X-ray powder diffraction (XRD) and Rietveld analysis were used to study the crystal structure. Also, neutron powder diffraction was used to study the magnetic peak intensity behavior with changes in temperature. Transport measurements were performed on both samples and activation energies (E_a) was calculated as 0.0694 eV and 0.06098 eV for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ and $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ respectively. The Rietveld fits confirmed that the material had tetragonal crystal system with space group P_4/mmm for both samples. The calculated β showed that this Mott insulator has the two dimensional Ising model. The volume of crystal increased with decreasing temperature while the atomic site occupancy increased. Also, the doping did not affect the crystal structure, however it suppressed the magnetic behaviour in $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$.

The second aim of this work was to study the structure of iron oxychalcogenides $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$, compare the short-range to the average structure, and understand the short-range behavior in this type of Mott insulators. Neutron powder diffraction (NPD) was used to study the short and average structure of $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$. The obtained NPD data were analyzed using Rietveld analysis and pair distribution function (PDF) method. We observe the presence of fluctuating nematic ordering from low temperature to room temperature. High values of the isotropic thermal parameter (U_{33}) for the oxygen atom O2 along c -axis was observed. The results also suggested the presence of short-range local distortion in both $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ materials which can be evidence of nematic behavior in the short-range of these materials.

The last part of this research investigated the transition metal dichalcogenides

(TMDs). TMDs are receiving a large amount of attention because they have been posited as a potential successor to silicon in the future of electronics manufacturing. The fabrication of large TMD crystals is currently an active area of industrial work. Most TMDs are low dimensional materials in the sense that their structures consist of stacks of hexagonally atomic layers of transition metal atoms or chalcogens sandwiched by transition metal (TM) layers. In addition to this, TMD electronic properties are primarily contained in the 2D TM planes. The last aim of this research was to study the transition metal dichalcogenide MoTe_2 in two of its three stable phases ($2H\text{-MoTe}_2$ and $1T'\text{-MoTe}_2$). Also, we studied the T_d phase, which results from the phase transition of $1T'\text{-MoTe}_2$ at low temperatures.

Powder diffraction techniques were implemented to study the detail of the crystal structure of bulk phases. Rietveld analysis was used to analyze the powder diffraction data of all MoTe_2 phases. Electron dispersion x-ray spectroscopy (EDX) and Raman spectroscopy were performed on both samples to check the purity of the samples. The EDX and Raman spectroscopy showed that the samples were clear from impurities. The Rietveld analysis determined the crystal structure of $2H\text{-MoTe}_2$, $1T'\text{-MoTe}_2$ and $T_d\text{-MoTe}_2$ were hexagonal $P6_3/mmc$, monoclinic $P2_1/m$, and orthorhombic $Pmn2_1$ respectively. Our results showed that temperature affected the atomic site occupancy in the studied MoTe_2 phases which might be related to the stacking faults in MoTe_2 layers.

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CHAPTER 1

INTRODUCTION TO STRONGLY CORRELATED ELECTRONIC SYSTEMS

Strongly correlated electronic systems (SCES) are fascinating systems that encompass rich phenomena from the perspective of fundamental science and offer possibilities for technological applications. Discovering the relationship between the complex degrees of freedom in those SCES has been a goal for condensed matter physicists in recent years. The mechanism of superconductivity in high transition temperature (high- T_c) superconductors (HTSC), the role of magnetic fluctuations, structural fluctuations, and even the homogeneity of the structures are topics of current interest. Furthermore, some new discoveries are groundbreaking enough to completely shift our understanding of these materials. The discovery of high- T_c superconductivity in iron-based materials, in 2008, paved the way for discovering a new superconducting family of materials [22, 23]. Figure 1 shows crystallographic structure and magnetic structure for some of FeSCs materials.

SCES often have remarkable properties and transitions between distinct, competing phases with dramatically different electronic and magnetic orders. These SCESs phenomena are often challenging to describe in a single definition due to their complexity. It is worth noting that in SCES, the interaction between electrons in solids is of fundamental importance as it governs the behavior of the whole system. SCESs show the strong interplay between different degrees of freedom, charge, orbital, spin, and lattice, which leads to novel material properties. These materials often have a complex phase diagram. SCESs includes much material such as conventional su-

Figure 1. Crystallographic and magnetic structures of (left) The tetragonal structures known to support superconductivity in FeSCs. (On right) the iron atoms planar layer which is common to all FeSCs (iron ions shown in red and pnictogen/chalcogen anions shown in gold) from reference [1].

perconductors and High-temperature superconductors, quantum hall systems (QHS), organic conductors, spintronic materials, multiferroics, Mott insulators, spin Peierls materials, and heavy fermion materials.

Two distinctive features of iron-based materials are their complex phase interplay and a surprisingly large chemical variety. The presence of high T_c superconductivity in doped Mott insulators such as the cuprates contradicts the conventional thought that electron repulsion is detrimental to the presence of superconductivity. Bloch theorem is used to describe conventional condensed matter materials by assuming non-interacting electrons to describe the band structure. Based on this assumption, the band structure of materials can be categorized as metals, semiconductors, and insulators, as illustrated in Figure 2.

In high-temperature superconductors, we can observe an unusual normal state which has resistivity, optical conductivity, lacks sharply defined quasiparticles, and Nernst effect. The mechanism of superconductivity at high temperatures seems to

Figure 2. Classification of materials based on their band structure

be related to electron-electron and electron-phonon interactions. We cannot use the standard model of band theory to describe novel quantum materials like SCESs. To describe strongly-correlated particles in a tight-binding lattice, the Hubbard model is the standard model to [24]. The Hubbard Hamiltonian (HH) offers a simple way to describe how the interactions between electrons.[25] (see Figure 3).

Strong correlations can have a significant effect on material properties. The interplay of electron-electron, spin, charge, orbital momentum, and symmetry can drive these materials to exhibit unusual ordering, especially at low temperatures. This makes SCES very sensitive to small changes from external parameters. Those effects can be a vast increase in resistivity through a metal-insulator transition. In heavy fermion systems, at low temperatures, electron mobility behaves as if electrons are very massive particles. Some SCES exhibit a tremendous thermoelectric response. SCES displays exciting phenomena such as conventional superconductors, high T_c superconductors, magnetic systems (ferromagnetism, antiferromagnetism), low-dimensional electron systems, quantum Hall systems, and heavy fermions systems. In iron-based superconductors (FeScs), the superconductivity pairing may be

Figure 3. Mott-insulator transition phase diagram based on the Hubbard model. The strength of Coulombic repulsion U and the temperature are plotted based, on the Hubbard model. At low temperature, the system had a long-range order (red). In the orange region, the model has two distinct solutions bounded by lines U_{C1} and U_{C2} , the dotted line indicates first order transition in equilibrium. The first order transition line terminates at a second order critical point. The Figure is from reference [2].

due to unconventional electron-electron Coulomb interactions. Applications of superconducting material are vast and include magnetic resonance imaging (MRI), nuclear magnetic resonance (NMR), beam-steering and focusing magnets used in particle accelerators, magnetic fusion device, electric power transmission lines, magnetometer for superconducting quantum interference devices (SQUIDs), electric motors and generators, fast digital circuits, RF and microwave filters, superconducting nanowire single-photon detector, fast fault current limiters, and the superconducting tunnel junction detector [26, 27].

Iron-based superconductors share a common crystal structure with a planar layer of iron atoms centered in a tetrahedrally stacking sequence of coordinated pnictogen or chalcogen anion separated by a layer of (alkaline earth or rare earth) and (oxygen or Fluorine). It is believed that the organization of these layers play an important role in high T_c superconductivity since it is similar in superconducting cuprates (Figure 1) [1]. In both FeSCs and cuprates superconductors, the doping or chemical substitution is

an important factor to induce the superconducting phase transition.

The physics behind FeSCs is far richer than initially anticipated in that they display exceptional and highly significant properties. Understanding the phases and states that lead to the superconducting phase in FeSCs will help to understand these complex materials. One of the phases that show in the iron pnictide phase diagram is the Mott localization. The electron correlations are associated with bad-metal behavior and magnetism, which can be the reason for the high T_c in FeSCs [28]. Studying Mott insulating behavior is important in understanding the process and explaining superconductivity in FeSC materials.

The free electron model, where electrons move freely in metal, can explain many physical properties in metals such as Ohm's law and the electrical and thermal conductivity. In a Fermi gas, at $T = 0$, particles will fill the lowest energy states up to The Fermi energy E_F occupying a radius of K_F . At temperature $T \neq 0$, some of the states will be thermally excited. The energy available for these excitations is $k_B T$, and the only possible excitations are from filled to unfilled electronic states. In order to include the electron-electron interactions and their effects, a material needs to be described using the Landau theory of a Fermi-liquid which assumes that momentum and spin number are good numbers to describe the quasiparticles, the electron-electron interaction can be turned on over some time (t), and the resulting excitation may be described as quasiparticles with lifetimes $\gg t$.

The BCS theory, which is the conventional theory to explain superconductivity, is based on the fact that a net interaction between electrons for transitions is less than the phonon energy $\hbar\omega$. In a superconducting phase, this interaction is favorable over the repulsive screened Coulomb interaction. This theory explains many conventional superconducting properties like second-order phase transition at the critical temperature T_c , the specific heat variation near the absolute temperature, the Meissner-Ochsenfeld effect. Despite the successes of the BCS theory failed to ex-

plain the unconventional high temperature superconductivity which remain not fully understood to date.

1.1 Mott Insulators

After the discovery of high T_c superconductors in cuprates by Bednorz and Muller in 1986, Anderson proposed that those materials are doped Mott-insulators, which generated a great interest in understanding them.

Mott insulators are named after its discoverer Sir Nevill Francis Mott, who shared the 1977 Nobel prize with Philip W. Anderson and J. H. Van Vleck, for his contribution for his work on the electronic structure of magnetic and disordered systems, especially amorphous semiconductors. Mott insulators can be defined as systems with strong electron-electron interactions that drive a quantum phase transition from a metallic phase to an insulating ground state [29]. Mott insulators are used in thin-film magnetic heterostructures, low power memory, thermal sensing, Field-Effect Transistors (FET), switches, junction Mott Transition Field-Effect Transistor (JMTFET), and high T_c superconductivity applications [30, 31, 32].

Novel physics often appears near a Mott quantum paramagnetic transition (QPT) and the type of this order, whether it is first-order or second-order, is important. The nature of these transitions, and quantum fluctuations near them, are of great interest because they help in understanding high T_c iron superconductors [33]. The mechanism of Mott insulator transition is not fully explained; however, many current scientific suggestions explain it by the opening of charge-transfer gap, orbital ordering, and charge ordering, but no experimental evidence to support these possible explanations has been found [33]. In the Mott insulating state, the charge degrees of freedom are frozen, and the associated spin degrees of freedom are considered as local moments. These local moments are coupled with each other through exchange interactions and frequently behave as an antiferromagnetic order [34]. The Mott-Hubbard transition is

one of the most spectacular direct effects of strong correlations and its understanding is believed to be essential to understand the behavior of FeSCs. The Mott-Hubbard transition is simply the process connecting a metallic state with a Mott-Hubbard insulator, a state in which the electronic conduction is inhibited by strong local Coulomb repulsion despite the partial filling of the band [35].

The iron oxychalcogenides crystal structure contains tetragonal symmetry with planes containing iron Fe and oxygen O atoms for which chalcogens alternate above and below those planes. Figure 1 shows the planar iron atom Fe arrangement in FeSCs which is similar to the arrangement in iron oxychalcogenide materials [9]. Iron oxychalcogenides such as $X_2O_2Fe_2OM_2$ (with $X = \text{Ca, La}$ and $M = \text{S, Se}$) are an important family to investigate. Iron oxychalcogenides are structurally related to the superconductors and because the substitution of the chalcogenide ion tunes the electronic bandwidth hence their proximity of a metal-insulator transition [36].

1.2 Iron-based Superconductors

Iron-based superconductors (FeSCs) are interesting; they have high critical temperature T_c , and in these materials, the electrons seem to form Cooper pairs via a Coulombic interaction without help from the ionic lattice [37]. The need to understand the pairing mechanism in the FeSCs had driven research into these materials. FeSCs material includes many iron pnictides and iron chalcogenides. Figure 1 shows the crystal structure of some pnictide and chalcogenide iron superconductors. The square lattice iron atom planar layer is shown on the right side of Figure 1, this layer is very common among FeSCs material structure. In iron-based superconductors, the superconductivity pairing may be due to unconventional electron-electron Coulomb interaction. Two distinctive features of iron-based materials are their complex phase interplay and a surprisingly large chemical variety. The presence of high T_c superconductivity in doped Mott insulators such as the cuprates contradicts the

conventional thought that electron repulsion is detrimental to the presence of superconductivity. Nematicity has been the focus of research and studies in the field of iron superconductors during the last decade. It leads to anisotropy in the magnetic properties, electric transport, orthorhombic structural distortions, and changes in the band splitting close to the Fermi level [38]. In the nematic phase (state) three different order parameter is present (non zero) and can be classified into the following three types: 1. structural distortion 2. charge/orbital order and 3. spin order [17]. Structural nematicity is short-range (local) fluctuations with or without a structural phase transition. Nematicity can be considered translational invariant even though it spontaneously breaks rotational symmetry. In many strongly correlated electron systems with very small structural anisotropy in the plane, such as cuprates and pnictides, ordered states of matter are characterized by a broken symmetry according to the Landau paradigm of continuous phase transitions [39]. Nematic ordering breaks the tetragonal symmetry of iron-based superconductors. It emerges from a regular structure transition of electric instability in the non-superconducting (normal) phase [20]. The susceptibility of the iron pnictides superconductor $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ distinguished an electric nematic state which is near the superconducting transition temperatures [39].

The presence of nematic order in iron-based superconductors is a well-established fact experimentally, although its origin remains controversial. Nematicity order state can happen because of a regular structural transition or as the result of an electronically driven instability in particular orbital order or spin-driven Ising-nematic order. The Ising-nematic order is a magnetic state that breaks rotational symmetry but preserves time-reversal symmetry. Symmetry dictates that the development of one of these orders immediately induces the other two, making the origin of nematicity a physics realization of the ‘chicken and egg problem’ [17].

1.3 Mott insulators in this study

New materials that exhibit strong correlations are continuously being developed. Recently the $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ has been synthesized and there are limited studies on its nuclear and magnetic structure. In addition, some materials like $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ lacks studies on the local structure using the Pair Distribution Function (PDF) analysis. In this work, both x-rays and neutrons scattering techniques were employed to investigate the behaviors of strongly correlated electronic systems. Mott insulating iron oxychalcogenides $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ and $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ in proximity to superconductors were studied. The nuclear structure of the newly reported $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ was studied to search for phase transition as well as lattice parameter temperature dependence to understand how atomic structure is related to the electronic and magnetic properties. Also, further analysis of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ magnetic structure and estimation of the order parameter (magnetic phase) was performed due to the unavailability of published data. Furthermore, we investigated the local structure of $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ by the neutron total scattering technique and the Pair Distribution Function (PDF).

CHAPTER 2

LOW-DIMENSIONAL SYSTEMS

In the past ten years, satisfying Moore’s law has required the adoption of new materials and new device geometries in order to continue improved performance. Two-dimensional materials (2DM) have been studied intensely for potential application are one of the most studied classes of materials due to the richness of unusual physical phenomena that occur when charge and heat transport is constrained in a plane. Many materials show special properties due to reduced dimensions, such as the layered transition metal dichalcogenides (TMDs), copper oxides, and iron pnictides. All of these systems which exhibit correlated electronic phenomena as varied as charge density waves and high-temperature superconductivity.

The isolation of graphene by Andre Geim and Konstantin Novoselov in 2004, from bulk graphite, has led to a tremendous focus on other 2DMs such as transition metal dichalcogenide. One of the challenges that face the 2DMs, to be used in devices and high volume manufacturing, is to grow large and high-quality single crystals. Many 2DMs crystals are now beginning to be investigated. There are hundreds of layered materials that hold their stability to the monolayers, having properties complementary to graphene. Transition metal oxides (TMOs) and transition metal dichalcogenides (TMDs) have a layered structure. In both TMOs and TMDs, atoms within layers are held together by covalent bonds, whereas different layers are held by van der Waals interactions. TMDs offer advantages in optoelectronics due to their transparency, mechanical flexibility, easy processing, and the ability to tune the bandgap by varying the number of layers that allows the detection of light at differ-

ent wavelengths. TMDs properties complement graphene's properties. For example, graphene is useful for broadband ultra-fast technologies, while semiconducting TMDs are better for applications requiring strong light absorption and electroluminescence. The Combined properties of both graphene and TMDs can be used to create multifunctional and high-performance materials that consist of heterogeneous stacks and hybrid devices [40]. 2DM are important in various applications such as optoelectronics, spintronics, catalysts, chemical, and biological sensors, supercapacitors, solar cells, digital circuits, light-emitting diodes, and lithium-ion batteries [3].

Figure 4. Different MX_2 compounds and binary compounds of group-IV elements and group III-V. The structure (H or T) is the ground state. The resulting structures (T or H) can be half-metallic (+), metallic (*), or semiconducting (***) with direct or indirect band gap [3].

2.1 Weyl Semi Metals

In condensed matter physics, the intersection of topology and the band theory has recently attracted the attention of researchers. The first topological material to show these effects was Weyl semimetals (WSM) [41]. Topological Weyl semimetals

(WSM) can be classified as either type-I WSM, which has a vanishing density of states at the Weyl nodes or type-II WSM, which have singular points of momentum space allowing for distinct topological properties. In 1929 Hermann Weyl proposed that the existence of Weyl fermions were massless chiral fermions in his paper "Gravitation and the Electron" [42], and he proposed a solution to Weyl equation derived from the Dirac equation. Weyl fermions as quasiparticles in a low-energy condensed matter system. Such quasiparticles were discovered in 2015, in the form of crystals known as Weyl semimetals, as a type of topological material.

Weyl semimetals are a gapless topological phase protected by the chiral anomaly, where the charge and the crystal translational symmetry are conserved. The absence of a bandgap in a weakly-interacting Weyl semimetal is sustained by the electronic structure topology and will remain intact as long as the symmetries and the anomaly are intact. This nontrivial topology also establishes in the Fermi arc surface states and topological response [43]. Weyl semimetal is the first example of a bulk gapless topological phase [41]. The vanishing gap of the bulk electronic structure in WSM is sustained by topology. The existence of closed surfaces in momentum space that carry nonzero Chern numbers creates the presence of a band-touching point inside the Brillouin zone (BZ) volume. In order to have a separation between the Weyl nodes in momentum space, an inversion or a time-reversal (TR) symmetry needs to be violated while maintaining the crystal translational symmetry.

Weyl semimetals show identification features like linear dispersion at Weyl nodes (or Weyl points), monopoles of Berry curvature originating at the location of the Weyl points in momentum space, and unique boundary modes known as Fermi arcs that connect projections of these Weyl nodes in the surface Brillouin zone [44]. Figure 5 illustrate the Weyl nodes (points) in WSM material. Type-I WSM, in which the density of states vanishes at the energy of the Weyl nodes, shows many essential physics properties like thermoelectric properties, [45] electro- and magneto-transport [46],

magnetic properties [47], and effect of disorder [48]. In type-I WSM, when the chemical potential is shifted slightly away from the nodal energy, the Fermi pockets enclosing the projections of the Weyl nodes are very small. In contrast, type-II WSM has an extended pocket of holes and electrons at the node energy. Doping away from the node energy will result in surface projections of the Weyl nodes becoming bounded within large Fermi pockets.

Figure 5. Schematics of the topological insulator and Weyl semimetal [4].

2.2 Transition Metal Dichalcogenide

In 1923, the crystal structure of molybdenite monolayers was studied by Dickinson and Pauling, and monolayer MoS_2 was investigated in 1986. Transition Metal Dichalcogenide (TMD) materials have the advantage over graphene of having extended bandgap tunability through composition, thickness, and possibly even strain control [49]. TMDs consist of hexagonal layers of metal atoms (M typically Mo, W, Nb, Re, Ni, or V) pack in between two layers of chalcogen atoms (X typically S, Se, or Te) with a MX_2 stoichiometry which gives more than 40 different combinations for TMDs as in figure 4. The bulk 3D crystals are stacked structures with van der

Waals bond between adjacent layers with strong covalent bonding within each layer. TMDs shows a range of electronic structures from insulators to metals with interesting properties including topological insulator effect [50], thermoelectricity [51], and superconductivity [52]. TMDs established themselves as fascinating building blocks for optoelectronic applications, with a strong focus on various photodetection platforms. The adaptability of TMDs enables their application in areas including ultrafast and ultrasensitive detection of light in the ultraviolet, visible, infrared and terahertz frequency ranges [40] which can be used in photonic components. Bulk TMDs are one of the most interesting classes of materials. They display a vast range of interesting properties such as semiconductivity, half-metallic magnetism [53], superconductivity [54], or charge density wave [55]. These properties made TMDs candidate for many applications in numerous areas, including lubrication, catalysis, photovoltaics, supercapacitors, and rechargeable battery systems [3]. Multi-level MoTe_2 -based resistive random-access memory (RRAM) devices with a new switching mechanism and speeds of less than five ns due to an electric-field induced $2H$ to $2H_d$ phase transition. These devices offer fundamentally better reliability and control for faster switching. MoTe_2 -based RRAM devices allow faster switching due to a transition between two crystalline states induced by an electric field. The phase transition from the stable semiconducting $2H$ phase to a more conductive $2H_d$ phase provides a potential path towards better stability [56].

