Structural, vibrational and transport properties of novel complex systems.

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STRUCTURAL, VIBRATIONAL AND TRANSPORT PROPERTIES OF NOVEL COMPLEX SYSTEMS

By
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B.S. Tribhuvan University, 2015
M. S. University of Louisville, 2017

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This dissertation is dedicated to my loving parents, Bhabindra and Urmila Karki, as well as my daughter Pensa and family.
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Electron correlation effects in quantum materials are very strong. It is critical to investigate the structure of quantum materials to better understand and manipulate their physical properties. Quantum effects are prominent at the atomic microscopic length scale, which can not be examined by average long range structural measurements using traditional diffraction methods. Instead, pair distribution function (PDF) analysis, a local structure probe, can effectively unveil the mystery of local structure, which is more sensitive to local behavior than bulk average features.

The first section of my dissertation will concentrate on the local structural study of the Iron oxy-chalcogenides, La$_2$O$_2$Fe$_2$O(S, Se)$_2$, which are layered materials formed by stacking layered units of La$_2$O$_2$ and Fe$_2$OM$_2$ ($M = S, Se$). Local crystal structure was studied using the PDF technique, which involves Fourier transforming the measured total scattering intensity to obtain a real space representation of inter-atomic correlations. This technique was used to study local, short range structural correlations that deviate from the average structure. PDF analysis for $M = S, Se$ shows short-scale structural distortions in a typical range of 1-2 nm, indicating nematic fluctuations. However, neutron powder diffraction (NPD) provides clear evidence that the average, long-range structure remains tetragonal throughout the high and
low temperature regimes. A comparable result was obtained for Fe$_{1.1}$Te. These findings highlight the ubiquity of nematic fluctuations in iron-based superconductors and related materials.

The second part of my research is focused on measuring the transport and vibrational properties of black phosphorus and related materials. Phosphorene, a novel two-dimensional (2D) material, is gaining researchers’ attention due to its exceptional properties, including a unique layer structure, a widely tunable band gap, strong in-plane anisotropy, and high carrier mobility. Strain in 2D materials can tune the material properties. The effect of tensile strain on the Raman spectra of black phosphorus (BP) was studied by using a simple custom strain device revealed clear red shifting of all three phonon modes, $A^1_g$, $B^2_g$ and $A^2_g$. We anticipate that our method of in-situ Raman spectroscopy could be an effective tool that can allow observation of strain effects directly, which is critical for future flexible electronic devices. Even though, black phosphorus has several unique properties, there are some limitations in its application in devices due to its environmental instability. Several passivation techniques have been employed, but just covering the surface may not be the long term solution. Doping engineering is found to be an efficient strategy in order to enhance the properties of BP, and its promising performance in electronic devices. We have synthesized a series of As$_x$P$_{1-x}$ ($x = 0, 0.2, 0.5, 0.83, 1$) alloys which show similar properties to black phosphorus and are more stable in comparison to BP. Temperature dependent transport properties of As$_x$P$_{1-x}$ alloys show that small arsenic doping greatly increases the thermoelectric power of black phosphorus. Thermoelectric properties of these materials provide an environmentally friendly solution for direct and reversible conversion between heat and electricity. They have potential applications in a wide range of fields, including transportation, industry, and power generators/solid-state refrigerators, and may also provide solutions for sustainable energy sources.
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Atoms, as the constitute of matter, make up everything. All matter is made up of elements, which have distinct chemical and physical properties and can’t be broken down into other substances by normal chemical reactions. In nature, there are only around a hundred different atom types to choose from, as recorded in the periodic table. On the other hand, various combinations of atoms in specific spatial configurations, will result in a plethora of colorful materials with various functionalities all over the world. This is the subject of condensed matter physics, which is currently the largest research field of physics, and is primarily concerned with understanding how atom interactions produce macroscopic and microscopic physical properties in condensed phases, including solids and liquids. Only a few of the frontier physical problems that can be solved by studying structures in the condensed phases are Superconductivity [3], superfluidity [4], and colossal magnetoresistance [5]. Quantum mechanics is a fundamental physics theory that describes the physical properties of existence at the level of atoms and subatomic particles. All quantum physics, including quantum chemistry, quantum field theory, quantum technology, and quantum information science, is built on this basis [6]. Quantum materials, such as transition metal oxides, Iron (Fe) and Copper (Cu) based high-temperature superconductors, topological insulators, quantum spin liquids, graphene, and Weyl semimetals, are compounds and phenomena where the result of quantum mechanics is substantially real [7]. Furthermore, the microscopic quantum effects in these quantum materials
are not subtle; rather, they influence the macroscopic behavior of the materials. In quantum materials, electrons are no longer considered to be independent of one another, but rather interact strongly and cause mutual excitations, which change the material’s properties. At the atomic level, strongly correlated electrons often result in complex behavior. However, most of the experimental methods used to analyze condensed matter are bulk probes that test average properties, such as the traditional x-ray or neutron diffraction approach, for determining a material’s average long-range crystal structure, and magnetic or electric susceptibility measurements are used to determine the average response to a magnetic or electric field. These bulk probes are ineffective at exposing quantum materials’ local behaviors. As a result, rather than calculating the average response, the field needs local probe techniques to understand the highly correlated electron systems and investigate local and microscopic activity. In addition, external stimuli such as strain and doping will change the structure and thus alter the transport properties of these material systems.

In this dissertation, I will describe experiments conducted on quantum materials that used a powerful local structure probe, namely, pair distribution function (PDF) analysis, which is a highly effective technique for measuring the local atomic structure of materials at the atomic length scale. Chapter 3 and 4 will discuss their average and local crystal structure using powder diffraction techniques. Following that, chapter 5 discusses the effect of strain on the phonon modes of black phosphorus and MoTe₂. In chapter 6, I will present the structural and thermoelectric properties of black arsenic phosphorus alloys. Finally, in chapter 7, I will present the phonon modes study of magnetic topological insulators CrX₃.

1 Mott Insulators

The idea of non-interacting or weakly interacting electron systems, also known as non-interacting band theory, was developed in the early years of quantum mechanics
It is the first successful theoretical description of how to differentiate between metals and insulators at zero temperature, based on the electron filling of energy bands. The periodic lattice structure of atoms in crystals, unlike free electrons, restricts electron movement, resulting in the formation of band structure of materials [9]. The Fermi level (also known as the chemical potential, \( \mu \)) specifies the energy level at which electrons are filled. The Fermi level in insulators is located between two bands, such that the highest filled band is totally filled and electrons can not easily move, resulting in low electrical conductivity. Metals, on the other hand, have the Fermi level inside a band, which means the band is partially filled, resulting in high electrical conductivity. Researchers realized in the early 1930s that some insulators can be further characterized as having a narrow energy band gap between the highest filled and lowest empty bands, which may not trap electrons due to thermal excitation at a finite temperature [10]. This type of material is known as a semiconductor, and it provides the basis for the invention of transistors. This classification based on band structure has proven successful in many materials, but it does not always work, as de Boer and Verwey initially pointed out with a series of transition-metal oxides with a partially filled \( d \)-electron band, such as NiO [11]. According to the noninteracting band hypothesis, these "strange" materials should be metals, yet they were discovered to be insulators in experiments. The significant electron-electron correlations, according to Mott and Peierls, could explain this mismatch, and the strong Coulomb repulsion between electrons could be the source of the insulating behavior [12]. Mott presented the first theoretical explanation of this topic in 1949 [13]. Mott insulators are the term given to this class of materials. He considered a simple lattice model in which each site had only one electronic orbital. Because the Coulomb repulsion between two electrons would be large if they were sitting at the same site, the single band could split into two bands, with the lower energy band made up of electrons that occupy an empty site and the higher energy band from
electrons that occupy a site that has already been occupied by another electron. Only one electron is allowed at each site in this method, therefore the bottom band is full and the system is in an insulating condition. Strong electron correlations have now become a key focus of condensed matter physics research.

While much progress has been made in this field, there are still a number of unanswered questions. Apart from the Mott insulating phase, understanding the metallic phase approaching the insulating state is a more difficult task. The spin, charge, and orbital correlations all fluctuate a lot in this regime. The anomalous metallic phase is the metallic phase with a strong fluctuation around MIT if the phase transition is first-order. Hubbard proposed a simplified many-body theory, known as the Hubbard model [14], to describe two opposing tendencies in the system, in which a kinetic term (t) allows particles to hop between lattice sites, and an on-site repulsion potential term (U) represents the energy cost of having two electrons on the same site. Bigger t in the system favors electron free motion through the lattice, whereas a larger U in the system favors strong localization of the electrons, preventing them from freely moving. Afterwards, Brinkmann and Rice expanded on the Hubbard model. Importantly, despite the strong fluctuation near MIT, the Hubbard model allows us to comprehend how a transition between the Mott insulator and the neighboring metallic phase can occur. The filling-controlled Mott transition [15] is another technique to effect the transition by doping electrons or holes to adjust the band filling, increasing or decreasing the chemical potential, respectively.

2 Property Tuning in 2D Materials via Strain

Two-dimensional (2D) materials are a novel family of atomically thin materials with promising features for next-generation ultrathin semiconductor devices [16]. Due to their excellent properties related to their unique structure, these materials have sparked a lot of scientific interest. Strain engineering is a powerful technique for
modifying the band structure of various 2D materials for enhancing the performance of opto-electronic devices \[17, 18, 19, 20, 21, 22\]. Such strains can cause significant changes in the electrical, optical, magnetic, transport, and chemical characteristics of 2D materials, resulting in fascinating phenomena-ripe with new physics and creative applications. Due to their extraordinary features, 2D materials such as black phosphorus (BP) and transition metal dichalcogenides (TMDs) have drawn a lot of attention in recent years \[23, 24, 25, 26, 27\]. The majority of TMDs are low-dimensional materials made up of stacks of transition metal atoms \(M = Mo, W\) sandwiched between two single layers of chalcogens \(X = S, Se\) \[28\]. Small amounts of strain can trigger the long-known semiconductor-metal transition in thin \(\text{MoS}_2\) and \(\text{MoTe}_2\) films, which is an exciting discovery \[29\]. As a result, it may be possible to readily construct suitable 2D TMD phases using in-plane tensile strain. This would make strain a very attractive tuning parameter for material properties and electronics applications.

Due to the absence of an intrinsic band gap, graphene-based transistors with high mobility have a low on/off ratio, whereas TMDs materials (monolayer with direct band gap but two or more layers with indirect band gap) have a high on/off ratio but low mobility \[30, 31, 32, 33\]. The thickness dependent band gap of few-layer BP, which possesses a direct gap regardless of layer number, lies between the band gap of TMDs and graphene.

3 Thermoelectric Materials

Massive usage of fossil fuels depletes their natural reserves and has long-term consequences for environmental challenges such as global warming, prompting increased research and development efforts for sustainable and environmentally acceptable alternative energy sources. Because of the growing demand for high-efficiency clean energy, it is critical to develop renewable energy devices to address energy concerns and prevent further environmental degradation \[34\]. Thermoelectric devices, solar
cells, wind-driven generators, and fuel cells have all gotten a lot of attention in recent decades and have shown to be reliable power generators. Thermoelectric devices, which are among these types of energy conversion technologies, have a wide range of applications, including power generators, cooling devices, and sensors [35, 36].

![Graphical diagram for thermoelectric power.](image)

**Figure 1.** Graphical diagram for thermoelectric power.

Because of the continuous growth of the information technology industry and other related industries, there is a growing demand for innovative thermoelectric (TE) materials, which are critical for the compactness and fast operation of current electronic devices. From TE generators to TE cooling and heating equipment, these materials have a wide range of uses. This is owing to their intrinsic capacity for converting thermal to electrical energy and vice versa, which could help to resolve the energy and environmental crisis. The dimensionless temperature-dependent quantity ($ZT$) characterizes these materials efficiency and TE performance.

$$ZT = \frac{S^2\sigma T}{k} \tag{1}$$

where $S$, $\sigma$, $T$, and $k$ are the Seebeck coefficient [TE power (TEP)], electrical conductivity, temperature, and thermal conductivity, respectively. Thermal conductivity
has the contribution from both electrons and phonons so, \( k = k_e + k_l \) [37]. In order to improve the TE performance, it is necessary to have a lower thermal conductivity and the suitable combination of electrical conductivity and electrical thermal conductivity [38] or in other words, higher power factor (PF) \( (S^2\sigma) \).