Density functional theory (DFT) calculations showed for bi-layer MoS_2 , WS_2 , MoSe_2 , and MoTe_2 that their fundamental indirect band gaps can be driven to zero by applying external electric field perpendicular to the layers which result in a gap tunability is much larger than in bi-layer graphene [3].

From studying strain effects on the electronic structures of monolayer $2H\text{-MX}_2$ sheets where $M = \text{Mo or W}$ and $X = \text{S, Se or Te}$ by using first-principles calculations, Yun et al. [57] found that even a small different lattice value from the bulk optimum

value could induce the direct-to-indirect bandgap transition, change the gap energy (the positions of the valence band maximum and the conduction band minimum) of the single-layer sheets. The ability of tuning MoTe_2 can affect its topological properties since the Weyl points are sensitive to changes in the lattice parameter of the MoTe_2 crystal.

2.3 Low-dimensional materials in this study

Low-dimensional materials have the potential to be used in a wide range of electronic devices due to their unique properties. In the current research, we evaluated the change in low-dimensional material structures with the change in temperature. We studied the structure in low-dimensional topological materials that show Type-II Weyl semimetal behavior in order to assess their viability as topological phase switches. The powder neutron and x-ray diffraction were used to estimate the phase transition and the coexistence range. Also, we evaluate the temperature dependence of the lattice parameters in $2H$ and $1T'$ phases of MoTe_2 .

CHAPTER 3

SCATTERING THEORY

3.1 Introduction to Scattering

The interaction between a beam of particles and a material will depend on the energy, charge, and spin of the incoming probe. Figure 6 shows how incoming x-ray and neutron beams scatter from a condensed matter sample.

Figure 6. Scattering process of a particle scattering from a sample in a) and b) shows the scattering vector $\vec{Q}$. This relation holds for any type of particles. In elastic scattering $|\vec{K}_i| = |\vec{K}_f|$, while for inelastic scattering $|\vec{K}_i| \neq |\vec{K}_f|$.

From conservation of momentum we can obtain the transfer momentum $\vec{P}$, by:

$$\begin{aligned}\vec{P} &= \hbar\vec{K}_i - \hbar\vec{K}_f = \hbar\vec{Q} \\ \vec{Q} &= \vec{K}_i - \vec{K}_f \\ E &= \hbar\omega = \frac{\hbar^2}{2m}(\vec{K}_i^2 - \vec{K}_f^2)\end{aligned}\tag{1}$$

Scattered particles can be classified as elastic, inelastic, coherent, and incoherent scattering. Elastic or inelastic scattering processes are identified by energy loss. If the energy describing the scattering process remains unchanged this means that it is an elastic case, or has a definite change in energy after interaction with the sample which leads to inelastic scattering. If the scattered particles have interference with

each other then this scattering is called coherent scattering. On the other hand it is called incoherent scattering when there is no phase relationship, and all of the scattered particles have different relative phases. X-ray, neutron, light and electrons are commonly used to provide a range of information about the studied material. The information that can be obtained depends on the interaction of the probe particle and the constituent of the material under study. Figure 7 show how x-ray and neutron interact with a sample. X-rays interacts mainly with the nucleus and this will produce information about the nuclear structure of the sample. Neutrons in the other hand interact with the nucleus and because they have a magnetic moment they also can interact with the magnetic moment of the electron to provide information about the magnetic structure of the sample.

Figure 7. The figure illustrates neutron interactions with the matter which produce nuclear and magnetic scattering

3.2 X-Ray Scattering

X-ray scattering is an impressive arsenal of tools that have been developed over the last century to understand the crystallography of materials. Currently, x-rays can determine the structure and provide insights into the functionality of systems from monolayers to bulk materials.

X-rays were discovered in 1895 by Wilhelm Röntgen, and since that time, it has been considered an essential tool for investigating the field of condensed matter [58]. In 1912 Max von Laue obtained the first diffraction pattern from a crystal. A year later, W.H. Bragg and W.L. Bragg, a father, and son, laid the foundation of crystallography [58]. This allowed the determination of crystal structure by introducing the famous Bragg formula, which describes the x-ray diffraction in terms of reflection of x-ray by lattice planes. Figure 8 illustrate Bragg law and Equation 2 states it. For an x-ray beam scattered from an electron, the scattering event exerts a force on the electron from the x-ray electric field. Then the accelerated electron radiates the scattered wave. If the wavelength of the scattered wave is the same as the incident one, then the scattering is elastic. If the scattered wavelength differs from the incident one, then the scattering is inelastic, and this is also known as the Compton effect [58].

$$n\lambda = 2d \sin\theta \quad (2)$$

The x-ray scattering intensity I is proportional to how efficient the particle in the sample scatter the radiation. This is given by the differential cross section ($\frac{d\sigma}{d\Omega}$) [58].

$$I \propto \left(\frac{d\sigma}{d\Omega} \right) \quad (3)$$

The differential cross section is defined by:

$$\left(\frac{d\sigma}{d\Omega} \right) = \frac{\text{Number of } x\text{-rays scattered per second into } d\Omega}{(\text{incident flux})(d\Omega)} \quad (4)$$

Figure 8. Illustration of Bragg Law, $\vec{K}$ is the incoming wave, $\vec{K}'$ is outgoing wave, and d is the interatomic spacing.

According to Nielson and McMArrow [58] the differential cross section for x-ray yields to:

$$\left(\frac{d\sigma}{d\Omega}\right) = r_o^2 P |F(\vec{Q})|^2 N \frac{\lambda^3}{v_c} \frac{1}{\sin 2\theta} \quad (5)$$

Where r_o is the Thomson scattering length, P the polarization factor, N is the total number of unit cells, λ is the incident beam wavelength, v_c is the volume of unit cell, θ is the integrated angle and $\frac{1}{\sin 2\theta}$ is called the Lorentz factor. $F(\vec{Q})$ is the structure factor which is defined as:

$$F(\vec{Q}) = \overbrace{\sum_j f_{atomic_j}(\vec{Q}, \lambda)}^{\text{Unit cell}} e^{i\vec{Q} \cdot \vec{r}} \overbrace{\sum_n e^{i\vec{Q} \cdot \vec{R}_n}}^{\text{Lattice}} \quad (6)$$

Where $\vec{R}_n$ is the lattice vector, $\vec{r}_j$ is the position of an atom within the unit cell, and the first term sum is over the basis of the atom and the second term is over the lattice. Using $\vec{Q} = \frac{\sin \theta}{\lambda}$, the atomic form factor is defined as:

$$f_{atomic}(\lambda, \theta) = f_o\left(\frac{\sin \theta}{\lambda}\right) + f'(\lambda) + if''(\lambda) \quad (7)$$

Where $f_o\left(\frac{\sin \theta}{\lambda}\right)$ is The atomic form factor that express the charge spacial profile inside the atom at high energies and is obtained by Fourier transform of the electron density [59]. The terms $f'(\lambda)$ and $if''(\lambda)$ are the atomic forwarding scattering factor (also called dispersion corrections) and their values depend strongly on λ . The scattering form factor for x-rays is shown in Figure 9. For the x-ray scattering, the form factor

diminishes monotonically with increasing θ and decreasing λ (as a function of $\frac{\sin\theta}{\lambda}$), has the same sign for all element and has a magnitude that is proportional to the atomic number Z of the scatterer atom.

Figure 9. Comparison between x-ray and neutron form factors. All form factors are normalized to unity at $\frac{\sin\theta}{\lambda} = 0$.

A common technique known as the Laue method uses a broad spectrum of x-rays. The Laue method is historically the oldest x-ray technique and was used in the original discovery of x-ray diffraction. Figure 10 illustrates Bragg and Laue diffraction. The Laue diffraction is used to orient single crystals and to determine their crystal quality. However, with the advent of synchrotron radiation and enormous improvements in computing power and detector technology, Laue diffraction has maintained a renaissance as a technique that provides a fast and efficient means to record diffraction data and is being used to significant effect in dynamical studies of transient crystalline states. One of the advantages of the synchrotron source is producing intense, brilliant photon beams on the very smallest of samples, which had a significant positive effect on the research in condensed matter physics. These x-rays beams can probe the inter-atomic distances in materials.

Figure 10. Comparison between Bragg and Laue scattering.

3.2.1 X-Ray Production

X-rays, which are commonly used for structural determination, can be obtained in labs by a benchtop machine or in a synchrotron. Although lab x-rays are beneficial tools and convenient for performing qualitative and quantitative studies, the quality of the data collected from a synchrotron beamline is of a high-resolution. In the early days of synchrotrons, x-rays were an undesirable by-product in high-energy particle accelerators facilities. In modern synchrotrons, electron beams are accelerated to speeds close to the speed of light, which generates the emission of *bremsstrahlung* radiation, which is emitted when the electron beams path is curved by magnetic fields. The sources of electrons in synchrotron are electron guns where cathode heated to 1000°C to produce a beam of electrons. Electrons are accelerated in an evacuated linear accelerator (LINAC) and then enter a booster ring where electron energy is boosted to the desired energy of the storage ring, which is in the range of GeV. In the storage rings, which can span over a few hundred meters of circumference, radiation is produced in the bending magnets. Bending magnets or undulators which are in the straight section of those rings. Electrons trajectories are controlled by

magnetic fields. A radio frequency (RF) source restores the energy to the beam on each subsequent pass. The x-ray radiation is then directed to beamlines. A beamline is the trajectory of the x-ray beam and the instrumentation that directs the beam towards the experimental assembly area. Each beamline is designed for a specific technique or a specific type of research. Figure 11 shows the different parts of a synchrotron and all beamlines at the Advanced Photon Source (APS) of the Argonne national laboratories, IL.

3.2.2 Synchrotron Beamline Used in This Research

3.2.2.1 Advanced Photon Source (APS) 11-BM

A dedicated high-resolution, high-throughput powder diffraction beamline, 11-BM is located at the Advanced Photon Source (APS) at Argonne National Laboratory. 11-BM is intended to facilitate high-resolution crystallographic structure determination from powder diffraction of complex polycrystalline materials. 11-BM supports a wide range of user interests, from pharmaceuticals through traditional materials science to questions in engineering, catalysis, chemistry, geosciences, physics, and electronics [60].

The x-ray beam size at the sample is ≈ 1.5 mm (horizontal) x 0.5 mm (vertical). The focused beam efficiently utilizes the bending magnet source and minimizes asymmetric diffraction peak broadening from axial divergence even at low angles. The 11-BM beamline couples an efficient focused x-ray beam with a high precision diffractometer circle and perfect Si(111) crystal analyzer detection to achieve high sensitivity and resolution. Instrumental resolution at high Q is better than $\Delta Q/Q \approx 2 \times 10^{-4}$, with a typical 2θ resolution of $<0.01^\circ$ at 30 keV. For mail-in samples, a Kapton capillary tubes will be supplied to the user. These capillary tube inner diameter of 0.80 mm, and an outer diameter that fits snugly inside 11-BM mounting bases. Figure 12 shows 11-BM mail-in Kapton capillary tubes. The capillary holding measured sample

ARGONNE NATIONAL LABORATORY 400-AREA FACILITIES

ADVANCED PHOTON SOURCE

(Beamlines, Disciplines, and Source Configuration)

ADVANCED PROTEIN CHARACTERIZATION FACILITY

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Figure 11. APS plan view shows every beamline and the different parts of the synchrotron from <https://www.aps.anl.gov/Beamlines>

Figure 12. 11-BM sample holder consists of a mounting base, a magnetic cap, and a capillary tube. The mounting base has a unique ten-digit barcode to track the sample at all steps of our mail-in service. A magnetic ring secures caps on mounting bases and provides some protection for sample capillary tubes during shipment. The Kapton tubes have an inner diameter of 0.80 mm, and an outer diameter that fits snugly inside 11-BM mounting base. On the left, the base and the tube filled with a sample is shown. On the right, the picture shows sample bases and capillary tubes, with the protective magnetic cap.

contributes a weak background to the total sample scattering.

3.3 Neutron Scattering

Neutrons were discovered by James Chadwick in 1932. Neutrons are subatomic particles with no net electric charge, a mass of $939.5656 \text{ MeV}/c^2$, and spin $\frac{1}{2}$. Neutron elastic and inelastic scattering has become an important tool for the determination of atomic, magnetic structures, and magnetic excitations. Neutron scattering, non-destructive techniques, are used in biology, chemistry, condensed matter physics, metallurgy, ceramics, and polymers providing information unobtainable by any other means. Sometimes this invaluable information is complementary to that obtained by more traditional methods [61]. Some of the advantages of the neutron scattering technique are neutron wavelengths and energies that well matched to interatomic spacings and excitations in condensed matter. Figure 13 shows length and time domains achieved by neutron scattering techniques. Neutron nuclear scattering does not associate with a form factor. Neutrons carry no charge and penetrate a large volume of the sample. A major disadvantage of this technique is that the scattering length varies irregularly among elements and isotopes for nuclear scattering. Another disadvantage is that neutron scattering is intensity limited, and it is costly to produce neutron beams.

Figure 7 illustrates neutrons interaction with matter. Neutrons interact with matter in two ways. First, they interact with atoms by nuclear forces. Second, they interact with the magnetic fields of unpaired electrons through magnetic dipole interactions. Neutron penetrates deeply into most materials, which makes neutron scattering suitable as a bulk probe.

Neutrons have de Broglie wavelength $\lambda \approx 1 - 2 \text{ \AA}$ and energies of $100\text{-}20 \text{ meV}$. Neutrons with these energies are called thermal neutrons. They are excellent probes of low-energy excitations such as lattice vibrations and spin waves with energies in the meV range. Neutron beams can be produced by fission reaction in a reactor or by spallation due to collisions of high-energy protons with a heavy metal target. Neutron

Figure 13. Length and time domains available with neutron scattering techniques compared to other investigation methods. Source <https://mlz-garching.de/englisch/neutron-research/experimental-methods/elastic-scattering.html>

scattering depends on the scattering length and not the atomic number. This results in light elements being highly detectable, and adjacent elements in the periodic table being easily distinguishable.

3.3.1 Nuclear Neutron Scattering

Travelling neutrons have a wavelength given by de Broglie equation:

$$\lambda = \frac{h}{m_n v} \quad (8)$$

Where m_n is the neutron mass, and h is Plank constant. As the neutron approaches the atomic nucleus, it can be scattered by the nuclear forces or by the spin-spin interactions. The magnetic moment of the neutron can interact with both the nuclear magnetic moments and the unpaired electron moments. The neutron wavelength is about $10^4 - 10^5$ times larger than the nuclear forces range which makes the nuclear neutron scattering just like a point scattering and the scattered neutron form factor, or scattering length b , for a given element is independent of $\frac{\sin\theta}{\lambda}$ (Figure 9) [59]. Similar to x-ray scattering, the nuclear neutron scattering intensity, is proportional to the differential cross-section as:

$$I \propto \left(\frac{d\sigma}{d\Omega} \right) = \frac{\text{Number of neutrons scattered per second into } d\Omega}{(\text{incident flux})(d\Omega)} \quad (9)$$

The Analysis of scattered neutrons from a random distribution of scatterer lead to the following expression for the differential cross section [62, 5].

$$\frac{d\sigma}{d\Omega} = |\bar{b}|^2 \left| \sum_n \exp(i\vec{Q} \cdot \vec{r}_n) \right|^2 + N \overline{|b - \bar{b}|^2} \quad (10)$$

Where $\bar{b}$ is the mean scattering length for all atoms, $\vec{Q}$ is the scattering vector, $\vec{r}_n$ is the position vector of the nth atom in the system, and N is the number of atoms in the measured system. In Equation 10 the first term represents the coherent scattering and the second is for the incoherent scattering.

3.3.2 Magnetic Neutron Scattering

As mentioned earlier, neutrons can be scattered due to the interactions between their magnetic moment and the orbital and spin magnetic moments of the atoms

in a crystal. The unpaired electron distribution is comparable to thermal neutron wavelength, and interference effects occur, which leads to a magnetic form factor. Figure 9 shows the neutron magnetic form factor compared to the x-ray form factor. The neutron magnetic form factor falls more rapidly compared to the X-ray form factor because only outer electrons are involved in the magnetic scattering [5]. The geometry of the magnetic neutron scattering is shown in Figure 14. The unit vectors $\hat{\kappa}$, $\hat{\mu}$, and $\hat{P}$ are the scattering vector, the atom magnetic moment, and polarization vector respectively. The magnetic interaction vector $\vec{q}$ is defined as:

$$\vec{q} = \hat{\kappa} \times (\hat{\mu} \times \hat{\kappa}) = \hat{\mu} - (\hat{\kappa} \cdot \hat{\mu}) \hat{\kappa} \quad \text{with } |q| = \sin \alpha \quad (11)$$

where α is the angle between $\hat{\mu}$ and $\hat{\kappa}$. Bacon [6] described the the magnetic cross section for neutron magnetic scattering for atoms with parallel or anti-parallel magnetic moments as:

$$\left(\frac{d\sigma}{d\Omega} \right)_{mag.} = q^2 S^2 \left(\frac{e^2 \gamma}{m_e c^2} \right)^2 |f|^2 \quad (12)$$

where S is the spin quantum number of the atom, e is the charge of the electron, m_e is the electron mass, c is the speed of light, γ is the magnetic moment of the neutron, and f is the magnetic form factor.

When the magnetic moments are highly correlated as in ordered magnetic structures, the magnetic neutron scattering is coherent and gives strong diffraction effects.

3.3.3 Neutron Beam Production

The main neutron beam sources for research are either a nuclear reactor or a spallation source. Each of the two methods is different and thus yield neutron beams of neutron beams of different characteristics energies. At nuclear reactor sources, a self-sustaining critical fission nuclear reaction produces excess neutrons as a by-product of the chain reaction. The coolant of the heart of the reactor acts as a reflector to concentrate neutrons. A moderator slows the neutrons. The resulting

Figure 14. Geometry of the neutron magnetic scattering. The vectors $\hat{k}$, $\hat{\mu}$, and $\hat{P}$ are the scattering vector, the atom magnetic moment, and polarization vector respectively. θ is the angle between incident or scattered neutron and the reflective plane. α is the angle between the scattering vector $\hat{k}$ and the magnetization vector $\hat{\mu}$. The magnetic interaction vector $\vec{q}$ lies in the plane of $\hat{k}$ and $\hat{\mu}$ and is perpendicular to $\hat{k}$ (adapted from [5, 6]).

neutrons are thermal neutrons with a Maxwellian distribution of wavelengths are in the range of 1 - 2 Å.

At a spallation neutron source (SNS), high-intensity neutrons are generated. The SNS ion source produces H^{-1} ions that are formed into a pulsed beam. This beam is delivered to a large linear accelerator (LINAC) where it accelerates to 1 GeV which is equivalent to 90% the speed of light. The LINAC consists of normal conducting and superconducting radio-frequency cavities that accelerate the beam and a magnetic lattice that provides focusing and steering. LINAC cavities are cooled with liquid helium to a temperature of 2 K. The H^{-1} ions pulse from the LINAC is wrapped into the ring through a diamond stripper foil that strips the electrons from the negatively charged hydrogen ions to produce the protons H^{-1} that circulate in the ring. Approximately a thousand turns are accumulated and then all these protons are “kicked” out at once producing a pulse less than 1 millionth of a second (10^{-6} seconds) in duration that is delivered to the target. At the target vessel which is a heavy metal

(like Pb, W, Ta or Hg). During neutron production, proton pulses collide with the target. When high-energy protons hit the nucleus of heavy metal atoms, neutrons are spalled or released. The neutrons emerging from the target are slowed down by moderators that are located above and below the target. Slowed neutrons, to low-energy neutrons suitable for research, are guided into beam tubes attached to instrument stations. The advantage of using a pulsed neutron source is that it provides highly effective intensity neutrons which are obtained for the same average neutron production. The pulse source defines one element of the resolution function. It has a lower background and nearly constant resolution. Spallation neutron sources are capable of providing peak thermal neutron fluxes at least an order of magnitude greater than those available from reactors. One disadvantage to the pulsed neutron beams is that time-of-flight (T.O.F.) techniques are obligatory [61].

3.3.4 Neutron Beamlines Used in This Research

3.3.4.1 POWGEN

POWGEN is a third-generation design of a time-of-flight (TOF) powder diffractometer at a spallation neutron source (SNS), ORNL. The instrument is optimized for both parametric studies of materials under a wide range of conditions like temperature, pressure, flowing gases, and ab-initio crystal structure determinations of complex solid-state materials. The geometric design of the instrument allows for all detected scattered neutrons to be focused onto a single diffraction profile yielding a high count rate while preserving good resolution data over d -spacings 0.3 - 10 Å with $\frac{\delta d}{d} = 0.0015$ at a $d = 1$ Å. The diffractometer consists of three major components, the sample vessel, secondary collimation, and detectors. The high-resolution requirement dictates that POWGEN has a long 60 m flight path from moderator to sample and consequently must be housed in a separate building outside the main instrumental hall. In order to control the sample environment, POWGEN diffractometer started

to use an orange cryostat with a temperature range from 2 K to 300 K and an IPNS Lucyfe furnace with a temperature range of 200 - 1000°C using a powder sample in vanadium can. In a time-of-flight powder diffractometer, the data is recorded as the number of neutrons as a function of time-of-flight. The de Broglie wavelength is modified to be as follows:

$$\lambda = \frac{ht}{m_n L} \quad (13)$$

Where h is the Plack's constant, t is the TOF, m_n is the neutron mass, and L is the total neutron flight path. The interatomic spacing d_{hkl} is given by:

$$d_{hkl} = \frac{ht}{2mL \sin \theta} \quad (14)$$

Where the units for t is μs , d is in $\text{\AA}$, and L is in meters ($L = 60$ m for POWGEN) [5, 63].

3.3.4.2 NOMAD

The Nanoscale Ordered MAterials Diffractometer (NOMAD) is a neutron time-of-flight diffractometer designed to determine pair distribution functions (PDF). It can be used for a wide range of materials from short-range ordered liquids to long-range ordered crystals. The determination of the PDF by diffraction experiments involves the measuring of the scattered intensity as a function of momentum transfer $\vec{Q}$. The momentum transfer is a Fourier transform of the pair distribution function (as discussed in the PDF section). High intensity, large accessible momentum transfer range, high stability, and good momentum transfer resolution are all requirements needed to get good results in PDF experiments. NOMAD, at the moment, is the fastest neutron diffractometer in its class with proportionate stability and precision. It is already a valuable tool for the determination of both disordered materials and crystalline structures [64].

3.4 Powder Diffraction

The rapid growth in scientific knowledge in the last few decades has led to the discovery and fabrication of new materials. These materials are highly desired in many fields and applications, such as medical equipment. The need for new material types continues in today's market. Presently, a noticeable effort of scientific research focuses on discovering, fabrication, and analyzing new materials with desired properties. Analyzing new fabricated materials is an essential step in understanding their properties. A critical part of the analyzing process is to determine how the material compounds are arranged. One of the well-understood techniques in determining material cell arrangement is powder diffraction. The powder diffraction method was developed independently in Germany by Debye and Scherrer in 1916 and the United States by Hull in 1917. Powder diffraction provides powerful means for the identification of unknown minerals, and it might be the most widely used technique for characterizing materials. It is a very effective method for providing information on unit cell dimensions and can be described as an analytical technique for phase identification of crystalline material. Generally, the samples are made into a powdery form, consisting of fine grains of single crystalline material to be studied. One of the significant advantages of using powder diffraction is that it provides explicit material determination with minimal sample preparation requirements. Since the pioneering papers of Hugo Rietveld (1967 and 1969), powder diffraction analysis has been improved, which made it perform well in many applications.

The determination of unknown solids is critical in studies of geology, environmental science, material science, engineering, and biology. Powder diffraction can be used to characterize crystalline materials, identify fine-grained minerals such as clays, determine unit cell dimensions, and measure the purity of a sample. With specialized techniques, powder diffraction can also determine crystal structures using Rietveld refinement, determine of modal amounts of minerals (quantitative analysis), charac-

terize thin film samples, and make textural measurements such as the orientation of grains in a polycrystalline sample.

To visualize diffraction from an ideal polycrystalline sample, we can use the Ewald construction, as shown in Figure 15 a and b. In a powder sample, we have a large amount of randomly oriented scatters. The superposition of reciprocal lattice Ewald points from a powder sample with the same d_{hkl} will form a cone, as shown in panel c from Figure 15. Since a crystal has many (hkl) planes with d-spacing d_{hkl} , a powder diffraction pattern will consist of a set of concentric cones known as Debye-Scherrer cones. In a 2D detector, those cones will show as rings, which can be represented as a radial plot that represents the diffraction angle 2θ with the scattered intensity from the powder sample. The diffraction rings and the corresponding diffraction pattern are shown in Figure 16.

One essential limitation of the powder diffraction method is the loss of information due to the peak overlap. Modern advances in powder diffraction helped to overcome some of its limitations. Advances in powder diffraction technique over the last several decades are related to the development of analysis methods like the Rietveld method, structural solution methods, instrumentation, and new software packages. Also, newly developed algorithms to determine the structure of powder diffraction data, had improved significantly in recent years especially the quality of the intensity extraction. Software packages are capable of deconvoluting non-equivalent overlapping reflections accurately for reciprocal space structure solution. The usage of synchrotron x-ray has added advantages over lab x-ray data such as tunability, high brilliance, and relatively low divergence. Data from synchrotron sources can be collected on very small samples by using smaller wavelength x-ray, which reduces systematic errors associated with larger wavelengths. Development of pulsed neutron sources and the availability of time-of-flight neutron diffractometers has allowed collecting a full diffraction pattern with a constant resolution, which is another achievement

Figure 15. Panels a and b show the Ewald construction. In panel a, the 2D section of the reciprocal lattice is shown, which represents a sphere with radius $1/\lambda$. The incident, scattered wavevectors are $\vec{k}_0/2\pi$ and $\vec{k}/2\pi$. The scattering vector is $\vec{\kappa}/2\pi$. The diffraction condition is satisfied when the scattering vector ends at a reciprocal lattice point. Panel b shows the Ewald construction for powder diffraction where randomly oriented crystallites cause lattice points to be replaced by concentric spheres. The dashed line shows the cone of diffraction (Debye-Scherrer), which results as an intersection between the concentric sphere and the reflection sphere. Panel c shows an illustration of Debye-Scherrer concentric cones as a result of scattering from a powder sample. All illustrations are from reference [5]

for the powder diffraction method. The non-ambient sample environment for diffraction methods such as low/high temperature, high-pressure, and the ability to apply magnetic fields has significant advantages.

Figure 16. A powder diffraction ring pattern from silver behenate (a layered organic crystal) and the radial line plot of the scattered intensity (from <https://www.physics.upenn.edu/heiney/datasqueeze/basics.html>).

CHAPTER 4

ANALYSIS METHODS

4.1 Rietveld Refinement

The development of computers and the ability to use programmed codes in the 1960s enabled the use of the least-squares methods to refine structures. These methods were first applied to the refinement of single crystal structures and later used to the analysis of powder diffraction data. Hugo M. Rietveld received the Gregori Aminoff Prize in 1995 in recognition of his development of profile refinement methods for the analysis of powder diffraction data. His pioneer work in developing this method is demonstrated in the famous papers published in 1967 and 1969 on structure refinement [65, 66]. Rietveld noticed that if a pattern could be modeled, the fit between a calculated pattern and measured data could be optimized. The Rietveld method, in the early 1980s, was developed to refine structural data collected with time-of-flight neutrons and synchrotron x-ray. This, along with the development of software packages for Rietveld refinement like DBWS and GSAS permitted a more precise and accurate data analysis from powder diffraction. Rietveld recognized that a diffraction pattern is a smooth curve that consists of Gaussian peaks on top of a smooth background and the best way of extracting the maximum information is to represent the observed intensity as:

$$Y_c = Y_b + \sum Y_{hkl} \quad (15)$$

where Y_c is the calculated model of the diffraction, Y_b is the contribution from the background, and Y_{hkl} is the Bragg reflection [59]. The model function Equation (15)

components are parametrized by the crystal parameters (atomic coordinates , thermal displacements parameters U_{xx} or U_{iso} , and site occupancies) and by the diffraction experiment parameters (unit cell (a, b and c), peak profile broadening (U, V, W or X, Y), instrumental parameter (Z, λ), etc.). The adjustable parameters are refined by the least-squares method in order to minimize the weighted difference between the observed and the calculated intensities. A minimization of:

$$M = \sum w(Y_o - Y_c)^2 \quad (16)$$

will give an estimate of the minimum variance. The weight w is computed from the variance of Y_o . The quality of the least-squares refinement is shown by the residual function R_p , the weighted residual function R_{wp} , the goodness-of-fit GoF, and the reduced χ^2 which are defined as:

$$R_p = \frac{\sum |Y_o - Y_c|}{\sum Y_o} \quad (17)$$

$$R_{wp} = \frac{M}{\sum wY_o^2} \quad (18)$$

$$GoF = \sqrt{\frac{\sum M}{N_{obs} - N_{var}}} \quad (19)$$

$$\chi^2 = \frac{\sum M}{N_{obs} - N_{var}} \quad (20)$$

where N_{obs} is number of observations and N_{var} is the number of variables during the refinement process. The

4.2 Pair Distribution Function

The Pair Distribution Function (PDF) method is a total scattering technique for determining the local order in nanostructured materials [67]. PDF was first published in 1915 soon after the first x-ray diffraction experiments were performed [67]. In

1927, Zernicke and Prins derived the Fourier relationship between the real-space pair density and the Debye scattering equation, which lead to the creation of the PDF method. The very first x-ray PDF experiments were carried out by Debye himself with Menke in 1930. [68]. The Debye equation was based on the average intensity distribution as:

$$I(Q) = \sum \sum f_i(Q) f_j^*(Q) \frac{\sin(Qr_{ij})}{Qr_{ij}} \quad (21)$$

where $Q = 4\pi \sin(\theta)/\lambda$, where λ is the scattering wavelength and 2θ is the scattering angle, f is the atomic form factor, and r_{ij} is the magnitude of the distance between any two of the N atoms in the sample [69].

The PDF is a measured probability of finding an atom at a given distance r from another atom. Therefore, the PDF method provides structural information about materials on different length scales. The PDF $g(r)$ is calculated by Fourier transforming the total scattering data which include Bragg peaks and the diffused scattering data. The reduced pair distribution function $G(r)$ is widely used and is related to $g(r)$ by $G(r) = 4\pi r[g(r) - 1]$. The advantage of using $G(r)$ over $g(r)$ is that it is calculated directly from Fourier transform (equation 22).

$$G(r) = 2\pi \int_{Q_{min}}^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ \quad (22)$$

The structure function, $S(Q)$, is extracted from the Bragg and diffuse components of x-ray, neutron, or electron powder diffraction intensity.

$$G_c(r) = \frac{1}{r} \sum_i \sum_j \left[\left(\frac{b_i b_j}{\langle b^2 \rangle} \right) \delta(r - r_{ij}) \right] - 4\pi r \rho_0 \quad (23)$$

The diffuse scattering offers important information about the local deviations from the average structure [67]. The calculated PDF, denoted $G_c(r)$, is calculated by equation 23 from the structural model [70]. Here, ρ_0 is the atomic number density of the material and $\rho(r)$ is the atomic pair density, which is the mean weighted density of neighbor atoms at distance r from an atom at the origin. The sum $\rho(r)$ is over all

Figure 17. PDF method measure the inter-atomic distances between atoms in the crystal. Each peak corresponds to a distance, where neighbouring atoms are most likely found in the sample.

the atoms in the sample, b_i is the scattering factor of atom i , $\langle b \rangle$ is the average scattering factor and r_{ij} is the distance between atoms i and j [68]. Figure 17 shows the PDF method and how the peaks in the total scattering data correspond to the inter-atomic distance of a sample.

PDF utilizes all diffraction information, including high Q values and diffused scattering data. This is important, especially in cases where disorder exists in a crystalline system [67]. In practice, values of Q_{min} and Q_{max} are determined by the experimental set-up, and Q_{max} is often held below the experimental maximum to eliminate noisy data from the PDF since the signal to noise ratio becomes unfavorable in the high Q region. Once the experimental PDFs are determined, they can be analyzed directly or modeled. PDF modeling, is performed by adjusting the parameters of the structure model, such as the lattice constants, atom positions, and anisotropic atomic displacement parameters in order to maximize the agreement between the calculated and an

experimental PDF. The goodness-of-fit parameter, which measures the agreement, χ^2 is calculated using equation 24. Where the sum is all measured data r_i and G_e is the experimental reduced pair distribution function $G(r)$, G_c is the calculated reduced pair distribution function, and σ is the estimated standard deviation. This procedure is implemented in PDFgui [71] and Diffpy-CMI [72], which are widely used for PDF analysis.

$$\chi^2 = \sum_{i=1}^N \frac{(G_e(r_i) - G_c(r_i))^2}{\sigma^2} \quad (24)$$

A powerful approach is simply to compare experimentally determined PDFs from samples under study and from known control samples. Insightful information can be learned simply from visual inspections and by taking differences to look for residual signals. Numerical tools that compare the likeness, or degree of correlation, between two curves also give insight.

The use of scattering techniques is very common in condensed matter physics. Scattering techniques provide unique results about the nuclear and magnetic structure of a material and its behavior. It is difficult to obtain similar information by using other techniques such as Raman scattering and NMR. For this reason we used neutron and x-ray scattering to understand the properties of the materials investigated in this work. For studying the nuclear and magnetic properties of Mott-insulators like $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ and the WSM MoTe_2 , powder neutron scattering was performed at POWGEN (ORNL) the Canada Neutron Beam Center. X-ray powder diffraction at 11-BM (APS) was performed to complement the neutron data. Rietveld refinement was used to analyze both neutron and x-ray powder diffraction data. In order to examine local structure of $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$, neutron total scattering experiments was performed at NOMAD, ORNL. PDF analysis was used to analyze this experimental data.

4.3 Electrical Resistivity

The relation between the temperature and the resistivity of a material can be shown as $\rho(T) = \rho_o[1 + \alpha(T - T_o)]$, where ρ_o is the resistivity at a standard T_o , and α is coefficient of resistivity. For metals, the coefficient of resistivity, α , is positive, and for semiconductor and insulators, it is negative.

In doped semiconductors, the Arrhenius temperature dependence resistivity follows equation 25.

$$\rho(T) = \rho_o \exp\left(\frac{E_a}{k_B T}\right) \quad (25)$$

where ρ_o is the pre-exponential factor, E_a is the activation energy and K_B Boltzmann constant. Many transition metal compounds display resistivity saturation at high temperatures, where the resistivity slope decreases significantly as a function of temperature [73]. The resistivity usually level close to Mott-Ioffe-Regel (MIR) limit of $\rho_{MIR} = 3\pi^2\hbar/e^2k_f^2a$, where a is the lattice parameter, is ≈ 100 - $3000 \mu\Omega \text{ cm}$ [74, 73].

In Mott insulators, the metal-to-insulator (MIT) transition can be driven by different kind of external perturbations, such as thermal energy, electric field, and optical stimuli [7]. In the initial state the material is in the insulating phase when a perturbation is introduced a reduction in the resistivity several order of magnitude. If the perturbation is removed the system return to its original insulating state (Figure 18).

4.3.1 Variable-Range Hopping

In Mott insulator, where the ground state is still insulating, a strong correlation between bad-metal state and Mott variable-range hopping model VRH localized state exists where the size of the Mott VRH activation energy E_a is linearly proportional to the critical temperature T_c [74]. The Mott VRH describes the hopping conduction at low temperatures in strongly disordered systems with localized charge-carrier states

Figure 18. Metal-insulator-transition features the figure from reference [7]. In Mott insulators, the metal-to-insulator (MIT) transition can be driven by different kind of external perturbations.

[75] as in equation 26:

$$\rho = \rho_o \exp(T_o/T)^{1/4} \quad (26)$$

where A is a pre-factor constant, T_o is a characteristic temperature [75]. This can be generalized to Equation 27:

$$\rho(T) = A \exp\left(\frac{T_o}{T}\right)^p \quad (27)$$

where A is a pre-factor constant, T_o is a characteristic temperature, and p denotes the value of the exponent reflecting the hopping dimensionality and Coulomb interactions [76]. The value for p represent the dimensionality of the hopping mechanism and is equal to $\frac{1}{(d+1)}$ where $d = 1, 2$, and 3 . A linear curve is expected when the $\ln(\rho)$ vs. $T^{1/p}$ and the Mott activation energy is calculated from its slope.

4.4 Magnetic Properties

In the presence of a magnetic field, the thermodynamic identity can be written as:

$$dF = -SdT - MdB \quad (28)$$

Where F is the free energy, B is the external magnetic field and M is the total magnetic moment of the system. Then the magnetization can be expressed as :

$$M = \left(\frac{\partial F}{\partial B} \right)_T \quad (29)$$

The energy of the magnetic dipole in the presence of a magnetic field is $E = -\gamma SB$ where S is the spin with values ± 1 and γ is the magnitude of the magnetic moment. The probability of a state having energy E is:

$$P_{\uparrow\downarrow} = \frac{e^{\pm\beta\gamma B}}{e^{\beta\gamma B} + e^{-\beta\gamma B}} \quad (30)$$

Then the expectation of the magnetic moment m is:

$$m = \gamma P = \gamma \tanh \left(\frac{\gamma B}{k_B T} \right) \quad (31)$$

For small magnetic fields where $\frac{\gamma B}{k_B T} \ll 1$ then :

$$m = \frac{\gamma^2}{k_B T} B \quad (32)$$

So $m \propto B$ and the constant of proportionality $\frac{\gamma^2}{k_B T}$ is called the magnetic susceptibility χ :

$$\chi = \frac{C}{T} \quad (33)$$

Equation 33 is called Curie's law and the constant $C = \frac{\gamma^2}{k_B}$. The Curie temperature T_c is the temperature above which the spontaneous magnetization vanishes; it separates the disordered paramagnetic phase at $T > T_c$ from the ordered ferromagnetic phase at $T < T_c$. In paramagnetic material, the magnetic susceptibility obeys the Curie law. In situations where there are short-range ferromagnetic or antiferromagnetic

domains, the magnetic susceptibility $\chi = \frac{C}{T-\theta}$ is called Curie–Weiss law, and θ is the Curie–Weiss temperature. In an antiferromagnet material, the spins are ordered in an antiparallel arrangement with zero net moments at temperatures below the magnetic ordering temperature or the Néel temperature. The susceptibility at $T = T_N$ of an antiferromagnet is not infinite but has a discontinuity. The temperature dependent magnetic susceptibility in paramagnet (Figure 19 a), ferromagnets (Figure 19 b), and antiferromagnets (Figure 19 c), where the magnetic transition temperature T_N shows as a kink in the magnetic susceptibility and has a maximum value.

Figure 19. Temperature dependent magnetic susceptibility behavior in different materials adapted from [8]

In iron oxychalcogenides, the temperature-dependent magnetic susceptibility has a very distinct feature, and it usually shows a broadening peak at the Néel temperature T_N . The sharp discontinuity shown in Figure 20 c is broadened. This indicates the onset of the long-range antiferromagnetic ordering for $T < T_N$ (Figure 20) [9, 10, 11, 77]. The broadening of magnetic susceptibility maximum and its deviation from the magnetic Curie-Weiss law, in the paramagnetic phase above T_N , indicates strong antiferromagnetic short-range correlations [77, 10].

Figure 20. Temperature dependant magnetic susceptibility in iron oxychalcogenides Mott insulators showing the broad maximum that characterize magnetic susceptibility in this material. Panels a and b show magnetic susceptibility in $\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$ and $\text{La}_2\text{O}_2\text{Fe}_2\text{OS}_2$ respectively, where a Curie tails are observed at low temperature from [9]. Panel c) shows a typical magnetic susceptibility in iron oxychalcogenides as in $\text{Sr}_2\text{F}_2\text{Fe}_2\text{OS}_2$ and $\text{Ba}_2\text{F}_2\text{Fe}_2\text{OS}_2$ from [10]

CHAPTER 5

STRUCTURAL STUDY OF CALCIUM IRON OXYCHALCOGINIDES

5.1 Introduction

The study of superconductivity high- T_c (HTSC) in iron pnictides and chalcogenides, like that of HTSC Cu-based superconductors, is largely focused on understanding the relevance of electron correlation to the onset of the superconducting phase. Iron-based materials and cuprates enter the superconducting phase from different conditions. Copper oxide parent material are Mott insulators with strong electron correlation. On the other hand, the parent compounds of Fe-based superconductors are generally designated as Hund's metals that may exhibit metallic, semiconducting, or semimetallic behaviour in the normal state. In FeSC, the electron correlation can be related to Hund's rule coupling whereas electron correlation in cuprates is thought to be an effective Hubbard interaction [78]. Numerous published works suggest that Fe-based superconductors are close to the Mott boundary; however, relatively few iron-containing materials, that show both Mott insulating behavior and superconductivity, have been discussed in the literature. The search for such materials has motivated further research of the iron oxychalcogenides $RE_2O_2Fe_2OM_2$ (RE = rare-earth atoms, M = S, Se). These are paramagnetic (PM) Mott insulators in the normal phase and it has been argued that they can be driven toward the metallic phase, and possibly superconductivity, by doping [79, 13]. However, superconductivity has not yet been reported in chemically doped variants of $RE_2O_2Fe_2OM_2$ materials.