4 Materials under study

4.1 Iron Oxychalcogenides

The discovery of superconductivity in iron-based superconductors (FeSCs) has attracted a large amount of attention due to the high transition temperature \( T_c \) at which they become superconducting. Although the precise pairing mechanism in these materials remains unknown, it is thought that electron-electron interactions play an important role. Such unconventional superconductivity is in contrast to the conventional electron-phonon coupling [39, 40] present in BCS superconductors. In order to examine the strong-Coulombic postulate for Fe pnictides and chalcogenides, studies were conducted [41, 42, 43, 44, 45, 46] to find iron-based Mott insulators that could be driven into the superconducting phase [47, 48]. The iron oxychalcogenides \( \text{La}_2\text{O}_2\text{Fe}_2\text{O}M_2 \) \((M = \text{S, Se})\) emerged as a candidate material because they are Mott insulators with structural similarities to the iron pnictides. Several attempts to induce SC in \( \text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2 \) have been made; however, to date, there are no published reports of SC in these systems [49]. Nevertheless, studying non-superconducting Mott insulators such as \( \text{La}_2\text{O}_2\text{Fe}_2\text{OM}_2 \) can enhance our understanding of the Mott insulating region of the iron-chalcogenide electronic phase diagram [39].

Hole-doped cuprates are prone to a variety of different type of electronic ordering like charge ordering and nematic ordering. The electronic nematicity, breaking the rotational symmetry while preserving the translational symmetry, has been observed in the pseudogap state of the cuprate superconductors. To date, several iron pnictides and cuprates show the presence of electronic nematic states, and it was thought
that the nematic phase is closely related to the superconducting mechanism in iron-based materials. Superconductivity in the cuprate superconductors is based on an electron or hole doping of a strongly correlated, Mott insulating phase \[50\]. Therefore, studying the Mott insulating phase in iron oxychalcogenides might enhance our understanding of the strongly correlated scenarios that lead to high temperature superconductivity \[51\].

Oxychalcogenides are mixed-anion compounds that contain oxide ions as well as anions from another group 6 element, most often S, Se, or Te. Following the finding of superconductivity in oxyphosphides in 2006 and the \(> 26\) K LaOFeAs superconductors in 2008, there has been a recent increase in the research of mixed anion materials \[52\]. While superconductivity has yet to be discovered in oxychalcogenide materials, there are a plethora of compounds with intriguing electrical, magnetic, and optical properties. The structural resemblance of oxychalcogenides to pnictide phases, as well as the large potential for doping these systems across the insulator-metal boundary, implies that more research into these systems is necessary. The iron oxychalcogenides \(\text{La}_2\text{O}_2\text{Fe}_2\text{OM}_2\) were first reported as antiferromagnetic (AFM) insulators by Mayer et. al. \[53\]. This layered mixed anion material 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 \[54\]. Furthermore, \(\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S,Se})_2\) allows the option for the tuning of electronic correlation strength by disorder-free chalcogen exchange of S and Se. These \(\text{FeOC}h\) is made up of stacked double-layered units \(\text{La}_2\text{O}_2\) and \(\text{Fe}_2\text{O}(\text{S,Se})_2\). An Fe-M layer exists in the \(\text{Fe}_2\text{O}(\text{S,Se})_2\) unit, which is analogous to the FeAs layer seen in pnictides. An additional O(1) atom is included in the rare-earth layer. In comparison to LaOFeAs, chalcogen substitution leads in a slightly larger Fe-square-lattice unit cell of \(\text{La}_2\text{O}_2\text{Fe}_2\text{OM}_2\) (\(M = \text{S, Se}\)). As a result of the decrease in electronic bandwidth \(W\), the Hubbard \(U\) increases, providing a parameter to change \(U/W\) across a key value for a Mott insulator phase. In this structure,
Figure 2. The crystal structure of $\text{La}_2\text{O}_2\text{Fe}_2\text{OM}_2$ ($M = \text{S, Se}$) is shown in the left panel. The right panel shows $\text{FeO}_2\text{Se}_4$ octahedra, where the Fe atom is surrounded by four $M = \text{S, Se}$ atoms and two $\text{O}(2)$ atoms. Black solid lines show the angle formed by Fe-O-Fe atoms while the dashed lines show $M$-Fe-$M$ angle.

$[\text{Fe}_2\text{O}]^{2+}$ consists of an anti-CuO$_2$ arrangement with an Fe$^{2+}$ cation coordinated by four M$^{2-}$ (above and below the plane) and two in-plane oxygen atoms, forming a tilted Fe-centered FeO$_2$Se$_4$ octahedron [53, 55, 56, 57, 51, 58]. Fig. 2 shows the crystal structure of $\text{La}_2\text{O}_2\text{Fe}_2\text{OM}_2$ and its octahedra. Structural studies using X-ray [57] and neutron [54] powder diffraction studies did not observe a structural phase transition in $\text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2$. However, an antiferromagnetic ordering was observed at Néel temperatures $T_N$ of 107.2 K and 90.1 K for $\text{La}_2\text{O}_2\text{Fe}_2\text{OS}_2$ and $\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$, respectively [54]. Experiments have indicated the AFM order to be consistent with a 2 - $k$ magnetic structure in which two spin stripe phases are oriented 90° with respect to each other. [54, 59, 60, 55]

Therefore, the structural and magnetic behavior do not have the same corre-
spondence that is observed in some iron-pnictides and iron-chalcogenides in which magnetic and structural phase transitions are coupled. The absence of a structural phase transition in the \( \text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2 \) Mott insulators motivates us to study the local structure to determine whether their short-range lattice symmetries undergo changes. In particular, we are interested in understanding whether local deviations from the average tetragonal structure occur and we seek to characterize lattice or atomic correlations with physical properties.

To date, several studies of FeSCs [61, 62, 63, 64, 65, 66] have revealed the presence of a long-range, non-superconducting state called the nematic phase [62] that precedes the superconducting phase transition. The short-range nematic phase, which has been observed in both iron pnictides and iron chalcogenides, develops at a structural phase transition temperature \( T_s \) higher than a magnetic transition temperature \( T_N \) [67]. The long-range nematic ordering is manifested by spontaneous rotational symmetry breaking while the translational symmetry is preserved [68, 69]. In iron pnictide superconductors symmetry is broken between x and y directions in the Fe-plane [62]. This reduces the rotational point group symmetry from tetragonal to orthorhombic while preserving the translational symmetry. [68, 66]. Nematic ordering was first observed in liquid crystals [70] a long time ago; however, recently quantum analogs of these phases have been discovered in electron fluids. In particular, quantum-Hall systems and many strongly correlated electron systems with very small in-plane structural anisotropy, such as cuprates and pnictides, display very large anisotropies in their physical properties [70, 66]. In the case of iron-based superconductors, the tetragonal symmetry of the normal state is broken, resulting in orthorhombic lattice distortions. Upon doping, the nematic state is suppressed and superconductivity emerges from the broken \( C_4 \) rotational symmetry state \( [71, 72] \) but often nematic ordering persists into the superconducting state as in LiFeAs [73]. The origin of nematic ordering is not yet fully understood. In the pnictides, it appears to be
related to the magnetism, but this may not be the case in iron chalcogenides such as FeSe, which does not show long-range magnetic ordering [67].

4.2 MoTe$_2$

Transition metal dichalcogenides (TMDs), having a general form $MX_2$ such that ($M$ = Mo, W, Ti, Zr, Hf, V, Nb, Ta, Tc, Re, Co, Rh, Ir, Ni, Pd, Pt) and ($X$ = S, Se, Te), have been studied for several decades [74, 75] because of their industrial applications. Recently, molybdenum-based TMDs have received theoretical and experimental attention because of their potential to advanced beyond silicon and graphene in developing a new generation of electronics devices [76, 77]. Recently, a great deal of interest in these materials has been ignited because of the wide range of electronics properties associated with these van der Waals (vdW) layered materials. Semiconducting two dimensional transition metal dichalcogenides are being intensely examined as the channel material for post-Si electronic devices [76, 78, 79, 80]. Furthermore, the ability to create single monolayer (1ML) TMD samples by exfoliation has opened the door of discovery for novel properties [81]. Unlike graphene, TMD monolayers can possibly exist in more than one crystal structure. As TMD thickness approaches a few layers, the materials undergo an indirect band gap to a direct band gap transition [82, 83, 84].

Among the TMDs, hexagonal molybdenum ditelluride MoTe$_2$ is a layered semiconductor currently has been studied for use in photo-electrochemical solar cells [85]. MoTe$_2$ has also been proposed as a base material for $pn$-junctions [86, 87], field-effect transistors [87], complementary metal-oxide semiconductor (CMOS) devices [88, 89], Schottky barriers [90] and gas sensors [91]. MoTe$_2$ is also being considered as an alternative to graphene [92]. The small band gap of molybdenum ditelluride MoTe$_2$ in addition to its large spin–orbit (SO) coupling splitting has lead to interest for optoelectronic, spintronic, and valleytronic applications. Because of its modest band gap,
high field-effect mobility, it is possible to tune the phases from $1T'/2H$ by means of and tunable phases [93]. Three-dimensional (3D) topological Weyl semimetals (TWSs) [94] 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, because they display a range of physical properties of promising usage [95]. Theoretical prediction claims that 2$H$ TMDs may become superconductors at high pressure. MoTe$_2$ shows superconductivity at transition temperature 0.1 K, and at high pressure (11.7GPa) the transition temperature gets up to 8.2 K [96].

Due to a trigonal prismatic crystal-field splitting of a filled nonbonding d$_{z^2}$ orbital, the group VIb ditellurides show deviation from a simple band model, which indicates semiconducting behavior. The ditellurides of Mo and W differ from their diselenides and disulphides in such a way that they can crystallize with a distorted octahedral coordination around the metal atoms, which are displaced from the center of the octahedra and form chains running through the crystal [97]. Electronic calculation paper by Bullett [97]. In-plane resistivity measurements suggest the existence of a first-order phase transition near 250K [98]. The group V and VI ditellurides form crystalline structures primarily in the 1$T$ polytype. A typical TMD shows the trigonal prismatic 2$H$ or the octahedral 1$T$ structures. In particular, MoTe$_2$ exhibits two polytype kinds. The 2$H$, called $\alpha$-MoTe$_2$ is a stable semiconductor [99, 100], while the 1$T$ distorted polytype is known as $\beta$-MoTe$_2$ which is unstable [101, 102]. Trigonal prismatic $\alpha$ form is stabilized by the opening of a hybridisation gap within the Mo $d$-band manifold, splitting off the full d$_{z^2}$ band. However, such a gap does not occur for ideal octahedral coordinate structure [103, 98]. Matthies calculated the band structure of MoTe$_2$ [103].

There is considerable interest in the phase transition behavior of transition metal dichalcogenides (TMDs) because the phase changes are often coupled with other
changes with these low dimensional systems \cite{104, 93}. Structural phase transition from 2\textit{H} to 1\textit{T}′ phase in few-layer MoTe\textsubscript{2} was found to be driven by electrostatic doping \cite{105} and by laser irradiation \cite{106}. Moreover, Structural phase transitions from the \textit{T}\textsubscript{d} to \textit{T}' phase can be driven by temperature \cite{107, 108}. In the monolayer, low-temperature phase \textit{T}\textsubscript{d}-MoTe\textsubscript{2}, is a type-II Weyl semimetal showing topological surface state Fermi arcs and chiral anomalies induced negative magnetoresistance is formed through temperature-induced phase transition from 1\textit{T}'-MoTe\textsubscript{2} \cite{109, 110}.