Figure 21. $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ resistivity and magnetic susceptibility from reference [11].

Transport measurements indicate that $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ is an AFM semiconductor with a strong electron correlation and narrow band gaps (see Figure 21) [11]. However, this electron correlation is unexpected because the Fe-Fe distance is the smallest among all the oxychalcogenides [11]. Band theory suggests that $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ should be more metallic than other iron-oxychalcogenides (which are insulators) because of the short ion-ion distance ought to yield greater Fe band overlaps [8, 80]. Further-

more, theoretical calculations, LDA+U [11] and LDA+DMFT [81], suggested that the stoichiometric variant $\text{Ca}_2\text{O}_3\text{Fe}_3\text{S}_2$ should be metallic but this compound has yet to be successfully grown [11]. This is surprising since the smaller Fe-Fe bond length might be thought to induce metallicity due to the greater iron band overlap. The Fe-Fe bond lengths in $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ are less than those in iron-pnictides, iron-chalcogenides as well as other iron oxychalcogenides.

Current theories of high temperature superconductivity suggest that electrons must organize into Cooper pairs in order for a material to exhibit superconducting behavior [82, 83]. Superconductivity often emerges from insulators that are altered by doping or external stimuli. Electrons in insulators experience significant repulsive interactions that tend to keep electrons localized at atomic positions. In contrast, electrons in metals are delocalized, interact weakly, and are free to conduct electricity. Therefore, the formation of Cooper pairs should have different mechanisms for metals compared to insulators. This contrast is central to the debate about the origin of high temperature superconductivity in iron based materials. Many iron-based materials are metallic in the normal phase; however, before entering superconducting phase these systems are believed to harbor insulating characteristics in close proximity to a Mott insulating phase. Figure 22 shows the location of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ on iron pnictide phase diagram.

The newly reported iron oxychalcogenide [11] $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ has space group $P4/mmm$ and consists of alternate stacking of antiperovskite like $[\text{Ca}_2\text{FeO}_2]^{2+}$ layers and $[\text{Fe}_2\text{OS}_2]^{2-}$ building blocks along the c axis as illustrated in Figure 23. Figure 23 (right) shows the Fe_2OS_2 plan where the Fe^{2+} ions are located between oxygen atoms forming a square-planar layer. This is an anti-configuration with respect to the CuO_2 layer of high- T_c cuprates. The two-dimensional $[\text{Fe}_2\text{OS}_2]^{2+}$ layers contain Fe_2OS_2 planar sheets separated from the $[\text{Fe}_2\text{OS}_2]^{2-}$ layers by Ca ions. The Fe2 ions in the $[\text{Fe}_2\text{OS}_2]^{2-}$ blocks are six fold-coordinated by two O ions and four sulfur ions, forming

Figure 22. Pnictide phase diagram near a magnetic quantum critical point. The blue dot denotes the quantum critical point determined by the critical tuning parameter w_c . The blue line is the line of the thermally driven antiferromagnetic transition and the dashed line is a structural transition [12]. The red star represents the location of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ within the phase diagram.

an FeO_2S_4 octahedron. The Fe(1) sites are fully occupied, while the Fe2 ions sites are about 20% deficient [11].

Figure 23. The crystal structure of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ is shown in panel a). Panel b) shows the Fe2 and O2 atoms forming the square-planer in the Fe_2OS_2 layer. The Fe-Fe distance ($D_{\text{Fe-Fe}}$) between any two iron atoms in this plane is 2.7902 Å.

Figure 24. The octahedra in $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ structure. Each octahedron consists of an Fe2 ion, two O2 ions, and four S ions forming FeO_2S_4 .

The decreasing of the Fe-Fe bond length ($d_{\text{Fe-Fe}}$) in $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ results in enhanced insulating properties instead of an expected increased metallicity [11, 77, 10]. This surprising behaviour illustrates the need for further study of calcium iron oxy-chalcogenide $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ as shown in Figure 25. For this reason, we investigated the structural and magnetic ordering implications of this effect. We also performed the first investigation of the structural behavior of chalcogen-doped variant of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$. We concentrated our efforts to better understand the nuclear structural therefor, the magnetic Rietveld refinement was not done in this work even though we collected magnetic data from neutron powder diffraction experiment. The presented work shows results of the structural Rietveld analysis of data obtained from neutron diffraction experiments conducted at POWGEN beamline at the ORNL, high-resolution XRD from 11-BM, APS and lab-based XRD.

Figure 25. Activation energy dependence of the Fe-Fe bond length (D_{Fe-Fe}) iron oxychalcogenides including the material in this study which are shown in gray and green stars. Pink markers shows iron based superconductors. Activation energy and bond length values used in this graph were from references [11, 13, 9, 14, 15]

5.2 Experimental Methods

5.2.1 Synthesis

Ca₂O₂Fe_{2.6}OS_{2-x}Se_x ($x = 0$ and 0.25) samples were fabricated at the Beijing National Laboratory for Condensed Matter Physics by Professor Minghu Fang's research group. The appearance of synthesized samples were shiny, black single crystals or polycrystalline materials. Powder samples were made by grinding reagents with an agate pestle and mortar and then pressing the mixture into pellets under glove box conditions. Pellets were placed in an alumina crucible and sealed inside an evacuated quartz tube. The sealed quartz tube was heated slowly to 1173 K and held at this reaction temperature for 24 hours before furnace cooling to room temperature. The resulting single crystalline material has a black plate-like form with typical sizes of 0.5x0.5x0.5 mm³. Efforts to produce large single-crystal of Ca₂O₂Fe_{2.6}OS_{2-x}Se_x have proven to be unsuccessful and, to the best of our knowledge, there are no published reports of large single crystals.

Figure 26. Powdering a sample with mortar and pestle as part of sample preparation for POWGEN experiment.

5.2.2 Diffraction Experiments

5.2.2.1 X-ray diffraction

High-resolution x-ray powder diffraction experiments were performed on two materials through the mail-in program at 11-BM, APS. The samples $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ and $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ were measured with a wavelength $\lambda = 0.457842 \text{ \AA}$ and at 295 K and 90 K.

Room temperature, lab-based x-ray powder diffraction measurements were performed at the University of Louisville, using a Bruker D8 Discover diffractometer with Cu $K\alpha$ radiation and a PANalytical Empyrean diffractometer with Cu $K\alpha$ radiation of $\lambda = 1.54056 \text{ \AA}$. The Rietveld refinements analysis for all x-ray powder diffraction data were performed using GSAS-II software. crystal lattice parameters, atomic positions, and other relevant parameter were refined during this process.

5.2.2.2 Neutron diffraction

We have performed neutron powder diffraction experiments on $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ and $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ at the POWGEN beamline of SNS in ORNL. All samples were prepared inside a glovebox. We used a mortar and pestle to pulverize materials into a fine powder. Vanadium cans of 3 mm diameter were filled with approximately 3 g of powder sample. Figure 26 shows the sample preparation for the POWGEN experiment. For all measurements, we used a chopper frequency of 60 Hz with a wavelength center at 1.5 Å with a minimum wavelength of 0.967 Å and a maximum wavelength of 2.033 Å. This corresponds to d -spacings of 0.4854 - 14.5795 Å. Samples were measured at 10, 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275 and 300 K approximately, for an hour each to get a full high-quality diffraction pattern. A temperature ramp measurement was performed on each sample as well. Each ramp measurement lasted about 5.8 hours. Seventy scans were collected where each scan lasted about 5 minutes. The ramp temperature started from 10 K up to 80 K. All data were reduced using the Mantid Plot program [84].

5.3 Results

5.3.1 Electrical Resistivity Measurements

The temperature-dependent resistivity $\rho(T)$ measurements for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ and $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ are shown in Figure 27. The $\rho(T)$ for both materials has a negative coefficient of resistivity, which indicates a semiconducting behavior, as we expected from this material [11]. The magnitude of the resistivity at 300 K for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ is 6.02 Ωcm and for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ is 0.53 Ωcm .

The $\text{Ln}(\rho)$ dependence with $\frac{1}{T}$ is shown in Figure 28 a) for the pure and b) for the doped sample. In the figure, both samples show a non-linear Arrhenius plots. In order to calculate activation energy E_a using the thermal activation model $\rho = \rho_0 \exp(\frac{E_a}{KT})$,

Figure 27. Temperature dependent of resistivity $\rho(T)$ for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ ($x = 0, 0.25$).

a fit function $f(x) = a_1 + a_2x$ was used to fit the temperature-dependent $\text{Ln}(\rho)$ (Table 1). Since those curves were non-linear, we selected 3 ranges where a linear fit would have better quality. For $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ sample we used the following ranges: for fit one from 275.546 K to 299.73 K, fit two from 205.198 K – 262.289 K and fit three from 159.645 K to 196.65 K. For $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ sample the fits were performed over the three temperature ranges: fit one from 249.576 K to 300.154 K, fit two from 180.174 K to 244.887 K and fit three from 150.649 K to 175.261 K. The values of activation energy E_a , for both sample, increases with temperature (Table 1).

Table 1. Activation energy calculation from the Arrhenius plots in Figure 28 using the fit function $f(x) = a_1 + a_2x$.

Temp. range (k)	fit param. a_o	fit param. a_1	χ^2	E_a (eV)
$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$				
275.546-299.730	-3.3451 ± 0.0568	1549.4 ± 16.4	0.0015	0.13352 ± 0.00141
205.198-262.289	-0.12399 ± 0.029	679.12 ± 7.02	0.0024	0.05852 ± 0.00060
159.645-196.65	1.6849 ± 0.0239	301.48 ± 4.23	0.0020	0.02598 ± 0.00036
$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$				
249.576-300.154	-3.557 ± 0.00535	877.67 ± 1.47	0.0016	0.07563 ± 0.00013
180.174-244.887	-3.1433 ± 0.0074	777.1 ± 1.55	0.0013	0.06697 ± 0.00013
150.649-175.261	-2.6448 ± 0.0273	687.65 ± 4.45	0.0008	0.05926 ± 0.00038

Figure 28. Resistivity measurement data above 150 K is used to fit the thermal activation model $\rho = \rho_0 \exp(\frac{E_a}{kT})$. Panel a) and b) show the fits for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ and $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$, respectively.

The Mott activation energy was calculated, for the pure and doped material as shown in Figure 29 and Table 2, using the Mott variable range hopping model $\rho(T) = \rho_0 \exp(T_0/T)^{1/4}$. In Figure 29 the $\text{Ln}(\rho)$ vs. $T^{-1/4}$ showed a non-linear curve when plotted for the temperature range from ≈ 80 K to 300 K. The activation energy E_a for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ sample was calculated for the most linear part of that curve, from 85.4 K - 140.9 K (Table 2 a) and its value was 1.38 ± 0.004 meV. The doped sample also showed non-linear curve for $\text{Ln}(\rho)$ vs. $T^{-1/4}$ which can be fitted in to two linear parts, the first with temperature from 84.91 K to 106.56 K and the second fit covered temperatures from 122.22 K to 241.28 K. The calculated activation energy E_a values for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ was 2.47 ± 0.05 meV for the first fit and 5.04 ± 0.008 meV for the second one.

Figure 29. Temperature dependant resistivity measurements are fitted to variable-range hopping VRH model.

Table 2. VRH model activation energy calculation using a fit function $f(x) = a_1 + a_2x$ (Figure 29).

Temp. range (K)	fit param. a_o	fit param a_1	χ^2	E_a (eV)
$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$				
85.433-140.9	-0.91453 ± 0.0152	15.993 ± 0.0495	0.0011	0.00138 ± 0.000004
$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$				
84.911-106.556	-5.6284 ± 0.19	28.700 ± 0.5940	0.0057	0.00247 ± 0.00005
122.221-241.281	-14.828 ± 0.0226	58.526 ± 0.0820	0.0146	0.00504 ± 0.000008

Figure 30. Temperature dependent magnetic susceptibility measurement showing antiferromagnetic behaviour for a) $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$, and b) $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$.

5.3.2 Magnetic Susceptibility Measurements

The magnetic susceptibility measurements with respect to temperature was performed in an applied magnetic field of 1000 Oe. The susceptibility of the two materials behave differently with temperature. The $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ susceptibility curve shows typical antiferromagnetic behaviour with a discontinuity at 74.092 K, which indicates that a magnetic phase transition occurs at this temperature. The $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ susceptibility shows a broad maximum around 74 K, with a

small peak centered at 64 K.

5.3.3 X-ray Diffraction

Figure 31 along with Tables 3 and 4 summarize the results of Rietveld refinement of lab based x-ray powder diffraction using GSAS-II software. The XRD was performed on both $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ and $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ at room temperature with $\lambda = 1.54 \text{ \AA}$. The calculated pattern (shown in blue) fits well with the measured pattern for both samples with intensity mismatched in some peaks. (Figure 31). Also, the samples have a similar peak profile. However, the relative peak intensity differs between $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ and the pure $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$. In Tables 3 and 4, using the tetragonal symmetry and space group $P4/mmm$ provides good fit for the XRD data as the R_w and χ^2 values are 0.041 and 0.015 for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$, 0.050 and 0.014 for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$. The refined lattice parameters, the atomic positions, isotropic thermal displacement parameter U_{iso} and atomic coordination are presented in those tables as well. During the Rietveld analysis, only the Fe atomic site occupancy was refined for the $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ sample. For $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ sample Fe, S and Se atomic site occupancy were refined, and the sum of S and Se atomic site occupancy was set to one.

The x-ray powder diffraction patterns obtained at 11-BM, APS are displayed in Figures 32 and 33. Data were collected at 90 K and 295 K. In Figure 32, the 295 K measurement has higher intensity than the 90 K for the pure sample. On the other hand, the diffraction pattern at 295 K showed higher peak intensities than the 90 K in the doped sample as shown in Figure 33. The diffraction experiment data were analyzed by Rietveld refinement method using GSAS-II software [85]. Tables 5 and 6 summarize the Rietveld analysis for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$, while Tables 7 and 8 summarize the Rietveld analysis for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$.

Figure 31. Rietveld Refinement profiles for the pure sample $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ in the upper panel and the doped sample $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ in the lower panel, from room temperature lab-based XRD.

Table 3. Rietveld Refinement results for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ from room temperature lab-based XRD. Space Group $P4/mmm$ $a = 3.94485(5)$ Å, $c = 8.7481(1)$ Å unit cell volume = $136.138(3)$ Å³.

$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$					
Atom	x	y	z	Occup.	$U_{iso}(\text{Å}^2)$
Ca	0.0	0.0	0.8063(8)	1.0	0.009(3)
O1	0.5	0.0	1.0	1.0	0.041(9)
O2	0.0	0.0	0.5	1.0	0.002(1)
Fe1	0.5	0.5	1.0	1.0	0.001(3)
Fe2	0.5	0.0	0.5	0.73(1)	0.027(5)
S	0.5	0.5	0.7039(9)	1.0	0.023(4)

Coordination

$d_{\text{Fe1}-\text{O1}}(\text{Å})$	1.97376(0)
$d_{\text{Fe2}-\text{O2}}(\text{Å})$	1.97376(0)
$d_{\text{Fe1}-\text{S}}(\text{Å})$	2.6073(9)
$d_{\text{Fe2}-\text{S}}(\text{Å})$	2.6564(6)
$d_{\text{Fe2}-\text{Fe2}}(\text{Å})$	2.79132(0)
$d_{\text{Ca}-\text{O1}}(\text{Å})$	2.5715(6)
$a_{\text{S}-\text{Fe2}-\text{S}}(\text{deg.})$	95.8(3)
$a_{\text{S}-\text{Fe2}-\text{S}}(\text{deg.})$	180.0(0)
$a_{\text{Ca}-\text{O1}-\text{Ca}}(\text{deg.})$	98.7(3)

$$\text{wR}_P=0.041 \quad \text{R}_P=0.053 \quad \text{GoF}=1.24 \quad \chi^2=0.015$$

Figure 32. X-ray powder diffraction from 11-BM, APS of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ at temperatures 90K and 295 K.

Table 4. Rietveld Refinement results for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ from room temperature lab-based XRD. Space Group $P4/mmm$ $a = 3.95089(6)$ Å, $c = 8.8094(2)$ Å unit cell volume = $137.510(4)$ Å³.

$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$					
Atom	x	y	z	Occup.	$U_{iso}(\text{\AA}^2)$
Ca	0.0	0.0	0.805(1)	1.0	0.0482(58)
O1	0.5	0.0	1.0	1.0	0.0044(96)
O2	0.0	0.0	0.5	1.0	0.0091(151)
Fe1	0.5	0.5	1.0	1.0	0.0218(56)
Fe2	0.5	0.0	0.5	0.76(1)	0.0442(76)
S	0.5	0.5	0.702(1)	0.86(3)	0.0757(93)
Se	0.5	0.5	0.702(1)	0.12(3)	0.0121(33)

Coordination

$d_{\text{Fe1}-\text{O1}}(\text{\AA})$	1.9754(0)
$d_{\text{Fe2}-\text{O2}}(\text{\AA})$	1.9754(0)
$d_{\text{Fe1}-\text{S}}(\text{\AA})$	2.623(10)
$d_{\text{Fe2}-\text{S}}(\text{\AA})$	2.661(7)
$d_{\text{Fe2}-\text{Fe2}}(\text{\AA})$	2.7937(0)
$d_{\text{Ca}-\text{O1}}(\text{\AA})$	2.617(7)
$a_{\text{S}-\text{Fe2}-\text{S}}(\text{deg.})$	95.9(4)
$a_{\text{O2}-\text{Fe2}-\text{O2}}(\text{deg.})$	180.0(0)
$a_{\text{Ca}-\text{O1}-\text{Ca}}(\text{deg.})$	98.0(4)

$$wR_P=0.0495 \quad R_P=0.057 \quad \text{GoF} = 1.17 \quad \chi^2=0.014$$

Figure 33. X-ray powder diffraction from 11-BM, APS of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ at temperatures 90 K and 295 K.

Table 5. Proposed model for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ from 11-BM XRD at 295K. Space Group $P4/mmm$ $a = 3.94552(1)$ Å, $c = 8.75195(2)$ Å unit cell volume = 136.243(1) Å³.

Ca ₂ O ₂ Fe _{2.6} OS ₂					
Atom	x	y	z	Occup.	U _{iso} (Å ²)
Ca	0.0	0.0	0.8127(1)	0.986(2)	0.0072(3)
O1	0.5	0.0	1.0	0.832(6)	0.0025(9)
O2	0.0	0.0	0.5	0.946(10)	0.0085(15)
Fe1	0.5	0.5	1.0	0.995(2)	0.0089(3)
Fe2	0.5	0.0	0.5	0.746(2)	0.0193(3)
S	0.5	0.5	0.7049(1)	0.951(3)	0.0056(3)
Coordination					
d _{Fe1-O1} (Å)	1.97276(0)				
d _{Fe2-O2} (Å)	1.97276(0)				
d _{Fe1-S} (Å)	2.5827(11)				
d _{Fe2-S} (Å)	2.6660(8)				
d _{Fe2-Fe2} (Å)	2.78990(0)				
d _{Ca-O1} (Å)	2.5652(6)				
a _{S-Fe2-S} (deg.)	95.46(4)				
a _{O2-Fe2-O2} (deg.)	180.0(0)				
a _{Ca-O1-Ca} (deg.)	100.54(3)				
wR _P =0.2685 R _P = 0.1850 GoF = 4.64 χ ² =0.2152					

Table 6. Proposed model for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ from 11-BM XRD at 90K. Space Group $P4/mmm$ $a = 3.94091(1)$ Å, $c = 8.70806(3)$ Å unit cell volume = $135.243(1)$ Å³.

$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$					
Atom	x	y	z	Occup.	$U_{iso}(\text{Å}^2)$
Ca	0.0	0.0	0.8116(1)	0.800(2)	0.0003(2)
O1	0.5	0.0	1.0	0.805(8)	0.0152(13)
O2	0.0	0.0	0.5	0.760(10)	0.0165(20)
Fe1	0.5	0.5	1.0	0.814(2)	0.0008(3)
Fe2	0.5	0.0	0.5	0.627(2)	0.0175(4)
S	0.5	0.5	0.7041(1)	0.778(3)	0.0006(3)

Coordination

$d_{\text{Fe1}-\text{O1}}(\text{Å})$	1.97045(0)
$d_{\text{Fe2}-\text{O2}}(\text{Å})$	1.97045(0)
$d_{\text{Fe1}-\text{S}}(\text{Å})$	2.5765(12)
$d_{\text{Fe2}-\text{S}}(\text{Å})$	2.6538(8)
$d_{\text{Fe2}-\text{Fe2}}(\text{Å})$	2.78664(0)
$d_{\text{Ca}-\text{O1}}(\text{Å})$	2.5642(6)
$a_{\text{S}-\text{Fe2}-\text{S}}(\text{deg.})$	95.89(4)
$a_{\text{O2}-\text{Fe2}-\text{O2}}(\text{deg.})$	180.0(0)
$a_{\text{Ca}-\text{O1}-\text{Ca}}(\text{deg.})$	100.43(3)

$$\text{wR}_P=0.2685 \quad \text{R}_P= 0.1850 \quad \text{GoF} = 4.64 \quad \chi^2=0.2152$$

Table 7. Proposed model for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ from 11-BM XRD at 295K. Space Group $P4/mmm$ $a = 3.952598(1) \text{ \AA}$, $c = 8.813372(2) \text{ \AA}$, unit cell volume = $137.692(1) \text{ \AA}^3$.