4.3 Fe\textsubscript{1.1}Te

The link between electronic nematicity, magnetic order and orbital order and their influence on high-\textit{T}\textsubscript{c} superconductivity is a highly controversial aspect in the physics of iron-based superconductors (FeSCs). This is due to the complexity introduced by the coupling of nematicity, orbital order, and magnetic order. It is believed that nematicity and superconductivity have a deep connection, since optimal superconductivity occurs near nematic instabilities in FeSCs. Exploring the role of an electronic nematic phase that breaks the \textit{C}\textsubscript{4} lattice symmetry of many different iron-pnictides and iron-chalcogenides is an outstanding goal among researchers. The field of iron-based high-\textit{T}\textsubscript{c} superconductivity (HTSC) faces a challenging perplexity since both magnetic and orbital fluctuations have been proposed as the cause of Cooper pair formation. Adding to the confusion is the question of which degree of freedom is the driver, orbital or spin? HTSC has been argued to be the result of spin fluctuations that form after the suppression of canted antiferromagnetic (CAFM) order by the introduction of doping or external pressure. Making universal understanding more difficult is the fact that some materials, such as FeSe, do not possess a long-range ordered magnetic phase. Adding to the complexity is the nearly universal observation of an electronic nematic phase that breaks the \textit{C}\textsubscript{4} lattice symmetry of many different iron-pnictides and iron-chalcogenides (FeCh). The detailed impact of the electronic
nematic phase on the formation of the Cooper pair is far from being understood. Previously, magnetic fluctuations were believed to trigger superconductivity in iron-based superconductors [39, 47]. It was reported that superconductivity arises solely near the magnetically ordered state, however, multiple studies [61, 62, 63, 64, 65, 66] revealed that there is another non-superconducting state also called as nematic state along side with magnetism [62]. Since, the superconductivity in the cuprate superconductors is based on electron or hole doping into a strongly correlated Mott insulating phase [50], studying the Mott insulating phase in iron chalcogenides might help us to understand the mechanism of high temperature superconductivity [51].

The parent compounds for iron pnictides are correlated materials on the border of Mott localization [51]. Better understanding of relatively simpler materials that are similar to FeSCs and the role of strongly coupled electron interactions can better explain superconductivity in non-conventional superconductors. The critical importance of electron-electron interactions, which give rise to new emergent collective electronic orders, including magnetism, electronic nematic order, and superconductivity, is outstanding among the many other challenges. These degrees of freedom are closely associated in iron-based superconductors. By studying their co-evolution across the phase diagram, the interplay between these orders can be deciphered. To understand the nature of the superconductivity mechanism, it is very important to know how superconductivity arises in these systems.

Iron pnictide and chalcogenide superconductors (FeSC) have parent phases that suffer antiferromagnetic (AFM) ordering during cooling and structural distortion lowering the high-temperature tetragonal (HTT) paramagnetic lattice symmetry, similar to cuprates [111, 112]. They also have strong magnetic fluctuations, which is a sign of unusual superconductivity [113]. The Fe-based materials, unlike cuprates, have multiple unfilled 3d bands. The Fermi surfaces of their parent magnetic phases are well-defined, indicating that they are metallic. The growth of theoretical models
and techniques is due to weak Mottness and itinerancy paired with orbital degeneracy linked with magnetic and lattice degrees of freedom. Strong coupling, in which physics is governed by the qualities of the electronic Fermi surface or mixed spin-orbital models. Fe$_{1.1}$Te is the last member of the FeSC chalcogenide family, where correlation effects are the strongest [114]. Crystal structure of Fe$_{1.1}$Te is shown in Fig. 3

Fe$_{1+x}$Te is a two-dimensional van der Waals antiferromagnet that becomes superconducting when the Te site is replaced with an anion. The amount of interstitial iron between the iron-tellurium layers affects the characteristics of the parent phase of Fe$_{1+x}$Te. As a function of iron concentration x, Fe$_{1+x}$Te has been discovered to have two spatially long-range correlated magnetic phases separated by a region of spatially short-ranged magnetic order. Fig. 4 shows the phase diagram of Fe$_{1+y}$Te with magneto-structural phases transition. Fe$_{1.1}$Te undergoes magnetic phase transition from paramagnetic to commensurate antiferromagnetic at temperature 70 K. Under a temperature where a structural transition from a tetragonal ($P_4/nmm$) to

![Crystal Structure of Fe$_{1.1}$Te](image_url)
a monoclinic ($P_{21}/m$) unit cell occurs, the magnetic structure is collinear for small interstitial iron concentrations $x \leq 0.12$ [115]. This indicates the strong magnetoelastic coupling in this material, since both structural and magnetic phase transitions occur at nearly the same temperature. The magnetic structure with low interstitial iron concentrations is known as a "double-stripe" structure, and it has been widely studied using unpolarized and uniaxial polarized neutron scattering [1]. Magnetic moments aligned along the crystallographic $b$ axis and magnetic Bragg peaks in the neutron cross section at $Q = (12, 0, 12)$ characterize this collinear magnetic phase. Because it is metallic at low temperatures and easily cleavable, surface techniques can be used to investigate the electrical and magnetic properties.

**Figure 4.** Temperature-composition phase diagram of Fe$_{1+y}$Te. AFM and IC AFM stand for antiferromagnetic and incommensurate antiferromagnetic phase, respectively.[1]
4.4 Black Phosphorus and its alloys

There has been a search for new two-dimensional (2D) materials since the discovery of graphene in 2004, with the aim of fully studying new basic phenomena arising from quantum confinement and size effects. This quest has sparked a flurry of new areas of research, both theoretical and experimental, targeted at technological breakthroughs. Among the newly discovered 2D materials, phosphorene, a monolayer 2D material exfoliated from black phosphorus, is one of the most intriguing due to its exotic properties [116] such as tunable bandgap (\(\sim 1.5\) eV for a monolayer to 0.3 eV for bulk BP), quantum confinement perpendicular to 2D plane, lack of dangling bonds, enhanced surface area, compatibility with heterostructures, and strong interaction with light, which makes it a good catalyst [117]. Furthermore, the compatibility of phosphorene with other 2D materials in so-called van der Waals heterostructures can provide solutions to important issues such as surface degradation, doping, and electronic structure control of the surface/interface, as well as enable novel functionalities and devices with unrivaled performance. In 1914, it was synthesized by heating white phosphorus at high pressures (12,000 atm). Black phosphorus resembles graphite in appearance, characteristics, and structure as a 2D substance, being black and flaky, a conductor of electricity, and having puckered sheets of connected atoms. Its outermost shell has five electrons and has a puckered shape. It has a simple cubic and rhombohedral crystal structure. The orthorhombic crystalline form, on the other hand, is one of a kind, promising structural stability of Black Phosphorus (BP) above White Phosphorus (WP). When monolayers of black phosphorus (phosphorene) are piled to form a bulk BP, the \(sp^3\) hybridization can be detected [118]. Within the plane of layers, phonons, photons, and electrons in layered black phosphorus structures behave in a highly anisotropic manner, showing promising applications in thin film electronics and infrared optoelectronics [119].

Despite the fact that phosphorene possesses a variety of intriguing features, produc-
ing few-layer phosphorene on a big scale remains a difficult task [120]. Phosphorene is unstable and degrades quickly in the environment, which limits its use in various applications [120, 121]. The development of liquid droplets on the BP flake is a common sign of black phosphorus degradation [122]. Several approaches, including surface functionalization and coatings, have been proposed and tested for successful passivation of BP flakes. It has been reported that double-layer Al$_2$O$_3$ and hydrophobic fluoropolymer can be used to make air-stable BP devices [123]. Gamage et al. investigated the efficiency of boron nitride (BN) encapsulation followed by Al$_2$O$_3$ coating in inhibiting BP degradation [124]. Nevertheless, simply covering the surface may not be the solution in all instances. Making layered materials out of BP alloys could be a viable alternative to coping with phosphorene’s limits while keeping (or perhaps improving) existing properties [125]. Some binary phosphide materials (MP$_x$), where M could be a group III, IV, or V element, have recently been discovered to be interesting candidates for this purpose [120, 126, 127]. Specifically, alloying BP with arsenic (As) gives As$_x$P$_{1-x}$ compounds, which have a layered structure similar to phosphorene’s puckered honeycomb structure and outstanding physical properties [38, 128, 129, 130, 131, 132, 133]. This structure has the same phosphorene lattice as the previous one, but certain P atoms have been substituted by As atoms (depending on $x$). A small outward movement of As atoms in the primitive unit cell, on the other hand, increases the lattice constants [120, 134]. According to a recent theoretical study, As$_x$P$_{1-x}$ monolayer structures may be more stable than phosphorene monolayer structures, with a larger anisotropy for thermal conductivity [135]. As$_x$P$_{1-x}$ alloys, in comparison to BP, have a significantly larger potential for efficient TE materials due to their significantly higher mobility and lower thermal conductivity. Furthermore, these material properties may be easily tuned by modifying the chemical composition during the synthesis stage. For example, the bandgaps of As$_x$P$_{1-x}$ have been discovered to be narrow and fully tunable [128, 132]. Later in
this dissertation, I will present the synthesis, vibrational and transport properties of black arsenic phosphorus alloys.

4.5 Chromium halides (Cr\textsubscript{X} \textsubscript{3})

Two-dimensional (2D) materials with unique electronic structures that can host novel magnetic, photonic, electric, and superconducting properties have recently attracted attention because of their potential applications in spintronics, quantum computing, quantum information, catalysts, and energy storage \cite{136, 137, 138, 139}. Among these 2D materials, Chromium trihalides (Cr\textsubscript{X} \textsubscript{3}, \textit{X} = Cl, Br, and I), despite being heavily studied more than half a century ago, have recently attracted much attention due to their unique low temperature magnetic orders in the monolayer and few-layer forms \cite{140, 141, 142}. In the monolayer, all Cr\textsubscript{X} \textsubscript{3} display the in-plane ferromagnetic (FM) order. In Cr\textsubscript{X} \textsubscript{3}, Cr\textsuperscript{3+} ions are arranged in a honeycomb network and located at the centers of edge sharing octahedral of six halogen atoms. CrI \textsubscript{3} is a ferromagnet with a Curie temperature (T\textsubscript{C}) 61 K, and CrCl \textsubscript{3} is an in-plane ferromagnet and out-of-plane antiferromagnet (AFM) with an ordering temperature (Neel temperature, T\textsubscript{N}) near 17 K. At ambient temperature, CrCl \textsubscript{3} has the monoclinic AlCl \textsubscript{3} structure (space group \textit{C}_2/m), whereas below 240 K, it has the rhombohedral BiI \textsubscript{3} structure (space group \textit{R}3). CrBr \textsubscript{3} undergoes the same crystallographic phase change, but at 420 K, resulting in a rhombohedral shape at room temperature \cite{140, 141, 143, 144}. Both CrCl \textsubscript{3} and CrBr \textsubscript{3} are Mott Hubbard insulators. Below roughly 17 K, the chloride layers stack antiferromagnetically, with Cr magnetic moments aligned ferromagnetically within each CrCl \textsubscript{3} layer. Below its Curie temperature (T\textsubscript{C}) of 37 K, CrBr \textsubscript{3} is ferromagnetic, and unlike the chloride, the bromide has Cr moments directed normal to the Cr\textsubscript{X} \textsubscript{3} layers, resulting in increased magnetic anisotropy in the magnetically ordered state \cite{145}. The out-of-plane spin coupling becomes antiferromagnetic (AF) in the bilayer, which changes to FM for trilayer/bulk for CrI \textsubscript{3} and CrBr \textsubscript{3} but CrCl \textsubscript{3} remains AF.
Because of the strong spin-lattice interaction and the hexagonal stacking order, the magnetic properties of Cr$_X_3$ depend sensitively on the number of layers and can be manipulated by the electric-field, magnetic-field, pressure, and strain.

5 Outline of the Thesis

The research work in this dissertation focuses on discovering the structure, vibrational and transport properties of various layered materials. Chapter 2 describes the experimental techniques that are used throughout this research. Mostly, x-ray/neutron diffraction techniques are used for structural and magnetic structure studies. Vibrational modes of black phosphorus were studied using Raman spectroscopy and, finally, transport studies were undertaken by measuring resistance and thermoelectric power. Chapter 3 explores local structural study of iron oxychalcogenides La$_2$O$_2$Fe$_2$O(S, Se)$_2$ using pair distribution function technique. We observed the presence of short-range nematic like fluctuations in a typical range of 2-3 nm. I investigated the local structure of Fe$_{1.1}$Te in Chapter 4. This material, like the iron oxychalcogenides, demonstrated the presence of nematic fluctuations. Average structure shows the first order structural phase transition from the tetragonal to the monoclinic structure. This finding highlights the ubiquity of nematic fluctuations in iron-based superconductors and related materials. In Chapter 5, we have investigated how tensile strain influences the vibrational modes of black phosphorus and MoTe$_2$. I have designed a custom strain device that was used to strain the crystals of black phosphorus and MoTe$_2$. In-situ Raman spectroscopy on BP revealed clear red-shifting of all three phonon modes of BP. We also observe a remarkable resemblance between donor-type intercalation induced vibrational properties and tensile stress-induced vibrational properties in BP. Our method of in-situ Raman spectroscopy can be an effective tool that can allow observation of strain effects directly, which is critical for future flexible electronic devices. Chapter 6 discusses the structural and electri-
cal transport properties of black arsenic phosphorus. In this work, we synthesized and reported a comparative study of thermoelectric power (TEP) and resistance of $\text{As}_x\text{P}_{1-x}$ ($x = 0, 0.2, 0.5, 0.83, 1$) alloys as potential TE materials. As the arsenic concentration, $x$, increases from 0 to 1, the 4-probe resistance of the $\text{As}_x\text{P}_{1-x}$ decreases by more than 3 orders of magnitude. The transport experiments demonstrate that samples with the greatest arsenic concentrations ($x = 1$ and 0.83) exhibit metallic behavior in the temperature dependence of resistance, with a small thermopower at room temperature. Finally, in Chapter 7, I discussed the synthesis, characterization, and vibrational properties of chromium halides ($\text{CrX}_3$) ($x = \text{Cl, Br, I}$). We observe the systematic shifting of phonon modes with respect to strain. Furthermore, despite the lack of energy resolution, it was discovered that RIXS is much more accurate at calculating the energy scales than XAS, and that determining these parameters by RIXS can greatly avoid the prohibition of the $d−d$ transition in Raman spectroscopy.
CHAPTER 2
EXPERIMENTAL TECHNIQUES

1 Scattering

1.1 Crystalline Materials

Crystalline materials have structures that show long range ordering and periodicity of atoms, ions or molecules. In contrast, amorphous materials don’t show a regular arrangement of atoms. A crystal structure is made up of a motif and a lattice, which is a collection of atoms arranged in a specific pattern. Motifs are located on the points of a lattice, which is an array of points repeated periodically in three dimensions. This periodic arrangement of a crystalline material is called a lattice, and the small repeating structural entity within a lattice is called the unit cell. If the arrangements of the atoms within the unit cell are known, then the crystal structure can be determined. Thus, when characterizing a crystalline material we solely characterize the dimensions and the contents of the unit cell. The orientation of a plane or set of parallel planes of atoms in a crystal is determined by a group of three numbers called as miller indices. These numbers are determined by the plane’s intersection with the crystallographic axes. The reciprocals of these intercepts are computed, and fractions are cleared to give the three Miller indices ($hkl$). There are seven crystal systems and fourteen Bravais lattices based on symmetry and dimensions of these unit cells, which are listed in Table 2.1.
Table 2.1. The seven crystal systems with their crystallographic axes and axial angles.

<table>
<thead>
<tr>
<th>No.</th>
<th>Crystal System</th>
<th>Crystallographic Axes and Axial Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cubic</td>
<td>$a = b = c, \alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>2</td>
<td>Tetragonal</td>
<td>$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>3</td>
<td>Orthorhombic</td>
<td>$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>4</td>
<td>Rhombohedral</td>
<td>$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$</td>
</tr>
<tr>
<td>5</td>
<td>Hexagonal</td>
<td>$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
</tr>
<tr>
<td>6</td>
<td>Monoclinic</td>
<td>$a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$</td>
</tr>
<tr>
<td>7</td>
<td>Triclinic</td>
<td>$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$</td>
</tr>
</tbody>
</table>

1.1.1 Basic theory of scattering

In 1914, Von Laue formulated the first X-ray diffraction pattern of crystal to investigate the atomic structure of a material. The intensity of the diffraction peaks are determined by the arrangement of atoms throughout entire crystals.

\[ I_{hkl} \propto |F_{hkl}|^2 \quad (2) \]

where,

\[ F_{hkl} = \sum_{j=1}^{m} N_j f_j e^{2\pi i (hx_j + ky_j + lz_j)} \quad (3) \]

Where, $F_{hkl}$ is the structure factor and $f_j$ is the form factor.

There are several uses of X-ray diffraction:

- Phase identification
- Crystal structure determination
- In situ analysis (Phase transitions, thermal expansion coefficients, etc.)
1.1.2 Bragg’s law of diffraction

Bragg’s diffraction was first proposed by Lawrence Bragg and his father William Henry Bragg in 1913 in a response of surprising patterns of reflected X-rays observed from the crystalline solids. Bragg’s law is a special case of Laue diffraction which determines the angles of coherent and incoherent scattering from a crystal lattice.

When X-rays are incident on particular atom, they make an electronic cloud move colloquial to an electromagnetic waves. Bragg diffraction occurs when radiation, with a wavelength comparable to atomic spacing’s, is scattered in a specular fashion by the atoms of a crystalline system. Similarly scattered radiation that undergoes constructive interference will produce diffracted intensity. In order for the waves to interfere constructively, the differences in the travel path must be equal to integer multiples of the wavelength. The path difference between two waves undergoing interference is given by $2d \sin \theta$, where $\theta$ is the glancing angle.

According to Bragg’s Equation:
Figure 2.6. Bragg’s law of diffraction

\[ n\lambda = 2d \sin\theta \]  

- The equation explains why the faces of crystals reflect X-ray beams at particular angles of incidence \((\theta, \lambda)\)
- \(d\) indicates the distance between the atomic layers and \(\lambda\) is the wavelength of the incident X-ray beam.
- \(n\) is an integer.

Since Bragg’s law is the basis for all diffraction, there are numerous applications in the field of science. In X-ray diffraction (XRD) the interplanar spacing or \(d\)-spacing of a crystal is used for the characterization and identification purposes. In the case of X-ray fluorescence spectroscopy, crystals of known \(d\)-spacing are used for analyzing crystals.
1.2 X-ray and neutron diffraction

Many remarkable advancements in the field of materials sciences have been made possible because of the discovery of X-ray and neutron diffraction. In the history of Nobel Prize victories, four Nobel prizes have been awarded for diffraction-based discoveries. In 1914 M. von Laue received the prize for discovering diffraction phenomena: diffraction of X-rays by crystals. W. H. Bragg and W. L. Bragg (1915) for developing the foundation for the crystal structure analysis with X-rays, and W. C. Rontgen (1891) was awarded for the discovery of X-rays. B. N. Brockhouse and C. G. Shull (1994) for their remarkable contributions in the development of neutron scattering techniques for studies of condensed matter systems. Both, X-ray and neutron diffraction basically follow Bragg’s law of diffraction and owing to some of their complementary characteristics simultaneous usage of both techniques provide combined advantages. X-rays are electromagnetic waves that interact with the electron density of atoms and the scattering power is directly proportional to the atomic form factor. Neutrons by contrast are charge neutral particles which interact with the nucleus of atoms and it’s scattering power is independent of the electron density. Instead it depend on the neutron scattering length and has no clear trend as the atomic form factors. Neutron cross sections and scattering lengths of different atoms can be found on the NIST website.

There are many advantages of using neutrons over x-rays. Neutron diffraction is more suitable for characterizing lighter elements such as oxygen. In a crystalline system which has both heavy and light elements, or having elements with similar atomic numbers, using both X-ray and neutron diffraction give optimum results. Due to the higher penetration power than X-rays, neutrons are more favored for bulk analysis [146]. As neutrons possess magnetic moment, neutrons are often used to characterize magnetic materials. Since, the magnetic moment of neutron interacts with the magnetic moment of the unpaired electron of the magnetic materials. Finally,
inelastic neutron scattering is an important probe to study the dynamic behavior of materials. This is because the energies of thermal neutrons (10-110 mev) are comparable to that of phonons in the crystal lattice. This is done by measuring the vibrational density of states.

Some of the drawbacks of neutron scattering are; neutron sources are very expensive compared to X-rays and it costs millions of dollars annually for operating nuclear research reactor. As neutrons are characterized by relatively low fluxes compared to X-rays sources they have limitation for studying rapid time dependent processes. Also, relatively large amount of samples are needed for neutron diffraction experiments.

1.2.1 Magnetic Neutron Scattering

Apart from nuclear scattering, the next important process is the scattering of neutrons by the magnetic moments of unpaired electrons [147, 148]. Magnetic neutron scattering comes by the magnetic dipole-dipole interaction between the magnetic dipole moment of the neutron and the magnetic field of the unpaired electrons, which has both spin and orbital angular momentum contributions. This magnetic neutron scattering allow us to study the magnetic properties of a sample on an atomic level.

Let us consider a neutron with the nuclear moment \( \mu_N \) is at position \( R \) with respect to an electron with spin \( S \), moving with a velocity \( v_e \).

The interaction potential between neutron with magnetic moment \( \mu_N \) and magnetic field due to unpaired electron is given by,

\[
V_M = -\mu_n . B
\]

where, the magnetic moment of the neutron is given by,

\[
\mu_n = -\gamma_n \mu_N . \sigma
\]

here, \( \sigma \) denotes the spin operator, \( \mu_N \) is the nuclear magneton and \( \gamma_n = -1.913 \) is the gyromagnetic factor of the neutron. The magnetic field \( B \) of an electron due to both
spin and orbital part is \( B = B_S + B_L \).

Thus, the dipole field of the spin moment is given by;

\[
B_S = \nabla \times \left( \frac{\mu_e \times R}{R^3} \right) ; \mu_e = -2\mu_B S
\]  

(7)

Now, the field due to the movement of the electron is given by according to Biot-Savart:

\[
B_L = -\frac{e\nu_e \times R}{cR^3}
\]  

(8)

\[ \text{Figure 2.7.} \] For magnetic neutron scattering, only the component \( M_\perp \) of the magnetization perpendicular to the scattering vector \( Q \) is of relevance.

Finally, the magnetic scattering cross section, where the neutron changes its wave vector from \( k \) to \( k' \) and the projection of its spin moment to a quantisation axis \( z \) from \( \sigma_z \) to \( \sigma_z' \) can be expressed within the first Born approximation:

\[
\frac{d\sigma}{d\Omega} = \left( \frac{m_n}{2\pi\hbar^2} \right)^2 | < k'\sigma_z' | V_M | k\sigma_z > |^2
\]  

(9)
substituting the value of $V_M$ in equation 9,

$$= (\gamma_n \gamma_0)^2 | - \frac{1}{2\mu_B} < \sigma_x | \sigma_z M_\perp(Q) | \sigma_z > |^2 \quad (10)$$

where, $M_\perp(Q) = \hat{Q} \times M(Q) \times \hat{Q}$. (Neutrons only see the component of the magnetisation perpendicular to the scattering vector as shown in Figure 2.7)

$$= (\gamma_n \gamma_0)^2 | f_m(Q) \sum S_{i\perp} e^{iQ.R_i}|^2 \quad (11)$$

Here, $f_m(Q)$ is the magnetic form factor, which is connected with the spin density ($\rho_s$) of an atom via fourier transform.

$$f_m(Q) = \int_{\text{Atom}} \rho_s(r) e^{iQ.r} d^3r \quad (12)$$

Considering only magnetic interaction between the unpolarized neutrons and the identical magnetic ions with localized electrons, and for spin only, the differential scattering cross-section is written as,

$$\frac{d^2\sigma}{d\Omega dw} = (\gamma r_0)^2 \frac{k_1}{k_0} F_M^2(Q) e^{-2W(Q)} \sum_{\alpha,\beta} (\delta_{\alpha\beta} - \frac{Q_{\alpha} Q_{\beta}}{Q^2}) S^{\alpha\beta}(Q, w) \quad (13)$$

with

$$S^{\alpha\beta}(Q, w) = \sum_{j,j'} e^{iQ.(R_j-R_{j'})} \sum_{\lambda_0,\lambda_1} p \lambda_0 < \lambda_0 | S_{j'}^{\alpha} | \lambda_1 > < \lambda_1 | S_{j}^{\beta} | \lambda_0 > \times \delta(hw + E_{\lambda_0} - E_{\lambda_1}) \quad (14)$$

the so called magnetic scattering factor. $F_M(Q)$ is dimensionless magnetic form factor, $e^{-2W(Q)}$ is the Debye-Waller factor and $S_{j}^{\alpha}(\alpha = x, y, z)$ is the spin operator of the $j^{th}$ ion at site $R_j$. The magnetic form factor falls off with the increasing modulus of the scattering vector $Q$. The polarization factor $(\delta_{\alpha\beta} - \frac{Q_{\alpha} Q_{\beta}}{Q^2})$ tells that neutrons can only couple to magnetic monment or spin fluctuations perpendicular to $Q$ which allows to determine moment directions or to distinguish between different polarization of spin fluctuations.
For elastic scattering \((\lambda_0 = \lambda_1)\), the scattering cross-section is obtained by integrating equation 13 w.r.t \(\omega\) which takes the form:

\[
\frac{d\sigma}{d\omega} = (\gamma r_0)^2 e^{-2W(Q)} F_M^2(Q) \sum_{\alpha,\beta} (\delta_{\alpha\beta} - \frac{Q_\alpha Q_\beta}{Q^2}) \sum_i e^{iQ.l} \langle \hat{S}_0^\alpha \hat{S}_l^\beta \rangle,
\]

where, \(l = R_j - R_{j'}\).