Ca ₂ O ₂ Fe _{2.6} OS _{1.75} Se _{0.25}					
Atom	x	y	z	Occup.	U _{iso} (Å ²)
Ca	0.0	0.0	0.8139(1)	0.990(37)	0.0079(2)
O1	0.5	0.0	1.0	0.967(35)	0.0171(10)
O2	0.0	0.0	0.5	0.905(33)	0.0058(13)
Fe1	0.5	0.5	1.0	0.988(37)	0.0044(3)
Fe2	0.5	0.0	0.5	0.774(29)	0.0247(3)
S	0.5	0.5	0.7034(1)	0.890(32)	0.0162(65)
Se	0.5	0.5	0.7034(1)	0.110(32)	0.0023(18)
Coordination					
d _{Fe1-O1} (Å)	1.97630(0)				
d _{Fe2-O2} (Å)	1.97630(0)				
d _{Fe1-S} (Å)	2.6143(10)				
d _{Fe2-S} (Å)	2.6680(7)				
d _{Fe2-Fe2} (Å)	2.79491(0)				
d _{Ca-O1} (Å)	2.5684(6)				
a _{S-Fe2-S} (deg.)	95.59(4)				
a _{O2-Fe2-O2} (deg.)	180.0(0)				
a _{Ca-O1-Ca} (deg.)	100.61(3)				
wR _P =0.1962 R _P = 0.1586 GoF = 3.11 χ ² =0.0969					

Table 8. Proposed model for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ from 11-BM XRD at 90K. Space Group $P4/mmm$ $a = 3.94752(1)$ Å, $c = 8.77023(2)$ Å, unit cell volume = 136.666(1) Å³.

$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$					
Atom	x	y	z	Occup.	$U_{iso}(\text{\AA}^2)$
Ca	0.0	0.0	0.8121(1)	0.949(32)	0.0082(2)
O1	0.5	0.0	1.0	0.971(32)	0.0218(10)
O2	0.0	0.0	0.5	0.857(29)	0.0002(11)
Fe1	0.5	0.5	1.0	0.923(31)	0.0064(3)
Fe2	0.5	0.0	0.5	0.732(25)	0.0239(3)
S	0.5	0.5	0.7027(1)	0.925(28)	0.0155(88)
Se	0.5	0.5	0.7027(1)	0.075(28)	0.0033(16)
Coordination					
$d_{\text{Fe1}-\text{O1}}(\text{\AA})$		1.9754(0)			
$d_{\text{Fe2}-\text{O2}}(\text{\AA})$		1.9754(0)			
$d_{\text{Fe1}-\text{S}}(\text{\AA})$		2.623(10)			
$d_{\text{Fe2}-\text{S}}(\text{\AA})$		2.661(7)			
$d_{\text{Fe2}-\text{Fe2}}(\text{\AA})$		2.7937(0)			
$d_{\text{Ca}-\text{O1}}(\text{\AA})$		2.617(7)			
$a_{\text{S}-\text{Fe2}-\text{S}}(\text{deg.})$		95.98(3)			
$a_{\text{O2}-\text{Fe2}-\text{O2}}(\text{deg.})$		180.0(0)			
$a_{\text{Ca}-\text{O1}-\text{Ca}}(\text{deg.})$		100.27(3)			
wR _P =0.1659 R _P = 0.2094 GoF = 4.02 χ^2 =0.1611					

5.3.4 Neutron Powder Diffraction and Order Parameter

Temperature dependent neutron powder diffraction patterns of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ are shown in Figure 34. Three magnetic peaks can be identified by comparing high temperature to lower temperature diffraction patterns. The highest intensity is the peak located at T.O.F. = $1.3179 \times 10^5 \mu\text{s}$ (intensity = 157.6), the second highest intensity peak is at T.O.F. = $86709 \mu\text{s}$ (intensity = 80) and the weakest magnetic peak intensity is at T.O.F. = $79535 \mu\text{s}$ (intensity = 84).

Figure 34. Neutron powder diffraction from POWGEN of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ at temperatures 10 K, 150 K and 300 K. the insert show the evolution of the most intense magnetic peak with temperature.

Figure 35 shows the temperature dependence neutron powder diffraction for the sample $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$. There are five magnetic peaks that can be identified. The highest intensity peak is located at T.O.F. = $1.324 \times 10^5 \mu\text{s}$ (highest intensity = 114.3), followed by the peak at T.O.F. = $61988 \mu\text{s}$ (intensity = 104.7), then at T.O.F. = $79619 \mu\text{s}$ (intensity = 100.8), then the peak at T.O.F. = $73912 \mu\text{s}$ (intensity = 82.5), and the lowest magnetic peak is located at T.O.F. $86523 \mu\text{s}$ with intensity = 75.6.

Figure 35. Neutron powder diffraction from POWGEN of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ at temperatures 10 K, 150 K and 300 K.

We have performed neutron powder diffraction during temperature ramps of 2 K steps at POWGEN beamline, ORNL. This experiment was aimed to calculate the magnetic order parameter for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ samples. For $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ sample, Figure 36 shows the result of order parameter fit analysis. The red dots represent the height of the selected magnetic peak with respect to changes in temperature. We have used equation $f(T) = c_1(1 - \frac{T}{c_2})^{c_3}$ for performing the fit analysis. The fit parameters for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ were: $c_1 = 179.64 \pm 2.35$, $c_2 = 75.01 \pm 0.0194$, and $c_3 = 0.24553 \pm 0.0127$.

Figure 36. Order parameter fitting for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ sample based on temperature dependence neutron powder diffraction calculated from the magnetic peak at T.O.F. $1.324 \times 10^5 \mu\text{s}$ ($d_{hkl} = 4.364 \text{ \AA}$). The order parameter describes the development of magnetic order. In $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ the continuous magnetic phase transition is from the paramagnetic phase for $T > T_N$ to the antiferromagnetic phase when $T < T_N$. The magnetic transition temperature T_N based on this fitting is $75.01 \pm 0.0194 \text{ K}$.

5.4 Discussion

5.4.1 Electrical Resistivity Measurements

Transition metal compounds usually display saturated resistivity, which has a substantial decrease in the slope of the resistivity as a function of temperature [73]. The temperature-dependent resistivity for both materials shows a semiconducting behavior (Figure 27), although the pure sample is one order of magnitude higher than the doped sample, signifying that the electron are more localized in the doped sample compared to the pure one [28]. The resistivity at 300 K for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ is $6.02 \text{ } \Omega\text{cm}$ and for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ is $0.53 \text{ } \Omega\text{cm}$ are well beyond the Mott-Ioffe-Regel (MIR). The measurements of the pure and doped samples have many similarities to the reported by Zhang et al. [11]. Our resistivity measurement curvature differs from what Zhang et al. results reported [11], and the values for their resistivity at temperatures higher than 250 K are more elevated than our measurements.

The calculated activation energy E_a for the pure sample shows a temperature dependence trend; it decreased with temperature. The doped sample shows the same trend with more consistent values of activation energy. Based activation energy E_a and the semiconducting behavior, the band gap (E_g) can be assumed to be $(E_g) = 2E_a$ yielding small band gap (E_g) below 14 meV for both material over all temperature ranges (Table 1) [74]. In the studied material doping with Se increase the lattice parameter and the unit cell volume while having a complex behavior with the activation energy. The activation energy at higher temperature (the first temp. range in Table 1 and Figure 28) decreases in value with doping. The average calculated activation energy E_a for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ was 0.07267 ± 0.00079 eV which is comparable to the reported value of 0.073 eV [11]. For the doped sample $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ the activation energy E_a was 0.06728 ± 0.00021 eV. For $\text{La}_2\text{O}_2\text{Fe}_2\text{OM}_2$, which is similar structurally to $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ and $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$, the activation energy were 0.19 eV and 0.24 eV, for $M = \text{Se}, \text{S}$ respectively [13].

Activation energy E_a values for some iron oxychalcogenides are presented in Table 9. The $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ and $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ materials which have the lowest E_a values compared to the other compounds.

Table 9. Activation energy values and critical exponent for the magnetic order parameter for some iron oxychalcogenides. The values for our E_a values are the average values for all temperature ranges from Table 1.

Compound	Activation Energy (eV)	β	Reference
$\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$	0.19	0.129	[14, 9]
$\text{La}_2\text{O}_2\text{Fe}_2\text{OS}_2$	0.24	0.133	[14, 9]
$\text{Ce}_2\text{O}_2\text{FeOSe}_2$	0.32	0.28	[14]
$\text{Ce}_2\text{O}_2\text{Fe}_2\text{OSe}_2$	0.26	0.11	[14]
$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$	0.073	-	[11]
$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$	0.07267 ± 0.00079	0.123	This work
$\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$	0.06728 ± 0.00021	-	This work

5.4.2 Magnetic Susceptibility Measurements

The pure sample magnetic susceptibility (Figure 30 a) shows an antiferromagnetic behavior with a discontinuity at 74 K indicating the magnetic phase transition temperature for the pure sample which is lower than the reported 77 K [11]. The presence of a sharp peak in the magnetic susceptibility indicates long-range AFM phase transition and it is different than the other iron oxychalcogenides that usually show a broad maxima [11, 9, 77, 10]. The broadening of the magnetic susceptibility maximum and its deviation from Curie-Weiss law indicates the strong antiferromagnetic short-range correlations. This behavior is similar to $\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$ [9] and $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ and indicates a 2D magnetic system [77]. Figure 20 shows the temperature dependence magnetic susceptibility in iron oxychalcogenides where all materials have the characteristic broad peak. $\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$ and $\text{La}_2\text{O}_2\text{Fe}_2\text{OS}_2$, panels a and b in Figure 20 respectively, and panel c shows both $\text{Sr}_2\text{F}_2\text{Fe}_2\text{OS}_2$ and $\text{Ba}_2\text{F}_2\text{Fe}_2\text{OS}_2$ with the former having a broader peak than the latter. Zhang et al. [11] studied the affect of doping on the $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ material and found that doping suppress the long-range magnetic ordering due to the increase of randomness in Fe2 vacancies with doping.

5.4.3 X-ray Diffraction

In this study we performed a detailed nuclear structural study of the Mott insulator $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ ($x = 0, 0.25$). We have performed, two x-ray powder diffraction experiments. The first used a lab-based x-ray diffractometer and the second used synchrotron x-ray at 11-BM, APS. The lab-based XRD enabled us to characterize our samples. $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ samples were measured at room temperature by a 1.54 Å wavelength lab based x-ray. The results of the Rietveld analysis are shown in Figure 31 and Tables 3 and 4. We have chosen the tetragonal crystal system with space group $P4/mmm$ to perform the Rietveld analysis. From the anal-

ysis we have concluded that the chosen crystal structure, and symmetry, fits well the measured diffraction pattern. The quality of the Rietveld analysis is illustrated in Figure 31 and the values of fit parameters (R_w, χ^2) in Table 3 and 4. Zhang et al.[11] reported powder x-ray diffraction for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ and concluded that tetragonal system with space group $P4/mmm$ best fit their data. They have found some unfitted peaks in their analysis and concluded that they might need to consider a super-cell with $\sqrt{8}a \times 2c$. For our lab-based XRD analysis we did not consider any superlattice because the Rietveld analysis fits had good quality without the need to include a superlattice in the refinement.

In order to further investigate the structure of this material with better precision, we conducted a high resolution x-ray powder diffraction experiment at 11-BM, APS. Both materials were measured with $\lambda = 0.4578 \text{ \AA}$ at room temperature and at 90 K. The peaks in the XRD data at 90 K for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ have lower intensity than the room temperature as in Figure 32. Studying the behaviour of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{1.75}\text{Se}_{0.25}$ XRD, we found that the peaks sharpen at low temperature compared to room temperature as expected.

Attempts to perform Rietveld fitting for $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ samples was not trivial. The fit quality represented by R_w and χ^2 values in Tables 5-8, were worse than our fits from the lab-based analysis. A probable explanation for this finding is that the high resolution synchrotron diffraction data had many smaller peaks that were not visible in the lab x-ray due to the presence of superlattice. Also, the synchrotron x-ray have greater penetration which can lead to greater scattering intensity.

The presented model to describe the crystal structure of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ resulted in poor Rietveld fits (Tables 5-8). This can be due to the presence of a superlattice, as suggested by Zhang et al. [11], contamination during the synthesis process, or the need to model the disorder in this material better and include this to represent a better-fitted crystal model to the measured diffraction data.

In order to investigate the reported superlattice structure presence in the pure $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$ material, we performed the indexing procedure and Pawley [86] refinement using GSAS-II software. We could not determine the reported [11] superlattice using the mentioned procedures by using Lab-based x-ray data. When using the high-resolution synchrotron data, we confirmed the presence of a supercell with space group $P4/mmm$ and lattice parameters $a = 11.13888 \text{ \AA}$, $c = 17.47045 \text{ \AA}$, and unit cell volume $= 2167.638390 \text{ \AA}^3$. The superlattice only present in the pure sample. Our investigation in the doped sample did not provide us with any structure. The presence of iron Fe2 vacancies has been linked to the superlattice structure in the pure samples. Zhang et al. [11] studied how the ordered Fe2 vacancies promote the presence of the superlattice. The evolution of superlattice peaks (at about 23.4° and 24.8° Figure 6 from reference [11]) with doping indicated that the superlattice peaks intensity decrease with increasing of the Se doping, which lead to their conclusion that the Se doping diminishes the superlattice related peaks in the XRD pattern.

5.4.4 Neutron Powder Diffraction and Magnetic Order Parameter

A temperature dependent neutron powder diffraction experiment was conducted at POWGEN beamline, ORNL. Diffraction patterns were obtained in 2 K steps from the base temperature up to 80 K to study the behavior of the magnetic peaks. The magnetic order parameter is proportional to the peak with the highest detected intensity, located at T.O.F. $= 1.324 \times 10^5 \mu\text{s}$, was used to perform the order parameter calculation. It is possible to study the magnetism within the sample because the neutron has a magnetic moment and interacts with the electrons moments around the atom. We can detect magnetic Bragg peaks caused by the arrangement of the magnetic atoms. The results of temperature ramps measurements were used to calculate the magnetic order parameter. Our magnetic order parameter results (Figure 36) showed that of the order parameter has a $\beta = 0.12277 \pm 0.0064$. Our β is

very close to $1/8$ value that corresponds to the two dimensional antiferromagnetic Ising model [87, 9]. This critical exponent value is similar to the values reported for $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S},\text{Se})_2$ and other Fe-based materials [9, 14] (see Table 9). The magnetic phase transition temperature based on the magnetic peak fit analysis is about 75 K, which is similar to the value obtained from the magnetic susceptibility measurement. For the doped sample, the analysis of the magnetic order parameter did not reveal any ordering.

5.5 Conclusion

Electrical resistivity measurement, magnetic susceptibility measurement, x-ray diffraction, and neutron diffraction were the main techniques used in this study. The high resolution powdered x-ray, and neutron diffraction experiments are among the first on $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$. High resolution x-ray diffraction is a powerful tool to identify the crystal structure and symmetry. The current study Rietveld analysis showed that the tetragonal structure with space group $P4/mmm$ was the best crystal structure to fit our materials. The unit cell volume increased with temperature, while the atomic site occupancies increased with decrease in temperatures. Also, the Fe2 atom had the lowest site occupancy which is equivalent to vacancies in the $[\text{Fe}_2\text{OS}_2]^{2-}$ plane about 20% to 30 %, the presence of Fe2 vacancies was expected and reported for the pure sample [11], our measurements confirmed the presence of those vacancies for the pure and the doped sample.

On the other hand, temperature dependent neutron diffraction was used to study the magnetic order parameter of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_2$. From the fit of the magnetic peak intensity with respect to temperature, magnetic phase transition temperature was determined to be at 75 K. Using the same analysis, $\beta = 0.12277 \pm 0.0064$ was determined and it corresponded to the two dimensional antiferromagnetic Ising model.

The $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ materials showed interesting features at low tempera-

tures. The unit cell volume of the sample increased as temperature decreased, and the atomic site occupancy increased. These two observation are most likely related since the increase in the unit cell volume will encompass larger numbers of atoms. The presence of AFM ordering in the Fe atoms might affected the crystal structure at low temperature. Although the doping did not affect the conducting behavior it had a greater impact on the magnetic susceptibility suppressed the magnetic ordering greatly.

5.6 Limitations and Future Work

One of the possible next steps is to study the magnetic structure in details for the $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ Mott insulators . There is currently limited understanding of the magnetic phase and magnetic structure of $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ which challenge our understanding of the Mott insulators behavior. The current work should support a detailed magnetic Rietveld refinement. The affect of doping on the magnetic structure to confirm the transport measurement across dopings. A limitation of the present study is the presence of vacancies in the atomic sites. These vacancies affected the quality of the Rietveld analysis fits. In future work, the vacancies can be modeled and implemented into the fit analysis process.

CHAPTER 6

LOCAL STRUCTURE OF LANTHANUM IRON OXYCHALCOGINIDES

6.1 Introduction

Superconductivity is one of the most exciting physics phenomena. Since the discovery of superconductivity, about a century ago, many researchers have worked to understand this phenomenon and the material that exhibits this property. Iron-based superconductors (FeSCs) had attracted tremendous attention among the superconducting materials because they have high-transition T_c temperatures. In FeSCs, the superconductivity is generated through the pairing mechanism of electron-electron Coulomb interaction. By comparison, conventional superconductors have a different superconductivity mechanism. In the conventional superconductors, the electron-phonon coupling initiates the superconductivity phase [88, 89]. FeSCs and cuprates share many similarities in their phase diagram, both High- T_c superconductors show the superconductivity in the vicinity of other competing phases like the nematic phase and spin-density-wave in FeSCs. Despite these similarities, FeSCs different compared to the cuprates in many aspects like the metallic phase of the parent, the conduction layer crystal structure, and the spin symmetry of the antiferromagnetic order[90].

In order to understand the nature of the superconductivity mechanism, it is essential to know how the superconductivity arises in FeSCs systems. Previously it was thought that magnetic fluctuations were the underlying origin of superconductivity since it arises near the magnetically ordered state. However, a more recent study revealed that there is another non-superconducting state, also called a nematic, besides

the magnetism [91]. Since the superconductivity in the cuprates superconductors are based on the electron or hole doping into a strongly correlated Mott insulating phase [92], it is crucial to study the Mott-insulating phase of iron superconductors in order to understand the mechanism of high-temperature superconductivity in these systems.

Nematicity is the condition of being nematic, or extent, to which a material is nematic. It was first observed in ordered crystalline liquids and in solid materials nematicity was seen in superconducting materials phase diagram before the superconducting phase. Mazin et al. [93] stated that “Nematic phases are frequently found in organic matter. The defining characteristic of these phases is orientational order in the absence of long-range positional order, resulting in distinctive uniaxial physical properties. It has also been proposed that nematic order exists in some electronic systems, and may even play a role in mediating high-temperature superconductivity”. The breaking of the electronic symmetry compared to the lattice is a distinguishing feature of electronic nematic phases. Therefore, nematic behavior can be defined as the existence of anisotropy in a property that locally breaks the symmetry of the crystal and/or reciprocal lattice structure but globally preserves it [94]. Strong evidence strongly leads to the electronic mechanism of nematicity, placing nematic order in the class of correlation-driven electronic instabilities [17].

Superconductivity originates near an antiferromagnetic (AFM) order, in both iron pnictides and iron chalcogenides. It is affected by the magnetism and the bad metal state [28]. The bad metal behavior is due to the proximity to a Mott transition. Song et al. [28] studied the Mott insulator $\text{NaFe}_{0.5}\text{Cu}_{0.5}\text{As}$ and suggested that the electron correlations are sufficient to place it in proximity to Mott transition. They concluded that in iron pnictides and iron chalcogenides, the high-temperature superconducting transitions are induced by the electron correlations, bad-metal behavior, and the magnetism. In this work, the local structure of the Mott insulating iron

oxychalcogenides $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ was studied. $\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$ has been described as a Mott insulator, and theoretical work suggested that it is more strongly correlated than LaFeAsO [95]. $\text{La}_2\text{O}_2\text{Fe}_2\text{OS}_2$ show Mott insulating properties due to the narrowing of the Fe d -electron band and correlation effects [77].

Figure 37. Crystal structure of lanthanum iron oxychalcogenide (left) and the octahedra (right), where the Fe atom is surrounded by four Se atoms and two O2 atoms.

Mayer et al. was the first to report the antiferromagnetic (AFM) insulator $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ [96]. These iron oxychalcogenides are layered mixed anion materials containing more than one anionic species in a single phase. $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ layers consists of a body-centered tetragonal crystal structure ($I4/mmm$) with Fluorite-like $[\text{La}_2\text{O}_2]^{2+}$ layers and $[\text{Fe}_2\text{O}]^{2+}$ sheets separated by M^{2-} anions where $M = \text{S}$ or Se . In this structure, $[\text{Fe}_2\text{O}]^{2+}$ consists of anti- CuO_2 arrangement with Fe^{2+} cations is four coordinated by M^{2-} (above and below the plane) and two in-plane oxygens, forming a tilted Fe-centered FeO_2Se_4 tilted octahedra [96, 95, 97]. Similar

to LaFeAsO and FeSe, the Fe plane has approximately 90° Fe-Se-Fe intersections. However, the Fe plane contains additional O^{2-} Ions [95]. Figure 37 shows the crystal structure of $La_2O_2Fe_2OSe_2$ and its octahedra. The $La_2O_2Fe_2O(S, Se)_2$ does not endure a structural phase transition at low temperatures.

$La_2O_2Fe_2O(S, Se)_2$ are structurally similar to parent compounds of iron pnictides, and it was thought that $La_2O_2Fe_2OS_2$ material could be driven into superconductivity through doping. To date, this was not achieved experimentally. The magnetic structure for $La_2O_2Fe_2O(S, Se)_2$ was studied intensively [98, 99, 79, 9]. The magnetic order temperature, also called Néel temperature (T_N), is the temperature above which an antiferromagnetic material becomes paramagnetic. It is the temperature at which the thermal energy becomes large enough to destroy the microscopic magnetic ordering within a material. In the $La_2O_2Fe_2O(S, Se)_2$, the transition is from antiferromagnetic (AFM) to paramagnetic (PM) ordering is at $T_N = 90.2$ K for $M=Se$ and $T_N = 107.1$ K for $M=S$ [9]. The AFM magnetic structure of $La_2O_2Fe_2O(S, Se)_2$ adopts a multicomponent 2- k magnetic structure [95].

The purpose of this investigation was to explore the local structure of the Mott insulators $La_2O_2Fe_2O(S, Se)_2$. Neutron powder diffraction (NPD) and the pair distribution function (PDF) technique were used to study the relationship between the structure and magnetism in those materials.

6.2 Experimental Methods

6.2.1 Synthesis

$La_2O_2Fe_2O(S, Se)_2$ were synthesized at the Beijing National Laboratory for Condensed Matter Physics by Professor Minghu Fang's re-search group. The samples were prepared by a solid-state reaction method from stoichiometric amounts of high purity La_2O_3 , S, Se, and Fe powders. The appropriate mixture of these powders was grounded properly, pelletized, and then heated in an evacuated quartz tube at 1030°

C for 72 hours, and the process was repeated three times. Samples obtained were confirmed by x-ray powder diffraction measurements to be of a high-quality single phase [9, 96].

6.2.2 Neutron Powder Diffraction

Roughly 5 g of powdered sample was needed to fill a 3 mm diameter vanadium sample holder. A time-of-flight (T.O.F.) neutron powder diffraction (NPD) measurement was performed at POWGEN diffractometer at the Spallation Neutron Source (SNS) of the Oak Ridge National Laboratory (ORNL). The center wavelengths and d -spacing range of neutrons were 1.5 Å and (0.49664 - 13.50203 Å) respectively. The data were analyzed using Rietveld refinement were performed using GSAS-II software [85].

6.2.3 Pair Distribution Function

We performed a neutron total scattering experiments using the Nano-scale Ordered Materials Diffractometer (NOMAD) beamline at SNS, ORNL. The measurements allowed the determination of the atomic pair distribution function. Both materials $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ powders were loaded and sealed in a vanadium can inside a glove-box. Samples were placed in an orange cryostat and exposed to the neutron beam at various temperatures from 30 K to 300 K. Sixteen measurements were performed for each sample with additional data points near the Néel temperature. Data were collected for approximately 2 hours at each temperature. An empty 3 mm vanadium can was also measured for 2 hours in order to collect a background measurement. The background measurement was used to perform background subtraction from the measured samples data.

The atomic pair distribution function (PDF), which involves the Fourier transformation of the total scattering data into real space to obtain the pair-wise atomic

correlation [67], was calculated by:

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho} \int_{Q_{min}}^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ \quad (34)$$

and $G(r) = 4\pi r \rho_0 (g(r) - 1)$

where $G(r)$ is the reduced pair distribution function, $S(Q)$ is the normalized structure factor, and Q is the scattering vector. The scattering vector is defined as $Q = \frac{4\pi}{\sin(\theta)}$, in which λ and θ are the neutron wavelength and scattering angle respectively. The calculated reduced pair distribution function $G_c(r)$ is obtained from the structural model using equation (35) [70].

$$G_c(r) = \frac{1}{r} \sum_i \sum_j \left[\left(\frac{b_i b_j}{\langle b \rangle^2} \right) \delta(r - r_{ij}) \right] - 4\pi r \rho_0 \quad (35)$$

where b_i is , b_j and $\langle b \rangle$ are the average scattering power of the sample atoms. The summation is over all atoms i and j in the model, and r_{ij} is the distance separating any given pair of atoms. PDF data were refined and analyzed using PDFGUI [71] programsuite for the PDF analysis values for Q_{min} and Q_{max} were 0.1 Å and 31.4 Å respectively.

6.3 Results

We have performed a neutron powder diffraction at POWGEN at SNS to confirm the average crystal structure. The NPD data were used to perform Rietveld refinement analysis using GSAS-II software [85]. Figure 39 (a) and (b) show the Rietveld refinement of neutron powder diffraction data measured at 300 K using neutrons of wavelength 1.5 Å. $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2$ showed nuclear structures that are consistent with a tetragonal system and space group $I4/mmm$, in agreement with the previous studies in literature [96, 9]. The Rietveld findings show that the lattice parameter and unit cell volume of $\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$ ($a = 4.08875(2)$ Å, $c = 18.6081(1)$ Å, unit cell

volume = 311.088(4) Å³) are larger than that of the La₂O₂Fe₂OS₂ ($a = 4.04388(3)$ Å, $c = 17.89412(19)$ Å, unit cell volume = 292.622(5) Å³) similar to results in reference [9]. Refinement fit results of both $M = \text{S}$ and Se are presented in Tables 10 and 11, respectively. The lattice parameters (a and c), the anisotropic thermal parameter U_{xx} , atomic site occupancy, and atomic coordination are presented in those tables. The La₂O₂Fe₂O(S , Se)₂ fit quality were characterized by the Rietveld fit parameters R_w whole pattern, crystallographic factor R_F , the goodness of fit GoF, and χ^2 which are presented at the bottom of Tables 10 and 11.

For both materials, The U_{11} value was found to be equal to U_{22} and differs U_{33} from for all atoms except the Fe atom. The O2 atom had the highest U_{33} value for both material and the Fe atom had different values for each U_{xx} parameter.

The high value of anisotropic thermal displacement parameter U_{33} along the c -axis for oxygen O2, corresponded to the displacement of O2 atom above and below the Fe₂O plane which can result in a distortion of Fe-O-Fe angle (in Figure 37, the Fe-O-Fe angle is highlighted by a solid black line in the octahedra). Another possible movement within the octahedra, is the movement of the sulfur/selenium atoms with respect to the Fe atoms along the c -axis. This motion can affect the M -Fe- M angle in the octahedra. Figure 38 shows Fe and O2 atomic movements in the octahedra. In panel a, the atoms are viewed along the a -axis, and in panel b, the view is slightly rotated to give an isometric view of panel a. When the O2 atoms in the Fe₂O plane move up or down, the angle Fe-O-Fe changes.

After confirming the average structure lattice symmetry for La₂O₂Fe₂O(S , Se)₂ samples, we investigated the local symmetry by the pair distribution function (PDF) method. The PDF method has been shown to be an effective method for studying local crystal structure nematic fluctuations [100, 101, 102, 103, 104, 105]. Studying the local structure of La₂O₂Fe₂OM₂ ($M = \text{S}$, Se) via PDF refinement method to determine the localized structural arrangement as a function of temperature and length

Figure 38. Panel a) shows possible Fe and the chalcogen atomic movement within the $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ octahedra. The dashed lines in b) show the O2 atom movement in the Fe_2O plane. The solid lines show Fe atom movement with respect to the chalcogen atom M [16].

scale was done using the PDFGUI program [71]. All lattice parameters, scale factor, atomic positions, and the thermal parameters were refined during the PDF analysis process. To make the refinement robust, we parametrized the lattice constants as $a = a_{mid}(1 + \delta)$ and $b = a_{mid}(1 - \delta)$, where $a_{mid} = \frac{a+b}{2}$ and $\delta = \left| \frac{a-b}{a+b} \right|$. We have used Nyquist grid to perform all refinements. Instrumental parameters q_{damp} and q_{broad} , which are the parameters that correct the PDF envelope function [106, 107] for the instrument resolution [70, 71], were fixed.

PDFGUI, through pre-written macros, allows data set fitting through a series of refinements that differ, one from another, by the corresponding fitting ranges [108]. Since we have performed PDF data sets over a wide range of temperatures, we used the PDFGUI T -series macro to study the details of the local to average structure crossover in our materials. This macros enable the set up of T -series sequential refinement fits where the same model is fitted over different temperatures of the PDF

Figure 39. Nuclear structure Rietveld refinement profile of NPD of a) $M = \text{S}$ and b) $M = \text{Se}$ at 300 K.

Table 10. Rietveld Refinement results for $\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$ from room temperature neutron powder diffraction. Space Group $I4/mmm$ $a = 4.08875(2)$ Å, $c = 18.6081(1)$ Å and unit cell volume = $311.088(4)$ Å³.

$\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$							
Atom	x	y	z	Occup.	$U_{11}(\text{Å}^2)$	$U_{22}(\text{Å}^2)$	$U_{33}(\text{Å}^2)$
La	0.5	0.5	0.18450(6)	0.972(5)	0.0029(3)	0.0029(3)	0.0076(6)
O1	0.5	0.0	0.25	0.996(6)	0.0040(4)	0.0040(4)	0.0112(8)
O2	0.5	0.5	0.0	0.970(11)	0.0055(6)	0.0055(6)	0.0218(14)
Fe	0.5	0.0	0.0	0.936(5)	0.0065(4)	0.0052(4)	0.0106(5)
Se	0.0	0.0	0.9666(6)	0.950(5)	0.0064(3)	0.0064(3)	0.0041(5)
Coordination							
$d_{\text{Fe}-\text{O1}}(\text{Å})$			4.6520(0)				
$d_{\text{Fe}-\text{O2}}(\text{Å})$			2.0444(0)				
$d_{\text{Fe}-\text{Se}}(\text{Å})$			2.723(8)				
$d_{\text{Fe}-\text{Fe}}(\text{Å})$			2.8912(0)				
$d_{\text{La}-\text{O1}}(\text{Å})$			2.3801(6)				
$d_{\text{La}-\text{Se}}(\text{Å})$			3.3212(8)				
$a_{\text{Fe}-\text{O2}-\text{Fe}}(\text{deg.})$			90.0(0)				
$a_{\text{Fe}-\text{SeFe}}(\text{deg.})$			64.13(2)				
$a_{\text{Se}-\text{FeSe}}(\text{deg.})$			97.32(4)				
$a_{\text{La}-\text{O1}-\text{La}}(\text{deg.})$			118.39(5)				
wR _P = 0.0675 R _P =0.0647 GoF = 5.35 χ^2 = 0.2836							

data [109]. We have performed extensive T -series PDF fits to determine the atomic structure as a function of temperature and length scale [101]. The evolution of the local structure (short-range) to the average structure (long-range) is presented in Figure 40. The most relevant structural parameter for describing the local distortion is the orthorhombicity. The orthorhombicity was determined, for both $M = \text{S}$ and Se , by using the results of T -series refinements based on the orthorhombic symmetry. T -series refinement was performed by PDF fits on low-temperature data first, a sequential PDF fits were performed for all of our data collected at various temperatures. Both $M = \text{S}$ and Se show high orthorhombicity in the short ranges for all temperatures at which data are collected.

Table 11. Rietveld Refinement results for from neutron powder diffraction at 300 K. Space Group $I4/mmm$ $a = 4.04388(3)$ Å, $c = 17.89412(19)$ Å and unit cell volume = $292.622(5)$ Å³.

La ₂ O ₂ Fe ₂ OS ₂							
Atom	x	y	z	Occup.	U ₁₁ (Å ²)	U ₂₂ (Å ²)	U ₃₃ (Å ²)
La	0.5	0.5	0.18082(5)	0.898(4)	0.0016(2)	0.0016(2)	0.0033(4)
O1	0.5	0.0	0.25	0.897(4)	0.0007(3)	0.0007(3)	0.0062(6)
O2	0.5	0.5	0.0	0.874(7)	0.0002(4)	0.0002(4)	0.0281(14)
Fe	0.5	0.0	0.0	0.871(4)	0.0082(4)	0.0020(3)	0.0112(5)
S	0.0	0.0	0.9397(15)	0.857(5)	0.0054(6)	0.0054(6)	0.0007(3)
Coordination							
d_{Fe-O1} (Å)			5.30933(0)				
d_{Fe-O2} (Å)			2.02194(0)				
d_{Fe-S} (Å)			2.6298(18)				
d_{Fe-Fe} (Å)			2.85946(0)				
d_{La-O1} (Å)			2.3708(5)				
d_{La-S} (Å)			3.2545(14)				
$a_{Fe-O2-Fe}$ (deg.)			90.0(0)				
$a_{Fe-S_{Fe}}$ (deg.)			65.87(5)				
a_{S-Fe_S} (deg.)			100.50(9)				
$a_{La-O1-La}$ (deg.)			117.05(4)				
wR _P = 0.0501 R _P =0.0561 GoF = 4.86 χ ² = 0.2336

Figure 40. The orthorhombicity determined from neutron PDF analysis for a) $M = S$ and b) $M = Se$. At the short ranges over all temperatures, we observe the presence of orthorhombicity for both samples.

6.4 Discussions

Neutron powder diffraction experiments established the average crystal structure as a tetragonal system with space group ($I4/mmm$) for both $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$. These findings match those observed in earlier studies on iron oxychalcogenides [96, 95, 98, 99, 13, 9]. Results from the neutron powder diffraction (Figure 39, Tables 11 and 10) clearly show that the thermal displacement parameter for O2 atom, along the c -axis (U_{33}), is larger than all the other thermal displacement parameters for both materials $M = \text{S}$ and Se .

According to Horigane et al. [110], deviations in the lattice parameter from the average crystallographic structure are caused by thermal displacement parameter U_{33} for O2 along the c -axis. It was claimed that this might be a similar case as of SrFeO_2 [111] which has a stronger temperature dependence of U_{33} for O2 (in-plane). In $\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$, the high U_{33} for O2 suggests the possibility of large distortion in O2 site. Also, a distortion in the Fe site makes it possible to have two Fe-Se correlation. In $\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$, the high U_{33} for O2 suggests the possibility of large distortion in O2 site. Also, a distortion in the Fe site makes it possible to have two Fe-Se correlation.

Figure 41 compares the phase diagram of iron pnictides (Figure 41 a) and $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ Mott insulators (Figure 41 b and c). In the phase diagram of FeSCs (Figure 41 a), the normal state is shown in light green color on the right/top part of the phase diagram. In this state, the FeSC is in the tetragonal crystal structure and paramagnetic magnetic phase at high temperatures. At lower temperature, the doping affects the behavior of the compound, it shows nematic fluctuation and ordering at $T_{nem.}$, a structural phase transition to the orthorhombic structure at T_c and magnetic phase transition to the antiferromagnetic structure at T_N as well as superconductivity properties that emerge at certain dopings.

In the pure sulfur and selenium compounds of $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ we have studied, we found evidence of nematicity at the shorter length scales (Figure 40 red lines

for $r = 0 - 15 \text{ \AA}$), which is shown in the phase diagram (Figure 41 b and c). Unlike iron pnictides, which undergo a structural phase transition from tetragonal to orthorhombic around T_s , $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2$ lattice symmetry does not change with temperature. Similar to iron pnictide superconductors, both $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2$ undergo a magnetic phase transition at Néel temperature T_N from a paramagnetic (PM) phase to an antiferromagnetic (AFM) phase. Nematic fluctuations appear around T_s in superconducting iron pnictides. These nematic fluctuations persist to a more ordered phase (nematic phase) until the temperature reaches the Néel temperature at which the magnetic phase transition occurs.

The superconductivity, in most FeSCs, is found in the proximity to a magnetically ordered state. However, a careful study of the phase diagram reveals that at a specific temperature of T_{nem} , there is another non-superconducting state besides magnetism. In this state, the system breaks its symmetry between x and y directions in the Fe-plane [17]. This system break reduces the rotational point group symmetry from tetragonal to orthorhombic while preserving the translational symmetry, also known as nematic fluctuations [101, 112].

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In FeSCs and other related materials, vital information can be understood not only from the nematic phase, which occurs above T_s but also from the nematic fluctuations which occur over a broad range of temperatures. These fluctuations, which deviates from the average structure, provide important information about the origin

Figure 41. A comparison of phase diagram in iron pnictides superconductors and the preliminary phase diagram of $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ Mott insulators. Panel a) after References [17, 18, 19, 20].

of nematicity and its relation to superconductivity mechanism [113, 114, 115, 116, 100, 117, 118, 119]. This question has become the key focal point of the field of iron-based high- T_c superconductivity. The findings presented in current study and in literature suggest that nematic fluctuations are not exclusively required for the onset

of a superconducting phase. In iron pnictides and iron chalcogenides, nematic fluctuations, along with other phases, appear to conspired to produce high-temperature superconductivity.

6.5 Conclusions

In this study, the average and local structure of the Mott insulating iron oxy-chalcogenides $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ were studied using neutron powder diffraction and pair distribution techniques. Neutron powder diffraction showed a similar average nuclear structure of $M = \text{Se}$ and S , with differences in volume and lattice parameters corresponding to differences in the atomic radii of the two chalcogens S and Se . Pair distribution function analysis showed the presence of local distortions from tetragonal to orthorhombic symmetry over the short-range, especially at lower temperatures. These results suggest the presence of short-range local distortions in both of these materials. These distortions can be evidence of nematic short-range ordering in the $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ materials despite the persistent tetragonal long-range crystal structure.

6.6 Future Work

Local structure investigation in similar materials, iron based superconductors and Mott insulators can be carried out using the PDF analysis to further examine the short range fluctuation in these materials and explore its nematic fluctuation and nematic ordering. Similar PDF analysis will be applied to other iron-based materials, including $\text{Fe}_{1.1}\text{Te}$ to investigate the presence of nematic fluctuations.

CHAPTER 7

STRUCTURAL STUDY OF MOLYBDENUM DITELLURIDE

$2H$ -MoTe₂ AND $1T'$ -MoTe₂

7.1 Introduction

Transition metal dichalcogenides (TMDs) have a general form MX_2 where M = Mo, W, Ti, Zr, Hf, V, Nb, Ta, Tc, Re, Co, Rh, Ir, Ni, Pd, Pt) and X = S, Se, Te. Molybdenum-based TMD materials have received theoretical and experimental attention because of their potential in advancing the development of a new generation of electronics devices beyond silicon and graphene [120, 121, 122]. A typical TMD shows the trigonal prismatic $2H$ or the octahedral $1T$ structures [123]. Figure 42 shows trigonal coordination of MoTe₂.

Molybdenum ditelluride MoTe₂ crystallizes into three stable phases: $2H$, $1T'$ and T_d while the $1T$ is considered to be unstable [123]. Table 12 provides the previously reported lattice parameters, space group and the crystal system of all phase of MoTe₂. The $2H$, called α -MoTe₂, is a stable semiconductor with hexagonal structure and $P6_3/mmc$ space group [124, 125]. The $2H$ -MoTe₂ does not undergo a structural phase transition with temperature, it may achieve superconductivity with applied pressure [126]. Hexagonal-phase molybdenum ditelluride MoTe₂ has been studied for use in photo-electrochemical solar cells [127]. Optoelectronic, spintronic, and valleytronic devices [128, 129] are possible applications for MoTe₂ due to its small bandgap and large spin-orbit (SO) coupling. α -MoTe₂ has also been proposed as a base material for pn -junctions [130, 131], field-effect transistors [131], complementary

Figure 42. Prismatic coordination of MoTe_2 . Panel a), b) and c) shows the coordination for $2H\text{-MoTe}_2$, $1T'\text{-MoTe}_2$, and $T_d\text{-MoTe}_2$ phase.

metal-oxide-semiconductor (CMOS) devices [132, 133], Schottky barriers [134] and gas sensors [135].

Table 12. Schematics of the structural polytypes of MoTe_2 .