1.3 Analysis of Powder diffraction patterns:

Crystalline materials are mainly classified into two groups ie. single crystals and powder/polycrystalline materials. In this thesis work, powdered samples are used for the diffraction measurement in order to extract their structural and magnetic structure information. Lab based powder diffractometer as well as national labs powder diffractometer are used to analyze polycrystalline samples. In x-ray diffractometer, X-rays are generally produced in x-ray tube, which are then scattered on a powder sample. The diffracted rays from the samples are detected by an X-ray detector. Diffracted pattern collected by the detector are then normalized to produce the plots of scattered intensity vs Bragg angle. These diffraction pattern can be analyzed both qualitatively and quantitatively to reveal the crystal structure and phase information of the material. Through the qualitative analysis, the collected diffraction pattern is matched with a database pattern using the data visualization software such as Diffract Eva or JADE, which allows the phase identification and identification of the presence of impurities in a material. Quantitative analysis provides the detail crystal structure information and is more complicated and there has been many recent advances in this regard. Here, we discuss several different quantitative methods that has been used in this research.

1.3.1 Le Bail Fit

This method was first put forward by Armel Lebail in 1988. It is a whole powder pattern fitting technique which extracts intensities from powder diffraction data [149].
This is mostly used to find intensities that are suitable to determine the correct space group, lattice parameters of a crystalline material and also it is helpful in checking phase purity. Algorithm in Lebail fit involves refining unit cell, profile parameters, peak intensities to match the measured experimental powder diffraction pattern. This method is useful for the analysis of in-situ diffraction pattern and phase transitions in high pressure and temperature experiments. The Lebail method is different from the Rietveld method as it uses fewer parameters, and also the structural factor and the related structural parameters of the material of interest doesn’t need to be known completely.

1.3.2 Rietveld Refinement

Rietveld refinement is a full profile quantitative analysis method which allows one to fit a structural model of an observed powder diffraction data. This method was first proposed by Hugo Rietveld in 1967 in which the calculated pattern is fitted with an experimental diffraction pattern using a least squared minimization algorithm [150]. The fundamental concept behind this method is to generate a powder diffraction pattern from a initial model, compare this with the observed pattern, refine the model using least square minimization algorithm and then iterate these steps until the better model is found. This method is different from a Lebail fit basically due to the fact that it looks to the content of the unit cell rather than just the edges and angles of the unit cell. One can refine a number of sample properties such as lattice parameter, atomic positions, thermal motion of the atoms in the sample, presence of impurity phases, site occupancies using the Rietveld refinement method.

In Rietveld refinement, the calculated intensity ($I_{\text{calc}}$) of a powder diffraction pattern is calculated using the following expression:

$$I_{\text{calc}} = I_{\text{bgg}} + S \sum_{hkl} C_{hkl}(Q)f_{hkl}^2(Q)P_{hkl}(Q)$$

(16)
where, the background intensity $I_{bkg}$ is generally expressed by a polynomial or power series expansion in terms of $Q$, $S$ is a scale factor, $C_{hkl}(Q)$ is a correction term to the instrument setup, $f_{hkl}^2(Q)$ is the structure factor which contains the information about the atomic positions, site occupancies, and thermal motions and $P_{hkl}(Q)$ is the profile term that provides the information about the particle size, texture and instrumental resolution. It should be noted that the unit cell information is uncorrelated to atomic position information, atomic positions are included in $f_{hkl}^2(Q)$ term and the lattice parameter information appearing in $\sum_{hkl}$ term. With this consideration, the need for improved statistics to obtain full structural characterization information, and the structural coherence of the sample will provide an answer about the lattice parameter and the symmetry very quickly.

The Bragg’s law illustrates the relationship between the $2\theta$ angle and the $d$-spacing in a diffraction pattern, where the interplanar spacing or $d$-spacing in a crystal is a function of lattice parameters. Fig. 2.8 shows the relationship between the interplanar distance and the lattice parameter for the 7 crystal systems where $a$, $b$, $c$ are the unit cell edges, $\alpha$, $\beta$, $\gamma$ are the angles and $h$, $k$ and $l$ are the miller indices of the crystal plane. Peak intensity of a powder diffraction data mainly arises from the electron densities of the atoms in the lattice which are described by the structure factor $F_{hkl}$ in the unit cell.

$$F_{hkl} = \sum g^i t^i(s) f g^i exp[2\pi i(hx^i + ky^i + lz^i)]$$ \hspace{1cm} (17)

where $g^i$ is the occupation factor of the $j$th atom and $t^i$ is the Debye-Waller factor which is a measure of atomic displacement of $j$th atom due to temperature. Square of the structural factor gives the integrated intensities of the powder diffraction pattern.

Rietveld refinement method revolutionized crystallography by solving complicated structural analysis through the robust algorithm, and it’s used has been resulted in ten fold increase in the publication of crystallographic data. The quality of the fits
Figure 2.8. Mathematical equations showing the relationship between \(d\)-spacing and the lattice parameters for seven different lattice systems.

produced by Rietveld refinement are judged commonly by various fit parameters such as: \(R_{wp}\), \(\chi^2\) which are produced directly from Rietveld codes. The residual function, \(R_{wp}\), is the measure of difference between the model and the experiment. It is calculated using the expression in equation 18, where \(y_{c,i}\), \(y_{o,i}\) are the calculated and observed intensity, respectively; \(w_i\) is the weighted factor which is used to avoid the overpowering of the refinement from intense peaks.

\[
R^2_{wp} = \frac{\sum_i w_i (y_{c,i} - y_{o,i})^2}{\sum_i w_i y_{o,i}^2}
\]  

(18)

Even though the objective of the Rietveld refinement is to minimize the \(R_{wp}\) value,
a low $R_{wp}$ value does not necessarily means a good fit. For instance, lab based x-ray
diffraclometer diffraction pattern generally gives a lower $R_{wp}$ because of the larger
background however, the diffraction pattern of synchrotron sources give relatively
higher $R_{wp}$ values due to high signal to noise ratio. For the proper refinement of
the diffraction data, one must consider other factor such as the calibration of the
diffraclometer, correct instrumental parameters.

1.3.3 Pair distribution function

Atomic pair distribution function (PDF) technique, a total scattering technique which
takes consideration of both Bragg and diffuse scattering, has been recently emerged as
powerful tool for studying local crystal structure of materials [147]. It is mostly used
to study materials which lacks long range lattice ordering such as liquids, amorphous
solids and nanomaterials. PDF is able to detect local distortions and can determine
the crossover from local to average structure, however at at high-r limit, the results
from the PDF refinement should agree with the Rietveld refinement for crystalline
data, as the effects of local distortion will be minimized at longer length scales.
PDF is defined as probability of finding any two atoms at a certain distance $r$ (see
Fig. 2.9b and Fig. 2.9c ) [151]. It basically has two important consequences: i)
Transformation to $r$ allows a direct analysis of real space instead of reciporcal space,
ii) PDF retains all information collected by the powder diffraction experiment. This
is contrast with Rietveld analysis which takes an account of only Bragg scattering and
considered the diffuse scattering as a background and thus provides the information
of average crystal structure only. Total scattering takes consideration of every point
of a diffraction pattern, including the background, which is generally ignored in a
conventional diffraction experiment. Figure 2.9a shows the crystal diffraction which
includes the scattering vector, Q. It is very important to understand the significance
of scattering vector Q before looking into PDF. The total scattering vector (Q) is
Figure 2.9. a) Depiction of momentum transfer, b) illustration of the evolution of PDF peaks and c) PDF peaks corresponding to atomic arrangement presented in b).

The difference between the incoming wave vector \( k \) and the scattered wave vector \( k' \) of the X-ray beam. It is perpendicular to the diffraction plane and has the dimensionality of an inverse length.

The reduced pair distribution function (PDF) \( G(r) \) is obtained experimentally by Fourier transforming the total scattering data as follows:

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

(19)
Where \( S(Q) \) is the normalized structure factor, and \( Q \) is the scattering vector, defined as \( Q = \frac{4\pi\sin(\theta)}{\lambda} \) in which \( \lambda \) and \( \theta \) are the neutron wavelength and scattering angle, respectively. \( Q_{\text{max}} \), the value of upper integral limit in eqn. 19, needs to be as large as possible to prevent termination ripples from appearing in the final PDF.

In addition, the total scattering function \( S(Q) \rightarrow 1 \) as \( Q \rightarrow \infty \). This is why in eqn.19, \( S(Q) \) has 1 subtracted in order to subtract contributions from the average continuum, since there is no diffraction in the infinite limit.

The calculated reduced pair distribution function \( G_c(r) \) is obtained from the structural model using equation (20) \([152]\).

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

where \( b_i, b_j \) and \( \langle b \rangle \) are the average scattering power of constituent atoms of the sample. The summation is over all atoms \( i \) and \( j \) in the model, where the distance separating any given pair of atoms is \( r_{ij} \).

**Figure 2.10.** Schematic diagram of NOMAD beamline \([2]\)
PDF data was collected at the Nanoscale Ordered Materials Diffractometer (NOMAD) stationed at Oak Ridge National Laboratory (ORNL). Figure 2.10 shows the schematic diagram of the NOMAD, which is a high-flux, medium-resolution diffractometer that employs the time of flight technique. This diffractometer uses a wide detector coverage and a huge bandwidth of neutron energy to obtain diffraction patterns up to a very large momentum transfer range, allowing structural assessment of local order in both crystalline and amorphous materials. A more detailed description of the instrument can be found elsewhere [2]. After properly calibrating detector deviations from orthogonality and masking invalid pixels, 2D X-ray diffraction data was integrated into 1D using FIT2D. The experimental background was subtracted from the data for diffraction profile studies. PDF data was reduced using PDFgetX2, which contains, inelastic scattering and energy-dependent detector response corrections, as well as experimental background and absorption corrections. In NOMAD’s data autoreduction algorithm, neutron scattering data for diffraction analysis was normalized and corrected bank-by-bank for experimental noise, merged, and reduced to PDFs. In addition to the standard adjustments for inelastic scattering contributions, an empirical correction to the hydrogen background caused by the interlayer water was used. The detector has maximum Q-range upto 100 Å⁻¹ but for typical experiment the Q-range for the Fourier transform was restricted upto 25 Å⁻¹, as that is the point at which the S(Q) is essentially flat for all compounds, showing the breakdown of the long-range structural coherence.

1.3.4 Magnetic pair distribution function

The importance of short-range structural correlations and phase fluctuations on the nanoscale is a recurring theme in the study of Strongly correlated electron systems [153, 154]. The PDF method has proven to be an effective probe of these local structure features that are difficult to study using traditional diffraction techniques.
Local magnetic structure, like local atomic structure, is important in a variety of condensed matter phenomena, including spin stripe correlation in cuprate superconductors [155], spin fluctuations in frustrated magnetic systems like quantum spin liquid herbertsmithite [156], and spin order in diluted magnetic semiconductors [157], to name a few. Neutron scattering has long been regarded as one of the most important experimental methods for studying magnetic structures. Conventional neutron diffraction techniques, on the other hand, are less successful due to the short-range existence of the magnetic correlations of interest. It is possible to determine magnetic structure using neutrons, but nuclear scattering usually dominates the PDF of magnetic structures [147]. The mean radius of the electron cloud in Ni, for example, is approximately 0.5 Å, implying that the magnetic peak’s full width will be 1.4 Å, which is significantly broader than the nuclear peak. Furthermore, since magnetic scattering has a shorter scattering length than nuclear scattering, the magnetic peak’s intensity is reduced significantly, rendering magnetic scattering a broad background to the PDF. To separate the magnetic portion, spin-polarized neutron scattering is usually needed.

2 Vibrational Properties under Strain

Figure 2.11 shows a schematic diagram of the setup used for a strain dependent Raman experiment. The setup includes a strain mount and a subminiature linear variable differential transformer (LVDT). The magnified image (within the orange circle) shows the part of the sample in which the Raman spectra were collected. The strain mount design has the form of a standard C-frame; the horizontal advancing screw is used to push apart the frame arms. Located at the end of the arms are two shims held by screws. In order to secure samples to the shims, double-sided tape is used for adhesion. Construction of the frame utilized 6061-T6 aluminum due to its higher yield strength compared to other aluminums. The shims were cut from 1100-
Figure 2.11. Schematic diagram of the setup used for strain dependent Raman study. The legend indicates the components of the setup.

H18 aluminum; the 0-80 UNF shim screws and the 2-56 UNC actuator screw were all 7075-T6 aluminum. Crystals of BP and MoTe$_2$ were exfoliated and mounted on the shims within the strain mount device using double-sided scotch tape. Mounted samples were strained by advancing the actuator screw in order to displace the frame arms. Depending on how far the screw was advanced, the amount of tension applied could be adjusted. The displacement of the frame arms moved the shims farther apart, which in turn placed the samples under tension.

A rigidly positioned torque actuator (DID-4A Digital Torque Screwdriver) was used to turn the advancing screw, and measure applied torque to ensure the displaced arms remained within the materials proportional limit. Staying within this limit meant general elastic stress-strain relationships remained applicable. This also allowed sample strain to be calculated by measuring frame arm displacement at the tip of the arm. Displacement was measured by using a sub-miniature linear variable differential transformer (LVDT). Since the frame arms possessed the same dimensions, shared
similar Young’s moduli, and were loaded within their elastic range, the assumption was made that differences between the two arms displacements were negligible due to differences being significantly smaller in value than the torque actuator and LVDT’s resolution.

In order to conduct strain dependent Raman studies, the strain mount setup was placed in a Raman spectroscopy stage (Renishaw inViaTM micro-Raman/PL spectrometer with a 632 nm He-Ne laser). Raman spectra at various strain values were recorded in-situ using a 50x objective lens with an exposure time of 10 sec and an accumulation of 10 times. BP samples used were stored inside a nitrogen filled glove box. We were able to mount the BP sample and perform the strain dependent Raman experiment in about 30-40 minutes. In order to minimize the degradation of BP in air during the strain experiment, we maintained a flow of nitrogen over the sample.

3 Transport Measurements

Electrical transport measurements are a fundamental material characterization technique that can reveal information about solid-state materials’ scattering mechanisms and band structure. Quantum mechanics describes macroscopic carrier transport as one of the most fundamental aspects of electronic material properties with prominent, gate-tunable effects in low-dimensional systems and at low temperatures. We used standard four-probe technique to measure the resistance and the thermopower was measured by the analog subtraction method.

To measure the Seebeck coefficient as a function of temperature, we employed a heat-pulse method involving a simple analogue-subtraction circuit and three instrumentation amplifiers (see Figure 2.12). This simple, low-cost approach uses only two thermocouples to make electrical contact with the sample, and this direct electronic coupling also increases thermal contact [158]. A PIC 16C56 microcontroller (Mi-
crochip Technology, Inc) was used to create a heat-pulse with variable pulse width and height that can be activated by an external TTL signal. The pulse height and duration can be adjusted between 0 and 10 V and 1 and 20 seconds, respectively. A temperature gradient of roughly 0.5 K is commonly produced and eased over a 5–20 s interval, depending on the thermal mass of the sample and heater block.

One end of the sample is placed in thermal contact with a heat sink, while the other end is placed in thermal contact with a heater in a typical experiment. Silver paint or silver-containing epoxy glue is commonly used to connect the two thermocouple connections to the sample. A schematic illustration of the sample holder is also shown in Figure 2.13. The heat source is a platinum resistor of type H2104 (Omega Engineering Inc) that is thermally clamped, or silver-epoxied, onto one of the copper pads. When the sample reaches the desired stable temperature, the PC triggers the pulse generator by sending a TTL pulse over one of the digital output lines of the analogue-to-digital converter (A/D) card DAS8 (Keithley MetraByte). As a result, the heater receives a voltage pulse of proper width and height, causing a temperature gradient to build and relax over time along the sample. As it raises and relaxes, thermopower data is gathered via the A/D card and PC [36].
4 Material Synthesis

I have used chemical vapor transport (CVT) and solid state reaction techniques for synthesizing various layered 2D materials.

4.1 Chemical Vapor Transport (CVT):

Chemical vapour transport (CVT), a technique pioneered by Schäfer, is a process in which a condensed phase, often a solid, is volatilized and deposited elsewhere in the form of crystals in the presence of a gaseous reactant (transport agent). Halogens and halogen compounds are common transport agents. A two-zone furnace (source T2 and sink T1), as well as the reactant and transport agent, are all sealed into one ampoule. Growth temperature, transport direction, mass transport rate, transport agent selection, and the free energy of the reaction are some of the characteristics that must be optimized for a successful CVT. Convection and diffusion are the two
processes that govern transport. Though larger crystals can be generated by favoring convection and enhancing transport rates, the crystals are inhomogeneous and prone to having more defects. As a result, optimizing each chemical system is critical. The source and sink temperatures must be adjusted based on the free energy of the reaction between the species. An exothermic reaction shows movement from the cold to the hot zone, while an endothermic reaction shows the opposite. Also, no transport occurs if the reaction between the species is highly exothermic or endothermic.

Precursor materials with the proper stoichiometric ratio will be loaded in the pyrex/quartz ampoule. Depending upon the annealing temperature, the choice of the ampoule can be made. The choice of Pyrex glass compared to quartz has some advantages such as an easier sealing process, but the Pyrex critical point is close to 600 °C which causes some difficulties in the high temperature annealing process. So, for high temperature synthesis, quartz ampoules are needed. The Pyrex/quartz tube was then evacuated to a pressure of 10^{-6} Torr using the vacuum system depicted in Figure 2.14. We employed a combination of two vacuum pumps, an oil diffusion pump, and a mechanical (rotary vane) pump to achieve such a high vacuum (10^{-6} Torr). A backup (roughing) pump is required since the diffusion pump can not start working at atmospheric pressure. The ampoule was sealed with an oxyacetylene torch. The sealed ampoule was then moved to the furnace for annealing with a temperature difference of (50 °C) between the two ends. Depending upon the materials, the temperature profile for each of them needs to be optimized. At the end of the annealing process, crystals will be formed at the colder end of the ampoule.

Single crystals of transition metal dichalcogenides (TMD), black phosphorus, black arsenic phosphorus, chromium halides and pnictides have been obtained by this method.
Figure 2.14. Vacuum system and furnace used for synthesis of 2D crystals by short way transport reaction methods.
4.2 Solid State Reaction:

At room temperature, solids are often regarded as chemically inert, and the most obvious evidence is frequently disregarded. In other words, solids do not appear to be reactive until they are heated. Solids, on the other hand, have atoms or ions that are constantly vibrating with the lattice and can "diffuse” from one location to another. Even at room temperature, if vacancies exist, they are constantly "filled” and "emptied.” Solids based on iron (Fe) are continuously oxidized, forming a coating called "rust.” As a result, solids aren’t totally stable and are constantly changing throughout time. A typical synthesis method for obtaining polycrystalline materials from solid chemicals is a solid-state reaction. A very high temperature is frequently used to initiate the reaction. Chemical and morphological features of the reagents, such as reactivity, surface area, and free energy change with the solid-state reaction, as well as other reaction parameters, such as temperature, pressure, and the reaction environment, all affect solid-state reactions. Simplicity and large-scale production are two advantages of the solid-state reaction approach. La$_2$O$_2$Fe$_2$OM$_2$($M = S, Se$) used in this dissertation were synthesized using this method.

5 Material Characterization

5.1 Raman Spectroscopy

Raman spectroscopy is a molecular spectroscopy technique which is an effective method for analysing the vibrational properties of two dimensional materials. It provides information about both inter- and intra-molecular vibrations. It is useful in studying lower frequency modes, and vibrations that give insight into crystal lattice and molecular backbone structure. It can be a quick method for the identification of the chemical compositions, analysis, and polymorph determination depending on the characteristics of a particular set of elements [159, 160]. This technique was first dis-
covered by Sir Chandrasekhara Venkata Raman and Sir Kariamanickam Srinivasa Krishnan in 1928 [161].

When a material is irradiated with photons of energy $\Delta E = h\nu_0$ as in fig.2.15, where $h$ is a Planck’s constant and $\nu_0$ is the frequency of incident photon, then the frequency of the scattered photon will be same or different then that of the incident photon. If the frequency is same then it is defined as Rayleigh scattering [162]. During the scattering process another frequency $\nu_m$ is also collected. This secondary frequency will be at a lower energy if a phonon is created (Stokes modes) or it will be
at higher energy if a phonon is absorbed (Anti-stokes modes) during the scattering process. Stokes mode are defined as $\nu_{\text{phonon}} = \nu_0 - \nu_m$, whereas $\nu_{\text{phonon}} = \nu_0 + \nu_m$ is called as Anti-Stokes modes (see fig. 2.16).

Raman spectroscopy is a measure in the shift of the frequency in relation to the excitation source, so called as Raman shift. All possible raman vibration are not active, this arises due to the incident light beam inducing a dipole moment in the molecule. Resulting dipole moment has the direct relationship with the rate of change of the polarizability at the equilibrium position. When the material is irradiated with the laser having a sinusoidal monochromatic wave, then the magnitude of the electric field it produces as a function of time can be represented as follows,

$$E = E_0 \cos 2\pi \nu_0 t$$  \hspace{1cm} (21)

Where, $E_0$ is the amplitude of the electromagnetic wave and $t$ is time. Due to this electromagnetic wave produced by the laser, it induces a dipole moment in the material which is directly proportional to the electric field and given as,

$$p = \alpha E$$  \hspace{1cm} (22)
Here, $\alpha$ is the proportionality constant, also called as the atomic polarizability. It should be noted that the above approximation is not valid if the electric field is too strong. The atomic polarizability can be expanded as a Maclaurin series about the equilibrium position in terms of the displacement as follow:

$$\alpha = \alpha_0 + \left( \frac{\delta \alpha}{\delta q} \right)_0 q + .....$$  \hspace{1cm} (23)

Here $q$ is the displacement of the molecule with the material having a vibrational state $\nu_m$ such that for small vibrations $\alpha$ is a linear function of $q$. $\alpha_0$ is the atomic polarizability at the equilibrium position and $\left( \frac{\delta \alpha}{\delta q} \right)_0$ is the rate of change of polarizability with respect to the displacement at equilibrium. Substituting eqn. 23 in eqn. 22 and inserting the equation for $E$ (eqn. 21), dipole moment can be written to a second order approximation as:

$$p = \left( \alpha_0 + \left( \frac{\delta \alpha}{\delta q} \right)_0 q \right) E_0 \cos \nu_0 t$$  \hspace{1cm} (24)

The form of $q$ will also have a similar plane wave form as that of the $E$ and can be written as follows,

$$q = q_0 \cos \nu_m t$$  \hspace{1cm} (25)

where, $q_0$ being the vibrational amplitude. Inserting this above eqn. 25 in eqn. 24 we get:

$$p = \alpha_0 E_0 \cos \nu_0 t + \left( \frac{\delta \alpha}{\delta q} \right)_0 q_0 E_0 \cos \nu_0 t \cos \nu_m t$$  \hspace{1cm} (26)

Using the trigonometric identities:

$$\cos(A \pm B) = \cos A \cos B \mp \sin A \sin B$$  \hspace{1cm} (27)

and combining these above equations with the dipole moment equation, we get,

$$p = \alpha_0 E_0 \cos \nu_0 t + \frac{1}{2} \left( \frac{\delta \alpha}{\delta q} \right)_0 q_0 E_0 \cos \nu_0 t \cos \nu_m t + \frac{1}{2} \left( \frac{\delta \alpha}{\delta q} \right)_0 q_0 E_0 \cos \nu_0 t \cos \nu_m t$$  \hspace{1cm} (28)

Here, in the above equation, the first term is for Rayleigh scattering. In the last two terms, it is seen that the derivative of the atomic polarizability with respect to
the displacement is directly proportional to the dipole moment. Anti-stokes Raman scattering arises due to the second term, while the Stokes Raman scattering is due to the therm term. We can see that, in order to Raman mode to be active the derivative of the atomic polarizability with respect to the displacement must be non-zero.