Phases	a (Å)	b (Å)	c (Å)	Space Group	Crystal System	Reference
$1T\text{-MoTe}_2$	-	-	-	Unstable	-	[123]
$1T_d\text{-MoTe}_2$	3.471	6.338	13.858	$Pmn2_1$ (no.31)	Orthorhombic	[136]
$1T'\text{-MoTe}_2$	6.338	3.472	13.861	$P2_1/m$ (no.11)	Monoclinic	[137]
$2H\text{-MoTe}_2$	3.519	3.519	13.964	$P6_3/mmc$ (no.194)	Hexagonal	[124]

The $\beta\text{-MoTe}_2$ ($1T'$ phase) has distorted octahedra showing monoclinic structure with space group $P2_1/m$ [137, 138]. $1T'\text{-MoTe}_2$ undergoes through structural phase transition with temperature to the $T_d\text{-MoTe}_2$ phase. The $T_d\text{-MoTe}_2$ version has attracted attention because it exhibited superconductivity at $T_c = 0.1\text{K}$ and a nontrivial π Berry phase at low temperature. $T_d\text{-MoTe}_2$ is considered to be the first type-II Weyl semimetal (WSM) [4, 139] and is predicted to be a topological superconductor [140, 141]. $T_d\text{-MoTe}_2$ is a WSM type-II which characterized by point-like Fermi

surface. Weyl fermions in T_d -MoTe₂ are very sensitive to their lattice constant. This provides a way to tune the topological phase transition by pressure or temperature [136].

The $2H$ -MoTe₂ phase consists of one layer of transition metal atoms sandwiched by two layers of chalcogen atoms with a prismatic coordination. The molybdenum Mo atom is surrounded by uniformly displaced 6 tellurium atoms Te arranged at the vertices of a triangular prism as shown in Figure 42, a. In $1T'$ -MoTe₂ and T_d -MoTe₂ phases the prism is distorted octahedrally coordinated by Te with alternating long and short distances between Mo atoms due to strong intermetallic bonding. Figure 42 b and c shows the Prismatic coordination of $1T'$ -MoTe₂ and T_d -MoTe₂ respectively. Both structure contain bonds between the metal atoms that dimerize along one of the lattice directions [142, 143].

There is considerable interest in the phase transition behavior of MoTe₂ because the phase changes are often coupled with other changes in these low-dimensional systems [144, 145]. The structural phase transition from $2H$ to $1T'$ phase in a few-layer MoTe₂ was found to be driven by electrostatic doping [146] and by laser irradiation [147]. Structural phase transitions from the T_d to $1T'$ phase, can be driven by temperature [148, 149], are accompanied by topological phase transition.

Trigonal prismatic (see figure 42 a) α -MoTe₂ form is stabilized by the opening of a hybridization gap within the Mo d -band manifold, splitting off the full d_{z^2} band. However, such a gap does not occur for the ideal octahedral coordinate structure (see figure 42 b) [150, 151]. Due to a trigonal prismatic crystal-field splitting of a filled nonbonding d_{z^2} orbital, the group VIb di-tellurides show a deviation from a simple band model, which indicates semiconducting behavior.

Three-dimensional (3D) topological Weyl semimetals (TWSs) [152] are novel topological quantum materials discovered and intensively investigated recently because of their intimate link between concepts of different fields of physics and material science.

Figure 43. The structure of different phases of MoTe_2 . Panel a) shows top view of $2H$ - MoTe_2 , panel b) side view of $2H$ - MoTe_2 . The top view of $1T'$ - MoTe_2 is shown in panel c), whereas panel d) shown the side view of the same phase. The T_d - MoTe_2 top view is shown in panel e) and the side view on panel f).

Topological TWSs display a range of physical properties of promising usage [153]. Theoretical prediction claims that $2H$ TMDs may become superconductors at high pressure. MoTe_2 shows superconductivity at transition temperature $T_c = 0.1$ K. At high pressure, about 11.7 GPa, the transition temperature T_c goes up to 8.2 K [141]. In the monolayer at low-temperature, T_d - MoTe_2 phase is a type-II Weyl semimetal.

Figure 44. single crystal $1T'$ -MoTe₂.

It shows topological surface state Fermi arcs and chiral anomalies. Induced negative magnetoresistance is formed through temperature-driven phase transition from $1T'$ -MoTe₂ [154, 155]. During the phase transition from $1T'$ -MoTe₂ to T_d -MoTe₂ where the electronic structure is largely preserved, but the topological character is changed. Using physical knobs such as strain or pressure at low temperatures the topological phenomena can be turned on and off by small changes in temperature. Where the structural transition also acts as a topological switch for surface states in $1T'$ -MoTe₂ [140].

Currently, there is ambiguity concerning the nature of the phase transition in $1T'$ -MoTe₂. There are less than a handful of high-resolution structural studies at low-temperature. We sought to examine the phase transitions of $2H$ -MoTe₂ and $1T'$ -MoTe₂. We used neutron powder diffraction and high-resolution x-ray powder diffraction to investigate both phases. Understanding the structure of MoTe₂ in few-layer and bulk configurations is important for enhancing our ability to deploy the material as topological devices.

7.2 Material

7.2.1 Synthesis

Samples used in the present experiments were obtained from two sources: commercial samples from HQ graphene and from the University of Tennessee. Hq graphene $2H$ -MoTe₂ and $1T'$ -MoTe₂ crystals were grown by the chemical vapor transport method. Figure 44 shows a picture of $1T'$ -MoTe₂ crystal obtained from hq graphene and the size of the longest edge of some crystals is about 5mm (0.197 in).

MoTe₂ samples were grown by the Yan group in the Materials Science and Engineering Department at the University of Tennessee at Knoxville. $1T'$ -MoTe₂ single crystals were grown out of a Te-rich binary melt using a canfield crucible set (CCS). Mo and Te shots in a ratio of 1:9 were loaded into a 5ml CCS and sealed in a quartz tube under vacuum. The quartz ampoule was held at 1000°C for a week. $1T'$ -MoTe₂ single crystals were isolated from Te flux by centrifuging. We have single crystalline samples of $1T'$ -MoTe₂. Single crystals grown in this manner have a residual resistance ratio (RRR) 500 and magnetoresistance (MR) of 40,000 which indicated no (or low) amounts of impurities and crystal defects. Samples sizes were plate-like with typical dimensions 2 mm x 4 mm x 0.3 mm.

7.2.2 Characterization

7.2.2.1 Raman Spectroscopy

$2H$ -MoTe₂ and $1T'$ -MoTe₂ samples were measured using a commercial Horiba LabRam HR Raman microscope in the back-scattering geometry at room temperature in Prof. Lui lab at University of California Riverside. The excitation light source was a 532 nm continuous laser. The incident laser power on the samples was below 1 mW, with a spot diameter of 1 μ m [156]. The present study performed detailed crystal structure analysis on MoTe₂ material by studying the structural changes of the

Figure 45. Left panel shows Raman Measurement on powder sample of $2H$ -MoTe₂ and $1T'$ -MoTe₂. Right panel shows the Raman spectra for both samples from reference [21].

$2H$ -MoTe₂ and $1T'$ -MoTe₂ phases with respect to temperature. To confirm the quality of both samples, $2H$ -MoTe₂ and $1T'$ -MoTe₂, we performed Raman spectroscopy. Raman measurements have been used previously to identify the type of material. Our Raman measurements were intended to determine whether the samples did not include contaminants. Also, Raman spectroscopy would have shown the different phases present in the material. The Raman spectroscopy results (Figure 45) confirm that only one phase exists in each sample which is essential for accurate study of the temperature effects on the structure of each phase. The Raman results also showed that both samples were clear from impurities. These results are similar to what is reported in the literature for both samples of $2H$ -MoTe₂ and $1T'$ -MoTe₂ [21].

7.2.2.2 Electron dispersion x-ray Spectroscopy (EDX)

$2H$ -MoTe₂ and $1T'$ -MoTe₂ samples were characterized using energy dispersion x-ray spectroscopy (EDX) measurements performed at the University of Louisville, CONN Center for Renewable Energy. Figure 46 shows the results of EDX for representative samples, panel a) shows the $2H$ -MoTe₂ and panel b) shows the results for $1T'$ -MoTe₂ sample. For both samples we notice that only peaks related to Molyb-

Figure 46. Stoichiometric analysis of a) $2H$ -MoTe₂ and b) $1T'$ -MoTe₂ by Energy-dispersive x-ray spectroscopy (EDX).

denum (Mo) or Tellurium (Te) are present. This indicates that our samples are of good quality and do not contain contaminants. Figure 45 shows the Raman measurement results for powdered samples of $2H$ -MoTe₂ and $1T'$ -MoTe₂. The present study performed detailed crystal structure analysis of MoTe₂ materials by investigating the structural changes of the $2H$ -MoTe₂ and $1T'$ -MoTe₂ phases with respect to temperature. EDX spectroscopy was used to study the elements present in the MoTe₂ samples. EDX spectroscopy is commonly used to quantify the impurities in synthesized materials. It has the ability to characterize different elements due to the fact that the element's unique atomic structure produces a set of peaks on its electromagnetic emission spectrum.

In the current study, EDX spectroscopy was performed on two samples. The first sample represented the $2H$ -MoTe₂ phase, and the second sample represented the $1T'$ -MoTe₂ phase. The EDX results for both samples, presented in Figure 46 a and 46b), show different elements by their dispersive energy plotted as peaks on an EDX spectrum. Both Figures (46a and 46b) show peaks related to molybdenum (Mo) and tellurium (Te). There was no other peaks present which indicates that the samples were clear from impurities. These results confirm that the elemental composition of both samples consisted only of molybdenum (Mo) and tellurium (Te). Impurities in the samples would have introduced new peaks in the x-ray powder diffraction, which would have affected the Rietveld analysis. The EDX spectroscopy was an important step to evaluate the purity of the studied samples.

7.3 Experimental Methods

7.3.1 X-ray Diffraction

In order to determine the structural model we used high-resolution x-ray powder diffraction. Data were acquired at two temperatures 295 K and 100 K using the mail-in program at beamline 11-BM of the Advanced Photon Source (APS) at Argonne National Laboratory. Data scans were taken over a 2θ angular range from 0.5 to 50° using a Si(111) double crystal monochromator at a wavelength $\lambda = 0.4127\text{\AA}$. For analyzing the powder diffraction data, we performed Rietveld refinement using the GSAS-II software suite [85]

7.3.2 Neutron diffraction

Temperature dependence neutron powder diffraction was performed at the Canadian Neutron Beam Centre (CNBC) at Chalk River Laboratories using C2 and C5 diffractometers. Data scans using C2 diffractometer were taken over a 2θ angular range from 2.9 to 117° at a wavelength $\lambda = 1.3\text{\AA}$ for temperatures from 5 K to 320

K. Another set of scan were performed with wavelength $\lambda = 2.37 \text{ \AA}$ at temperatures from 5 K to 325 K. Data scans using C5 diffractometer were taken over a 2θ angular range from 4.5 to 120° at a wavelength $\lambda = 2.44 \text{ \AA}$ over a range of temperatures from 1.77 K to 293 K.

7.4 Results

The results of high resolution x-ray diffraction experiments, performed at 11-BM, APS and neutron powder diffraction, Chalk River, on both $2H$ -MoTe₂ and $1T'$ -MoTe₂ are presented here.

7.4.1 $2H$ -MoTe₂ Powder Diffraction

7.4.1.1 Synchrotron X-rays

APS synchrotron x-ray diffraction data collected from $2H$ -MoTe₂ is presented in Figure 47. The diffractogram shows intensity versus the scattering angle 2θ . Figure 47, a) shows the x-ray diffraction pattern for $2H$ -MoTe₂ phase at 100 K and 295 K. The difference between the diffraction patterns is shown in panel b) of the same Figure. The major difference between the 295 K and 100 K data is the peak height mismatch at 2θ value from 2.5° to 15° . The peak at 3.4° shows the largest peak height difference between the two diffraction patterns. Figure 48, Tables 13 and 14 summarize the attempted Rietveld refinement analysis for $2H$ -MoTe₂ phase. The Rietveld refinement of the x-ray powder diffraction experiment data from 11-BM was performed using GSAS-II [85]. Figure 48 a and b for temperatures 295 K and 100 K respectively. The calculated diffraction pattern using GSAS-II software is shown in green curve, the measured x-ray diffraction pattern is in red. The difference between the calculated and the measured patterns is in blue, the background is shown in black. The blue tick marks represent the Bragg angles based on the modeled lattice symmetry studied with the Rietveld analysis.

Table 13. Proposed model for 2H-MoTe₂ based on 11-BM XRD at 295K. Space Group $P6_3/mmc$ $a = 3.51981(3)$ Å, $c = 13.96812(7)$ Å unit cell volume = 149.867(2) Å³.

2H-MoTe ₂					
Atom	x	y	z	Occup.	$U_{iso}(\text{\AA}^2)$
Mo	1/3	2/3	1/4	0.962(3)	0.0059(2)
Te	1/3	2/3	0.6205(1)	0.958(3)	0.0070(2)
Coordination					
$d_{Mo-Mo}(\text{\AA})$	3.51981(0)				
$d_{Mo-Te}(\text{\AA})$	2.7204(5)				
$d_{Te-Te}(\text{\AA})$	3.51981(0)				
$a_{Mo-Te-Mo}(\text{deg.})$	80.620(17)				
$a_{Te-Mo-Te}(\text{deg.})$	83.34(3)				
wR _P =0.1690 R _P = 0.1021 GoF = 3.00 χ^2 =0.0899					

Table 14. Proposed model for 2H-MoTe₂ from 11-BM XRD at 100K. Space Group $P6_3/mmc$ $a = 3.51473(2)$ Å, $c = 13.94093(7)$ Å unit cell volume = 149.144(2) Å³.

2H-MoTe ₂					
Atom	x	y	z	Occup.	$U_{iso}(\text{\AA}^2)$
Mo	1/3	2/3	1/4	0.998(3)	0.0007(2)
Te	1/3	2/3	0.62022(4)	0.993(3)	0.0011(2)
Coordination					
$d_{Mo-Mo}(\text{\AA})$	3.51473(0)				
$d_{Mo-Te}(\text{\AA})$	2.7187(4)				
$d_{Te-Te}(\text{\AA})$	3.51473(0)				
$a_{Mo-Te-Mo}(\text{deg.})$	80.542(14)				
$a_{Te-Mo-Te}(\text{deg.})$	83.440(18)				
wR _P =0.1685 R _P = 0.0837 GoF = 2.94 χ^2 =0.0866					

The lattice parameters (a, b, c) and atomic positions (x,y,z) that were refined during the analysis are presented in Tables 13 and 14. The weighted profile R-factor (R_w) and χ^2 values indicate the quality of the Rietveld refinement analysis; at 295 K, R_w and χ^2 were 0.1690 , 0.0899, and at 100 K the values were 0.1685, and 0.0866. These values indicates the quality of the fit for the hexagonal symmetry with space group $P6_3/mmc$. The lattice parameters, as well as the unit cell volume, increases with

Figure 47. Panel a) presents the x-ray diffraction pattern from 11-BM at APS of $2H\text{-MoTe}_2$ at 295 K and 100 K. Panel b) shows the diffraction difference between the patterns.

temperature from 100 K to up to room temperature. The change in unit cell volume and the lattice parameters are due thermal expansion at higher temperature. The atomic positions (x,y,z) and the atomic occupancy changed slightly temperature. The atomic occupancies, for molybdenum and tellurium, decreased when the temperature increased from 100 K to room temperature. A higher occupancy value will represent higher possibility for this particular atomic site to be occupied with a certain atom,

Figure 48. Rietveld refinement profiles of x-ray diffraction data from 11-BM at APS of $2H\text{-MoTe}_2$. a) At 300 K, b) at 100 K.

and the lower possibility for vacancies in the atomic site.

7.4.1.2 Neutron Powder Diffraction

Temperature dependent neutron powder diffraction patterns for $2H\text{-MoTe}_2$ collected at C2 diffractometer of CNBC is shown in Figure 49 where the diffraction pattern of $2H\text{-MoTe}_2$ material are shown at temperatures 5, 200 and 320 K using a neutron wavelength $\lambda = 1.3 \text{ \AA}$.

Figure 49. Panel a) shows $2H\text{-MoTe}_2$ neutron powder diffraction data from C2 diffractometer at Chalk river with $\lambda = 1.3 \text{ \AA}$ performed at temperatures 5, 200 and 320 K. Panel b) shows magnification of the diffraction pattern highlighting the 2θ from 81.5° to 97.5° .

At $2\theta = 3^\circ$ there are no shifts in the peaks. At $2\theta = 82.35^\circ$ for $T = 5 \text{ K}$ we can observe a new peak which is not presented in the 200 and 320 K data. At $2\theta = 94^\circ$ and 95° there are 2 peaks (twin) at 320K the first peak has higher intensity, at 200K they are almost equal and at 5 K the peak at $2\theta = 95^\circ$ has higher intensity. Overall, most peaks sharpen and shift toward higher 2θ as the temperature increases as is expected for a thermal contraction of the lattice. Neutron powder diffraction patterns using wavelength $\lambda = 2.37 \text{ \AA}$ at temperatures 5, 16, 132, 200, 208, 291 and

320 K are shown in Figure 50. The diffractograms in this figure over different angular ranges: data collected at temperatures 16, 132, 208 and 291 K have 2θ range from 2.9° to 83° and data collected at temperatures 5, 200 and 320 K have a 2θ range from 2.9° to 117° .

Figure 50. $2H$ - MoTe_2 neutron powder diffraction data from C2 diffractometer at Chalk river with $\lambda = 2.37 \text{ \AA}$ performed at 5, 132, 200, 208 and 320 K.

7.4.2 $1T'$ - MoTe_2 Powder Diffraction

7.4.2.1 Synchrotron X-rays

High-resolution x-ray diffraction patterns of the $1T'$ - MoTe_2 phase collected at 100 K and 295 K is shown in Figure 51, in panel a) the full x-ray powder diffraction pattern for both temperatures are superimposed. The lower scattering angle range up to $2\theta = 15^\circ$ showed the largest differences between the two patterns. Panel b) shows the difference between the two patterns where peaks at angular $2\theta = 3.4, 6.8,$ and 13.7° represents the highest peak intensity differences.

Data presented over specific scattering angular ranges in order to highlight the differences between the $1T'$ - MoTe_2 at low and room temperature as shown in Figure 52, all panels. In this figure low temperature is shown blue line and room temperature data is shown by a red line. Panel a show the height difference and peak position shift

Figure 51. X-ray diffraction pattern from 11-BM at APS of $1T'$ -MoTe₂ at 295 K and 100 K. Panel a) shows the full diffraction pattern and panel b) shows the difference between the patterns.

in the highest intensity peak in the diffractogram in the $1T'$ -MoTe₂ phase. Panel b focused on the angular range 2θ from 6.5° to 17° , where we see new peaks emerged at 100 K at $2\theta = 7.7, 10.7^\circ$. These new peaks are related to the structural phase transition from $1T'$ -MoTe₂ to T_d -MoTe₂. Panel c contains data collected over the angular range 2θ from 16° to 26° ; we can see that a new peak raised at low temperature at $2\theta = 23.36^\circ$. Other noticeable change is that some peaks merge into one peak for

Figure 52. Focused section for the comparison from the x-ray diffraction pattern of data taken at 11-BM at APS, of $1T'$ -MoTe₂ at 295 K (red) and 100 K (blue). The full patterns are shown in figure 51.

example the two peaks around $2\theta = 20^\circ$ at room temperature merge into one at low temperature. Panel d focus on the diffraction from $2\theta = 26$ to 34° where two peaks at $2\theta = 27.79^\circ$ and 27.98° merged to one peak located at $2\theta = 28.89^\circ$. In panel e new peaks emerge at low temperatures located at angular $2\theta = 36.4$ and 36.7° .

The $1T'$ -MoTe₂ proposed model lattice parameters and atomic positions are presented in Tables 15 and 16. The $1T'$ -MoTe₂ phase is reported [157, 158] to undergo a structural phase transition at temperature below 200 K. For this reason we collected x-ray powder diffraction data at 100 K which is well below the expected transition temperature.

The difference between $1T'$ -MoTe₂ and T_d -MoTe₂ crystal symmetry is mainly the value of angle β which changes from 90.0° in orthorhombic T_d to $92.54889^\circ(19)$ in

Table 15. Proposed model for $1T'$ -MoTe₂ from 11-BM XRD at 295K. Space Group $P2_1/m$ $a = 6.32049(19)$ Å, $b = 3.47182(14)$ Å, $c = 13.83659(27)$ Å, $\beta = 92.5489^\circ(19)$, unit cell volume = $303.325(13)$ Å³.