5.2 Scanning electron microscopy

Since it surpasses the resolution limit of the optical microscope, the scanning electron microscope is an extremely useful instrument for investigating the surface of a sample. The SEM scans the sample using a focused beam of electrons. An electron gun at the top of the SEM column produces the electrons. The thermionic emission of electrons occurs when a filament is heated to a temperature of 2000-2700 K. The electron beam is focused on the sample using a set of electromagnetic lenses. Elastic and inelastic scatterings arise from the interaction between the sample and the electron beam. The most popular SEM mode for imaging surface topography is by detecting secondary electrons, which are inelastically scattered electrons. Low-energy particles emitted by atoms near the sample surface are known as secondary electrons. Backscattered electron imaging is another popular mode. They are scattered elastically from nuclei with no energy loss. In comparison to secondary electrons, this approach has a greater penetration depth and is less sensitive to the sample surface. This mode, on the other hand, offers valuable information about the nuclei’s atomic mass. The release of high-energy X-ray photons from a targeted sample is another possible form of emission. EDAX stands for energy dispersive study of X-rays, and it’s a technique for probing with X-rays. This technique is used to determine the elemental composition of a sample.
5.3 Transmission electron microscopy

An electron beam is often used in TEM to photograph a sample. An electron gun is used as a beam source, similar to SEM. The beam is then centered on the sample through electromagnetic lenses. Only a fraction of the electrons pass into the sample, while the remainder scatter. To construct the image, TEM uses a fluorescent screen to detect the transmitted electrons. Owing to electron absorption, thicker parts of the sample or regions with higher atomic density appear darker, whereas thinner parts appear brighter. An aperture can be used to block the scattered electrons in this mode. The transmission intensity depends on the sample’s electron transparency and thickness. This emphasizes how important sample preparation is in TEM imaging. The sample thickness must be less than 100 nm, which restricts the types of samples available. Electrons scatter according to Bragg’s law in crystalline samples, resulting in a diffraction pattern. The diffraction strength is determined by the atomic planes’ orientation in relation to the electron beam. The electromagnetic lenses detect elastically dispersed electrons, resulting in a pattern of spots. Each dot corresponds to an atomic plane. Sample phase information, atomic arrangements, and plane orientation can all be determined using this method.
CHAPTER 3

LOCAL STRUCTURE OF IRON OXYCHALCOGENIDES

La$_2$O$_2$Fe$_2$OM$_2$ (M = S, Se)

Recently, the pair distribution function (PDF) technique [147, 163] has been used to study the local atomic arrangement and structural nematic fluctuations in iron-based superconductors for both normal and superconducting phases. PDF methods can be used to measure local scale deviations from the global crystal symmetry of a material [164, 62]. In FeSe$_{1-x}$Te$_x$ systems, PDF investigated the reduction of local crystal symmetry which enhances the local moment formation leading to magnetic instability [165]. X-ray and neutron PDF on FeSe and (Sr, Na)Fe$_2$As$_2$ revealed the presence of short-range orthorhombic distortions at temperatures well above the static nematic and orthorhombic ordering temperature $T_s$ [72, 164, 69, 68]. The observation of nematic fluctuations in iron-based superconductors, by using neutron and x-ray PDF analysis, provided evidence that nematic degrees of freedom exist near the superconducting phase [68]. Horigane et. al [166] conducted PDF studies of La$_2$O$_2$Fe$_2$OS$_2$ local structure and found a large anisotropic thermal displacement parameter for the O(2) atom along the c-axis ($U_{33}$). That study concluded that the crystal structure is strongly coupled to the magnetism in this system.

We report the use of the neutron pair distribution function (PDF) technique to study the local structure of La$_2$O$_2$Fe$_2$O(S, Se)$_2$ and to investigate the relationship between the structure and magnetism. The experimental methods are discussed in Section II, the results of this study are presented in Section III, section IV includes
the discussion and the conclusions are presented in section V. Our results indicate the presence of short-range orthorhombic distortions suggestive of short-range nematicity in both materials \( \text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2 \), despite the persistence of tetragonal symmetry in the average structure at all temperatures. We discuss the behavior of these fluctuations as a function of temperature. It appears that the change in the chalcogen from S to Se does not affect this behavior.

1 Experimental

\( \text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2 \) samples were prepared by a solid-state reaction method \cite{53} from stoichiometric amounts of high purity \( \text{La}_2\text{O}_3 \), S, Se, and Fe powders. The appropriate mixture of these powders was grounded thoroughly, pelletized then heated in an evacuated quartz tube at 1030\(^\circ\) C for 72 hours. This process was repeated three times. After being pulverized into fine powders, lab-based x-ray powder diffraction showed the materials to be of the high-quality and single phase \cite{53, 54, 51}.

Time-of-flight (TOF) neutron powder diffraction measurements were performed at the POWGEN diffractometer of the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). Five grams of \( \text{La}_2\text{O}_2\text{Fe}_2\text{O}_2 \) and 4.5 g of \( \text{La}_2\text{O}_2\text{Fe}_2\text{O}_\text{Se}_2 \) powders were placed in vanadium cans. Room temperature (300 K) measurement were performed, on each sample, for approximately one hour. The center wavelength and \( d \)-spacing range of neutrons in this experiment were 1.5 \( \text{Å} \) and 0.49664-13.50203 \( \text{Å} \) respectively. Rietveld refinements were conducted using GSAS-II software \cite{167}.

Neutron total scattering data were collected using the Nano-scale Ordered Materials Diffractometer (NOMAD) beamline at the SNS in ORNL. \( \text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2 \) powders were loaded and sealed in the vanadium cans inside a glove-box and were placed in an orange cryostat. A total of sixteen measurements were performed on
each sample at various temperatures ranging from 2 K to 300 K. A higher number of
data points were taken, in small steps, around the Néel temperature. Data were col-
lected for approximately two hours at each temperature. In order to obtain structural
information relevant to the samples, an empty vanadium sample can was measured
for two hours for background subtraction.

2 Results

2.1 Nuclear Structure

We confirmed the crystal structure of our samples through the neutron powder diffrac-
tion. The Rietveld refinement of neutron powder diffraction data was performed using
GSAS II software [167]. Fig. 3.1(a) and (b) show the Rietveld refinement of neu-
tron powder diffraction data measured at 300 K using neutrons of central wavelength
1.5 Å. Both \( M = S, Se \) materials show similar nuclear structures having space group
\( I4/mmm \) (space group No. 139) which is consistent with the previous studies [53, 54].
Our findings show that the lattice parameters of \( \text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2 \) \( (a = 4.0887(5) \, \text{Å}, \)
c\( = 18.6081(3) \, \text{Å}) \) is larger than that of the \( \text{La}_2\text{O}_2\text{Fe}_2\text{OS}_2 \) \( (a = 4.0439(9) \, \text{Å}, c = 17.8945(6) \, \text{Å}) \), as expected for the larger Se atoms. Rietveld refinement parameters
of both \( M = S, Se \) are tabulated in Table 3.1 including lattice parameters \( (a \text{ and } c) \)
as well as the anisotropic thermal displacement parameters \( U_{33} \) for all atoms. It was
observed that \( U_{33} \) for O(2) site is much larger than all the other sites. The quality
of the presented fits was characterized by the listed Rietveld parameters: \( R \)-whole
pattern \( R_w \), crystallographic factor \( R_F \) and goodness of fit tabulated in Table 3.1.

Having obtained a confirmation of the global lattice symmetry for our samples, we
then investigated the local symmetry [72, 68, 168, 169, 170, 171]. The local structure
data of \( \text{La}_2\text{O}_2\text{Fe}_2\text{OM}_2 \) \( (M = S, Se) \) was analyzed by using the PDF refinement pro-
gram PDFGUI [163] to determine the localized structural arrangement as a function of
Figure 3.1. Neutron Rietveld refinement of the nuclear model of a) $M = S$ and b) $M = Se$ at 300 K as a function of momentum transfer $Q$. The details of the fit are provided in the text.

temperature and length scale. During the refinement process the lattice parameter, scale factor, atomic positions, and the thermal parameters were fitted. In order to allow for local orthorhombic symmetry breaking, we parameterized the lattice constants as $a = a_{mid}(1 + \delta)$ and $b = a_{mid}(1 - \delta)$, where $a_{mid} = \frac{a + b}{2}$ and $\delta = \frac{|a - b|}{a + b}$. All refinements were performed on the Nyquist grid. Instrumental parameters $q_{damp}$ and $q_{broad}$, which are the parameters that correct the PDF envelope function [172, 173] for the instrument resolution [152, 163], were fixed by using an independent measurement of a standard Si sample. A direct comparison of quality of fit parameters of pseudo-orthorhombic symmetry and tetragonal symmetry PDF fits of room tem-
<table>
<thead>
<tr>
<th></th>
<th>La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}OSe\textsubscript{2}</th>
<th>La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}OS\textsubscript{2}</th>
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<tr>
<td>(a) (Å)</td>
<td>4.0887(5)</td>
<td>4.0439(9)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>18.6081(3)</td>
<td>17.8945(0)</td>
</tr>
<tr>
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<td>0.02049</td>
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<tr>
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<td>292.64(1)</td>
</tr>
<tr>
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<td>(I_4/mmm)</td>
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<td>(R_w) (%)</td>
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<td>6.79</td>
</tr>
<tr>
<td>(R_F) (%)</td>
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</tr>
<tr>
<td>Goodness of fit</td>
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<td>6.57</td>
</tr>
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</table>

**Table 3.1.** Refined parameters from Rietveld analysis of neutron powder diffraction data of La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}O(S, Se)\textsubscript{2} at \(T = 300\) K.

Temperature data of La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}OM\textsubscript{2} (\(M = S, Se\)) is shown in Table 3.3 and Fig. 3.2. It is clear that pseudo-orthorhombic model provides a improvement to the fit over the tetragonal model.

In Fig. 3.3, refined PDF data is presented for La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}O(S, Se)\textsubscript{2}. The observed data \(G_{obs}\) is shown in black and the calculated data \(G_{calc}\) is shown in red, while the difference between the observed data and the calculated data, \(G_{diff}\), is shown in green. We observed that the third peak of Fig. 3.3a, representing a Fe-Se distance of 2.72 Å at 300 K, shows a clear modification into Fe-Se at 2.67 Å and Fe-Fe, O(1)-O(1) at 2.87 Å at low temperature (see Fig. 3.3b). The peak change indicates two slight changes of Fe and O positions that affect the associated interatomic positions. The
Table 3.2. Atomic site, occupancy and fractional atomic coordinates of \( \text{La}_2\text{O}_2\text{Fe}_2\text{O(S, Se)}_2 \) at \( T = 300 \text{ K} \) extracted from Rietveld analysis.

Table 3.3. Comparison of the PDF fit quality parameters of pseudo-orthorhombic and tetragonal models of room temperature data within the range \( 1.8 \ \text{Å} \leq r \leq 20.0 \ \text{Å} \).