$1T'$ -MoTe ₂					
Atom	x	y	z	Occup.	$U_{iso}(\text{\AA}^2)$
Mo1	0.1748(8)	1/4	0.0051(5)	0.432(4)	0.0060(10)
Mo2	0.3468(13)	-1/4	0.5087(6)	0.329(4)	0.0037(18)
Te1	0.5907(8)	1/4	0.1091(3)	0.530(4)	0.0129(13)
Te2	0.1026(9)	-1/4	0.1493(4)	0.407(5)	0.0054(17)
Te3	0.5833(11)	-1/4	0.3584(5)	0.401(5)	0.0354(28)
Te4	0.0423(7)	2/3	0.6202(4)	0.562(5)	0.0223(16)
Coordination					
Atomic distances					
$d_{Mo1-Mo1}(\text{\AA})$	2.818(8)				
$d_{Mo2-Mo2}(\text{\AA})$	2.605(13)				
$d_{Te1-Te1}(\text{\AA})$	3.611(7)				
$d_{Te2-Te2}(\text{\AA})$	4.601(11)				
$d_{Te3-Te3}(\text{\AA})$	4.458(13)				
$d_{Te4-Te4}(\text{\AA})$	3.309(7)				
$d_{Mo1-Te1}(\text{\AA})$	2.806(7)				
$d_{Mo1-Te2}(\text{\AA})$	2.704(7)				
$d_{Mo2-Te3}(\text{\AA})$	2.557(8)				
$d_{Mo2-Te4}(\text{\AA})$	2.942(7)				
Bond angles					
$a_{Te1-Mo1-Te1}(\text{deg.})$	117.02(19)				
$a_{Te2-Mo1-Te2}(\text{deg.})$	76.76(16)				
$a_{Te3-Mo2-Te3}(\text{deg.})$	119.4(3)				
$a_{Te4-Mo2-Te4}(\text{deg.})$	78.3(3)				
wR _P =0.3142 R _P = 0.2334 GoF = 5.07 χ^2 =0.2565					

the monoclinic $1T'$ (Figure 43 d and f). The graphical presentation of the Rietveld refinement analysis of the $1T'$ -MoTe₂ phase x-ray powder diffraction is given in Figure 53. Panel a) shows the refinement at room temperature 295 K using the monoclinic symmetry and panel b) shows the 100 K data refined using the orthorhombic symmetry.

Table 16. Proposed model for T_d -MoTe₂ from 11-BM XRD at 100K. Space Group $Pmn2_1$ $a = 3.46675(29)$ Å, $b = 6.30310(53)$ Å, $c = 13.85899(39)$ Å, $\beta = 90.0^\circ(0)$, unit cell volume = $302.837(31)$ Å³. The fit quality here is low and the negative values of the U_{iso} and the large fit quality parameters listed below.

1T'-MoTe ₂					
Atom	x	y	z	Occup.	U _{iso} (Å ²)
Mo1	0.0	0.6259(8)	0.5075(4)	1.0	-0.0029(14)
Mo2	0.0	0.0175(8)	0.0132(4)	1.0	-0.0053(11)
Te1	0.0	0.8579(7)	0.6532(2)	1.0	-0.0200(4)
Te2	0.0	0.6564(8)	0.0994(3)	1.0	0.0084(18)
Te3	0.0	0.3110(8)	0.3584(5)	1.0	0.0119(18)
Te4	0.0	0.2125(6)	0.6202(4)	1.0	-0.0151(4)
Coordination					
Atomic distances					
d _{Mo1-Mo1} (Å)	3.46675(0)				
d _{Mo2-Mo2} (Å)	3.46675(0)				
d _{Te1-Te1} (Å)	3.46675(0)				
d _{Te2-Te2} (Å)	3.46675(0)				
d _{Te3-Te3} (Å)	3.46675(0)				
d _{Te4-Te4} (Å)	3.46675(0)				
d _{Mo1-Te1} (Å)	2.493(7)				
d _{Mo1-Te2} (Å)	2.792(6)				
d _{Mo1-Te3} (Å)	2.689(6)				
d _{Mo1-Te4} (Å)	2.992(7)				
d _{Mo2-Te1} (Å)	2.718(6)				
d _{Mo2-Te2} (Å)	2.571(8)				
d _{Mo2-Te3} (Å)	2.795(8)				
d _{Mo2-Te4} (Å)	2.740(5)				
Bond angles					
a _{Te1-Mo1-Te2} (deg.)	90.2(2)				
a _{Te1-Mo1-Te3} (deg.)	121.38(19)				
a _{Te1-Mo2-Te2} (deg.)	85.64(19)				
a _{Te2-Mo2-Te4} (deg.)	78.12(17)				
wR _P =0.3502	R _P = 0.2838	GoF = 5.82	χ ² =0.3382		

7.4.2.2 Neutron Powder Diffraction

Figure 54 shows temperature dependence neutron powder diffraction pattern for the $1T'$ -MoTe₂ phase from the C2 diffractometer at the Canadian Neutron Beam

Figure 53. X-ray diffraction pattern from 11-BM at APS of 1T'-MoTe₂ At 295 K and 100 K. Panel a) shows the full diffraction pattern where panels b-f shows focused portions of this pattern.

Centre. Samples were measured at the following temperatures 5, 20, 92, 113, 161, 200, 293, 320 and 325 K using a wavelength $\lambda = 1.33$ Å. The resulting diffraction patterns are shown in the upper panel of Figure 54. Temperatures 5, 200 and 320 K cover the full detector range in which the scattering angle 2θ varies from 3° to 117°. While data for the temperatures 20, 113, 161 and 293 K cover a 2θ range from 3° to 83° and data for temperatures 20 and 325 K cover a 2θ range from 37° to 117°.

Peaks with 2θ greater than 30.469° shift to higher 2θ values at low temperature.

Figure 54. Panel a) $1T'$ - MoTe_2 temperature dependence neutron powder diffraction data from C2 diffractometer at Chalk River with $\lambda = 1.33 \text{ \AA}$. Panel b) $1T'$ - MoTe_2 temperature dependence neutron powder diffraction data from C2 diffractometer at Chalk River with $\lambda = 2.37 \text{ \AA}$.

The lower panel of Figure 54 shows measurements of $1T'$ - MoTe_2 phase at temperatures 5, 200, 203, 205, 240 and 320 K using a wavelength $\lambda = 2.37 \text{ \AA}$. Neutron powder diffraction patterns were taken at temperatures 5, 320 K over the full detector range in which the scattering angle 2θ varied from 3° to 117° . Diffraction patterns

Figure 55. $1T'$ -MoTe₂ temperature dependence neutron powder diffraction data from C5 diffractometer at Chalk river with $\lambda = 2.44 \text{ \AA}$.

taken at temperatures 203, 205, and 240 K covered a 2θ range from 37° to 117° . The measurement at 200 K covered angular range 2θ from 3° to 83° . We observed two dips in the measurements one is at $2\theta = 52.33^\circ$ (except for temperature 203, 205 K no dip was found) and at $2\theta = 86.323^\circ$ for all temperatures. Peaks with 2θ greater than 60° tended to shift to higher 2θ at lower temperatures. New peak appears at 5 K temperature at $2\theta = 64.862^\circ$, which is related to the structural phase transition from $1T'$ -MoTe₂ phase to T_d -MoTe₂ phase.

Figure 55 shows temperature dependence neutron powder diffraction pattern for the $1T'$ -MoTe₂ phase from C5 diffractometer at Chalk river. We measured this sample at temperatures 1.77 and 293 K with wavelength $\lambda = 2.44 \text{ \AA}$. In this measurement, peaks from both temperatures coincides around or before $2\theta = 52.145^\circ$ which is the highest intensity peak. Peaks with 2θ greater than 62.954 shift to higher 2θ at low temperature.

7.5 Discussion

7.5.1 $2H$ -MoTe₂ Phase

The primary structural analysis of $2H$ -MoTe₂ was performed using x-ray and neutron powder diffraction. These experiments provide structural characterization of atomic coordinates and detailed structural parameters of the particular material phase. The x-ray powder diffraction data obtained from the 11-BM measurement were analyzed using Rietveld analysis by GSAS-II suite. Rietveld analysis was used to identify the crystal structure and its symmetry as well as the lattice parameters, atomic positions, and atomic site occupancy at different temperatures. At room temperature, the crystal structure parameters were similar to values reported in literature [123, 159, 160]. Puotinen et al. performed x-ray powder diffraction and reported hexagonal system with space group $P6_3/mmc$ with similar lattice parameters a and c [160]. They reported that their lowest R_W value was 17%, which is similar to our fit quality values, and attributed that to preferred orientation effects.

The diffraction indicates that $2H$ -MoTe₂ sample has hexagonal crystal symmetry with space group $P6_3/mmc$ remains the same at room temperature and 100 K. We notice this fact by direct comparison of diffraction data collected at these temperatures (see Figure 47). The persistence of the diffraction pattern profile from room temperature to 100 K, confirms that the bulk $2H$ -MoTe₂ maintains the same symmetry. Only a slight reduction in lattice parameters is observed upon lowering the temperature and this is expected to result from the lattice contraction.

Atomic positions values, for all atoms, increased slightly with temperature (Tables 13, and 14) while the occupancies of the atomic sites changed. At lower temperatures both atoms, Mo and Te, have less occupancy than room temperature.

We have performed a temperature dependence powder neutron diffraction experiment at Canadian Neutron Beam Centre, Chalk River. $2H$ -MoTe₂ was measured

with different wavelengths for many temperatures (Figures 49 and 50). Except for a temperature based peak shift no major changes in the peaks, which was expected due to lack of phase transition in $2H$ -MoTe₂ phase.

7.5.2 $1T'$ -MoTe₂ Phase

Similar to $2H$ -MoTe₂, x-ray diffraction was performed on $1T'$ -MoTe₂ at room temperature and 100 K. These temperatures were appropriate for the current study, since 100 K is lower than the reported phase transition temperature in $1T'$ -MoTe₂ phase. Rietveld refinement was used to analyze the diffraction experiment data and determine the structure of the material. Tables 15 and 16 showed the proposed crystal structure for the collected data before and after the structural phase transition. The analysis for $1T'$ -MoTe₂ at room temperature is confirmed to have a monoclinic symmetry. At 100 K the crystal symmetry was modeled as orthorhombic. Our low-temperature measurement at 100 K was below the phase transition temperature and the coexistence region [157], we expected that the $1T'$ -MoTe₂ would undergo a structural phase transition to T_d -MoTe₂. This was further confirmed by our Rietveld refinement analysis. In $1T'$ -MoTe₂ the change from monoclinic to orthorhombic structure is based on a slight change in the lattice parameters. However, the symmetry change is thought to be mainly due to tilting in the c -axis by few degrees in the out-of-plane direction. In our measurements the tilting angle β is about 2° (β changes from $92.5489(19)^\circ$ to 90.0°) when the phase transitions from monoclinic to orthorhombic. It has been suggested that MoTe₂ layers might easily shift due to the weak Van der Waals forces [161]. Our findings further confirm the role the Van der Waals forces on the MoTe₂ layers. The similarity of the layers and the ease of movement between them is ideal for symmetry change through the structural phase transition, this is also the reason of the coexistence region where some of both phases exists. Kim et al. showed that the slight change in the interlayer bonding did affect the bulk symmetry

in MoTe_2 [123].

We have considered several sample-related features that might hinder better Rietveld refinement quality. We performed measurements to check the quality of our samples and quantify the impurity level prior to diffraction experiments by using EDX and Raman spectroscopy. Our materials were powdered prior to all the measurements. We were concerned about the effect of powdering the single crystal on the quality of the crystal. It could have been possible that the weakly connected layers would shift or atoms might create vacancies within the crystal. However, studies on small single-crystals of $1T'$ - MoTe_2 indicates that layer shifting is already present [161]. The formation of oxides in all phases of MoTe_2 was ruled out because the material was not expected to react with ambient atmosphere. Our results indicate that the weakly attached atoms may affect the crystallinity which can lead to reduced quality of the diffraction pattern quality make the pattern harder to refine. We compared our x-ray powder diffraction data to simulated patterns created by GSAS-II software. The data for phases $1T'$ - MoTe_2 and T_d - MoTe_2 showed a large number of wide closely peaked peaks that resulted in very broad peaks instead of many well-defined peaks. The behavior of our bulk powdered $1T'$ - MoTe_2 and T_d - MoTe_2 materials is similar to the powdered few-layer nano-sheets $1T'$ - MoTe_2 reported by Sun et al. (Figure 56). This behavior also impacted the attempt to refine data from MoTe_2 phases, specially $1T'$ - MoTe_2 and T_d - MoTe_2 , although it is less in $2H$ - MoTe_2 phase.

Figures 54 and 55 showed the The temperature dependence powder neutron diffraction experiment at CNBC, Chalk River data for $1T'$ - MoTe_2 phase. The initial purpose for this experiment was to map $1T'$ - MoTe_2 and T_d - MoTe_2 coexistent region and phase transition, to confirm the x-ray powder diffraction structural determination results, and to identify the transition temperature. We wanted to study the structural changes through the coexistence region and determine how the crystal structure behaves in this region and how it changes from $1T'$ - MoTe_2 phase to T_d - MoTe_2 phase.

Figure 56. Comparison between X-ray powder diffraction patterns from APS experiment and simulated patterns using GSAS-II software. Panel a) shows a full range patterns for $1T'$ -MoTe₂ and T_d -MoTe₂. A focused portion of the patterns are shown in b) and c) for phases $1T'$ -MoTe₂ and T_d -MoTe₂, respectively.

Unfortunately, the neutron powder diffraction patterns was not reliable to perform a Rietveld analysis using GSAS-II. Figure 54 panel b at 64.8° shows a peak that appear at 5 K and disappear at 240 K which might be evidence to the phase transition. It is worth mentioning that due to the low intensity in the neutron diffraction patterns, the changes in peaks that might represent a phase transition might not be visible. Since the coexistence area is not mapped very clear in the literature, we sought to determine its temperature range. Based on our data, we believe that the sample phase coexistence region is between 205 K and 240 K.

A limitation of this study was the unintended low intensity neutron powder diffraction data which made it very difficult to analyze the data from CNBC using Rietveld analysis. Large single crystals are difficult to obtain by practically all growth methods. This makes the collection of single crystal diffraction data challenging. Nevertheless high-resolution single-crystalline data would be useful in understating the crystal model of $2H$ and $1T'$ MoTe₂.

7.6 Conclusion

MoTe₂ is an interesting material with very promising uses in the industry and physics theory. While MoTe₂ maybe already in use for some applications, many applications utilized this material as thin films or few layers. Accurate analysis of bulk MoTe₂ is difficult which has resulted in a limited understanding of the material. A probable explanation is that the MoTe₂ a vdW material and its layers are loosely stacked. This makes it easy for the different layers to slide in, and therefor the atomic position alter, which makes it challenging for resolving the crystal structure. Also, the presence of vacancies was common in the studied phases of MoTe₂. This indicates that atomic movements within the crystal structure is accessible to both Mo and Te atoms. Knowing the crystal structure and lattice parameters are important since they greatly effect the number and positions of Weyl points in the T_d -MoTe₂ phase. Our current study provides a new detailed study of bulk MoTe₂.

The main aim for this study was to characterize bulk MoTe₂ phases. We performed measurements to check the quality of our samples and quantify the impurity level prior to diffraction experiments by using EDX and Raman spectroscopy. We employed on high resolution x-ray powder diffraction to analyze the crystal structure of $2H$ -MoTe₂ and $1T'$ -MoTe₂ phases at room and 100 K. Our results were similar to what is reported in the literature. We identify the presence of vacancies specially at low temperature. These defects are related to the stacking faults in the MoTe₂ material. We believe that its due to the weakly layer binding Van der Waals forces that allowed layers to lose with respect to other layers. We identified the coexistence region in $1T'$ -MoTe₂ phase to be between 205 K and 240 K.

7.7 Further work

Further study to investigate the local structure of $1T'$ -MoTe₂ as the phase changes to T_d -MoTe₂ is needed. This will aid in understanding the phase transition and the coexistence region on the short scale.

The current work has initiated studies of the stacking faults and layer disordering particularly in $1T'$ -MoTe₂. Studies on MoTe₂ phases should investigate into details of twining of crystals and the stacking faults that might be present. The phase transition in $1T'$ -MoTe₂ can be used in many application such as pressure devices fabrication.

CHAPTER 8

CONCLUSIONS

The current work was intended to provide a deeper understanding of the crystal structure of materials related to superconductivity. Superconducting materials are influential in the rapidly expanding field of condensed matter physics. The first aim of the present research was to investigate the crystal structural details of relatively new Mott insulator the $\text{Ca}_2\text{O}_3\text{Fe}_{2.6}\text{S}_2$ and its doped variant $\text{Ca}_2\text{O}_3\text{Fe}_{2.6}\text{S}_{1.75}\text{Se}_{0.25}$. The magnetic structure of those materials was evaluated by estimating the order parameter through temperature dependent powder diffraction. The research's second aim was to assess the short-range fluctuations in another Mott insulator, $\text{La}_2\text{O}_2\text{Fe}_2\text{OM}_2$ where $M = \text{S}, \text{Se}$ using the total neutron scattering and pair distribution function (PDF). The last aim of the study was to examine in detail the crystal structure of bulk MoTe_2 . The phases $2H\text{-MoTe}_2$ and $1T'\text{-MoTe}_2$ were studied using high-resolution synchrotron x-ray powder diffraction.

One of the main findings of this study was the presence of high iron atom vacancies in the pure and doped samples. Our results estimated the vacancies to reach approximately 30% of the total iron atomic sites. Such high vacancies $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ or similar materials will affect the quality of the diffraction pattern, electrical transport properties, and the magnetic structure. Another important finding was the similarity between $\text{Ca}_2\text{O}_2\text{Fe}_{2.6}\text{OS}_{2-x}\text{Se}_x$ and $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S}, \text{Se})_2$ based on the critical β value. Our temperature-dependent neutron powder diffraction revealed that $\text{Ca}_2\text{O}_3\text{Fe}_{2.6}\text{S}_2$ has the critical exponent β of 0.1228. This β value implies that this Mott insulator

is similar to $\text{La}_2\text{O}_3\text{Fe}_2\text{M}_2$, which has a comparable critical exponent value and thus can be associated with the two dimensional antiferromagnetic Ising model.

The short-range structural study on $\text{La}_2\text{O}_2\text{Fe}_2\text{OM}_2$ for $M = \text{S}$ or Se , showed the strong presence of orthorhombic distortion on the short scale while the average scale maintained its tetragonal symmetry. These structural distortions are strong evidence of nematic behavior on the short scale in these Mott insulators. The study shows strong evidence of short-range symmetry breaking in iron-based materials. This behavior of the Mott insulator is similar to iron pnictides superconductors.

The discovery of graphene laid the ground for diverse applications based on 2D material. Naturally, closer attention was given to other materials that exhibit similar properties as graphene. One of those materials was the transition metal dichalcogenide MoTe_2 which has three stable phases. In the $2H$ - MoTe_2 phase that we studied, vacancies were found at room-temperature and increased at low temperatures. The presence of these vacancies made it very difficult to evaluate the structure through Rietveld analysis. While not confirmed by this study, we believe that the presence of these vacancies affects the transport measurements. MoTe_2 is a topological superconductor and a type-II Weyl semimetal. Understanding the details of the MoTe_2 crystal structure will help in determining the positions of the Weyl points (WP). $1T'$ - MoTe_2 phase transition is also estimated based on temperature dependence powder diffraction to be between 200 K and 240 K.

Detailed analysis of crystal structure is a significant step when determining the properties of the studied material. It gives information about the connectivity, accurate bond lengths and angles, and three-dimensional packing of the specific material. Based on the precision information of the crystal structure density functional theory (DFT) calculation can be made, magnetic structure analysis can be determined, and the quality of the crystal can be verified. The total neutron scattering and PDF analysis are powerful tools to investigate the short-range symmetry in materials. The

work done in this research can be beneficial for further studies of TMDs, iron-based superconductors, and Mott insulators.

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APPENDIX A: COMMONLY USED ACRONYMS

AFM - Anti FerroMagnetic
BZ - Brillouin zone
CVT - Chemical transpor vapour
DFT - Density functional theory
FM - Ferromagnetic
High- T_c - High temperature superconductor
HTSC - High temperature superconductor
MIT - Metal-to Insulator transition
PDF - Pair Distribution Function
LINAC - Linear Accelerator (linac)
LMDC - Layered Metal Chalcogenides
QPT - Quantum Phase Transition
SCES - Strongly Correlated Electronic Systems
SNS - Spallation Neutron Source
TMD - Transition Metal Dichalcogenide
TMO - Transition metal oxide
TOF - Time-of-Flight
2D - Two-Dimensional
2DM -Two-Dimensional Material
WSM - Weyl Semi Metal

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Publications

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2. Local structural study of novel Mott-insulating cousins of the iron pnictides. Karki, B., Alfaiakawi, A., Frandsen, B.A., Neufeld, J.C., Everett, M. and Freelon, B. Crystallography, 75, p.a376. (2019)

Posters

1. 3rd Annual Modern Methods in Rietveld Refinement for Structural Analysis, school poster title: Exploring the Phase Diagram of Novel Iron Oxychalcogenides

2. GSA meeting march 2018, University of Louisville, Poster title : Structural and Magnetic Properties of a New Mott Insulator.