The lattice constants were obtained as a function of temperature using PDF analysis. Fig. 3.4 shows the temperature dependence of the lattice parameters \( a \) and \( c \) for both \( \text{La}_2\text{O}_2\text{Fe}_2\text{O(S, Se)}_2 \) samples in the range of 1.8 to 49.99 Å, where the data are fitted using an Einstein model of thermal expansion. Following previous work [57], the Einstein fitting model was calculated using equations (29) and (30) under the assumption that the thermal expansion is proportional to the internal energy of a quantum mechanical oscillator [174]. Fig. 3.4 also shows that the lattice parameter \( a \) increases with increasing temperature and fits well with the Einstein model of ther-
Figure 3.2. Room temperature PDF fits of a) $M = S$ and b) $M = Se$ fitted with both tetragonal and pseudo-orthorhombic model within the range of $1.8 \, \text{Å} \leq r \leq 10.0 \, \text{Å}$.

However, the lattice parameter $c$ shows a kink near 90 K in the case of $M = Se$ (see discussion).

$$a(T) = a_0 \left[ 1 + \alpha \theta_E f_E \left( \frac{\theta_E}{T} \right) \right] \tag{29}$$

$$f_E \left( \frac{\theta_E}{T} \right) = \frac{1}{\exp \left( \frac{\theta_E}{T} \right) - 1} \tag{30}$$
Figure 3.3. PDF refinement of $M = \text{Se}$ fitted with pseudo-orthorhombic model at a) 300 K and b) 2 K within the range of $1.8 \ \text{Å} \leq r \leq 4.5 \ \text{Å}$. Observed and calculated PDF patterns are represented by $G_{\text{obs}}$ (black) and $G_{\text{calc}}$ (red), respectively, with the difference profile by $G_{\text{diff}}$ (green).

Here, $a$ is the lattice constant, $a_0$ is the lattice constant at 0 K, $\alpha$ is the high temperature thermal expansion coefficient, and $\theta_E$ is the characteristic Einstein temperature. In our plots, we have used $\theta_E = 211 \ \text{K}$ as reported by Free et al. [57].
Figure 3.4. Lattice parameters as a function of temperature for $M = S$, Se determined from temperature-series sequential PDF refinement. a) $a$- and c) $c$-lattice parameter are shown for $M = S$ and b) $a$- and d) $c$-lattice parameter are shown for $M = Se$. Blue dotted lines represent an Einstein model of lattice thermal expansion (see text).

2.2 Magnetic Structure

Upon cooling, we observed extraneous intensity in the diffraction profiles of $M = S$ and Se which we attributed to magnetic phase transition behavior. These peaks were assigned a magnetic origin on the basis of their temperature dependence and the complete Rietveld refinement of the diffraction patterns. The Se end member has been well-characterized by Free and Evans [57]. It was argued [57] that the “AFM3” model [175] provides the best fit to the magnetic structure of the Se end-member. We used the SARAh suite of programs [176] to analyze the representations and provide
Figure 3.5. Refined fits (Calculated) of neutron powder diffraction data (Observed) at low angle for La$_2$O$_2$Fe$_2$OS$_2$ is shown for a) 290 K and b) 4 K. Red (Blue) labels indicate the (HKL) indices of the nuclear (magnetic) Bragg diffraction peaks. The difference (purple) is Observed - Calculated.
the basis vectors for refinement with FullProf. [177, 178] The “AFM3 model” may be written as Fe\{1/2, 0, 0\}\Gamma_2\psi_1 + Fe\{1/2, 0, 0\}\Gamma_3\psi_2, the irreducible representations being labeled with the scheme of Kovalev [179] and the basis vectors that of Sarah [176]. \Gamma_2\psi_1 and \Gamma_3\psi_2 generate the same geometric ordering scheme on the two independent sites; during refinement, the standard Fe^{2+} magnetic form factor is assumed, and the additional constraint is applied that both independent sites possess the same size ordered magnetic moment.

We initially verified the “AFM3” model [175] also gives the best fit to the magnetic structure of our data from La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}OSe\textsubscript{2} compound. In close similarity to what was described previously for \( M = \text{Se} \), our analysis of magnetic structure of the \( M = \text{S} \) compound reveals that the magnetic cell of \( M = \text{S} \) is commensurate and is doubled in \( a \) and \( c \) with respect to the structural cell. The magnetic ordering in La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}OS\textsubscript{2} is associated with an ordering vector \( \mathbf{k} = (1/2, 0, 1/2) \), and the single Fe site on \{1/2, 0, 0\} in the nuclear \textit{I4/mmm} cell is described by two distinct orbits governing the two \{1/2, 0, 0\} and \{0, 1/2, 0\} Fe sites that are independent in the magnetically ordered state. Propagation vector \( \mathbf{k} = (1/2, 0, 1/2) \) suggest the mangetic unit cell is two times that of nuclear unit cell. In Fig. 3.5 the low angle region of the powder diffractograms of La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}OS\textsubscript{2} is shown at 290 K (panel a) and 4 K (panel b). The data (Observed) are presented in order to show magnetic Bragg peaks \( Q_M = (000), (−101), (002) \) and \( (−103) \) (blue label) that develop at low-temperatures in addition to the structural Bragg peaks are present (red) for both high- and low-temperatures. In addition to the data, the Rietveld refinement fits (Calculated) are shown in both temperature regions.

There are two independent Fe sites for both La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}O(S, Se)\textsubscript{2}. By performing a full Rietveld refinement and analysis of the neutron powder diffraction data, the ordered Fe\textsuperscript{2+} moment of La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}OS\textsubscript{2} was determined to be 2.32(4) \( \mu_B \) at 4 K. For La\textsubscript{2}O\textsubscript{2}Fe\textsubscript{2}OSe\textsubscript{2} a range of values from 2.8 to 3.50(5) \( \mu_B \) has been reported. [55] Thus
the magnetic ground state of both compounds is composed of the Fe ions in a high spin, non-collinear antiferromagnetically ordered state.

2.3 Temperature Dependence of Thermal Displacement Parameters

Fig. 3.6 shows the temperature dependence of the anisotropic thermal displacement parameters $U_{11}$ and $U_{33}$ for both $M = S$, Se. We note the relatively high values of $U_{11}$ parameter for the $M = S$, Se sites and the $U_{33}$ parameter for the O(2) site. The large $U_{33}$ parameter for the O(2) site agrees well with the neutron powder diffraction results (See Table 3.1). The large an anisotropic thermal displacement parameter $U_{33}$ corresponds to O(2) displacement above and below the Fe$_2$O plane. This displacement can be accompanied by a distortion of Fe-O-Fe angle (See Fig. 2 where this angle is highlighted by a solid black line in the octahedra). An additional atomic movement along the c-axis is that of sulfur/selenium atoms with respect to the Fe atoms in the octahedra. This motion would affect the $M$-Fe-$M$ angle in the octahedra (See Fig. 2 where this angle is highlighted by dashed black lines in the octahedra).

Fig. 3.7 provides views of the atomic displacements under discussion. Panel a) shows a view along the a-axis while panel b) provides an isometric perspective view by presenting slight rotations about the a and c crystal axes. In panel b) black solid lines show the Fe atom movement and the black dashed lines show the movement of O(2) atoms. When the O(2) atoms in the Fe$_2$O plane move up or down the angle Fe-O-Fe changes causing buckling of the Fe$_2$O plane. O(2) atoms are displacing out of the plane by $\sim 0.015$ (0.0016) Å. Allowing the z-coordinates of the two O(2) atoms to displace opposite to each other results in the $U_{33}$ parameter for the O(2) site dropping down to a value that is in line with other atomic sites. This result suggests that local buckling of the Fe$_2$O plane may occur through small displacements of the O(2) atom above and below the plane.
2.4 Local Orthorhombicity

The use of pre-written macros allows PDFGUI to fit data sets through a series of boxcar refinements that differ one from another by corresponding fitting ranges [180]. Since we have performed PDF data sets over a wide range of temperatures, we used PDFGUI $T$-series and $r$-series macros to study details of the local to average structure crossover in our materials. These macros allow the setup of boxcar fits, in which the same model is fitted over different real space intervals ($r$-ranges) for different temperatures of the PDF data [181]. We have performed extensive $T$- and $r$-series PDF fits to determine the atomic structure as a function of temperature and length scale [68]. The evolution of the orthorhombicity of the local structure (short-range) to the average structure (long range) is presented in the color maps of Fig. 3.8. The most relevant structural parameter for the local distortion is the orthorhombicity. Color
Figure 3.7. Panel (a) shows possible Fe and Se/S atomic movement within the La$_2$O$_2$Fe$_2$O(S, Se)$_2$ octahedra that result in the bucking of the Fe$_2$O plane. (b) The dashed lines show Fe atom movement in the Fe$_2$O plane and the solid lines show Fe movement with respect to $M$. 

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Figure 3.8. Color maps of the refined orthorhombicity determined from neutron PDF analysis for a) $M = S$ and b) $M = Se$.

Maps of orthorhombicity were prepared, for both $M = S$ and Se by using the results of $T$- and $r$- series refinements based on the orthorhombic symmetry. We did the $T$-series refinement by performing the PDF fits on low temperature data at first, then we run the sequential PDF fits for all of our data collected at various temperatures. For each temperature data, we have performed the $r$- series refinement in a sliding 20 Å data window from [1.5 - 21.5 Å] to [29.5 - 49.5 Å] in 1 Å steps, resulting in 29 fits per temperature. Orthorhombicity and $c$ lattice parameter were extracted from all of these fits for all temperatures to produce the color maps. Color maps were made using the ORIGIN software [182]. In these color maps, the midpoint of the fitting range $r_{mid}$ is shown on the x-axis, the temperature is shown on the y-axis, and orthorhombicity
Figure 3.9. Color maps of \( c \)-lattices for \( \text{La}_2\text{O}_2\text{Fe}_2\text{O(S, Se)}_2 \) derived from \( T \)- and \( r \)-series PDF refinements for a) \( M = \text{S} \) and b) \( M = \text{Se} \).

is shown on the color bar as indicated by the brightness of the colors from light blue to dark blue. The dark blue color denotes high orthorhombicity, light blue represent zero orthorhombicity \( i.e. \), tetragonality. The maps indicate that at short ranges, over all temperatures, the presence of orthorhombicity is observed, but it diminishes over longer length scales.

Fig. 3.10 presents the local orthorhombicity \( \delta \) as a function of the midpoint of the fitting ranges for two representative temperatures. Data were fitted with exponential decay functions. Fig. 3.10(a) shows the orthorhombicity of \( M = \text{S} \) at 28.45 K and 214.0 K. At both temperatures, the orthorhombicity is largest at short fitting ranges and gradually decreases to form a plateau at larger fitting ranges. A black
Figure 3.10. Orthorhombicity as a function of fitting range for a) $M = S$ and b) $M = Se$ at low and high temperature.

solid (dashed) line shows the exponential fitting function for 28.45 K (214.0 K) with decay lengths of 6.42 ± 2.2 Å (3.52 ± 0.93 Å), respectively. Fig.3.10(b) displays the orthorhombicity at different fitting ranges for $M = Se$ at temperature 2.57 K and 211.47 K. Black solid (dashed) line shows the exponential fitting function for 2.57 K (211.47 K) with decay length of 7.52 ± 1.38 Å (7.92 ± 1.6 Å), respectively. Figs. 3.10(a) and (b) provided evidence of the greater orthorhombicity at shorter ranges.

The color maps of the $c$-lattice parameter for $M = S$, Se determined from $T$- and $r$-series refinement of pair distribution function analysis are presented in Fig. 3.9. In this figure, the x-axis is the midpoint of fitting range $r_{mid}$, the y-axis is the temperature, and the color bar shows the $c$-lattice parameter with light blue for the high intensity and black for low intensity. $c$-lattice color maps show the evolution of $c$-lattice from the local structure (short-range) to the average structure (long range). For both La$_2$O$_2$Fe$_2$O(S, Se)$_2$ materials, we can see an increase in the $c$-lattice as the temperature increases overall $r_{mid}$ ranges.
Neutron powder diffraction experiments confirmed the average crystal structure of La$_2$O$_2$Fe$_2$O(S, Se)$_2$ as tetragonal systems with space group ($I4/mmm$) (see Fig. 3.1) in agreement with the previous studies on these materials [53, 55, 56, 57, 51, 54]. Unlike many iron pnictides which undergo a structural phase transition from tetragonal to orthorhombic symmetries near $T_s$, La$_2$O$_2$Fe$_2$O(S, Se)$_2$ lattice symmetries are not observed to change with temperature. However, both La$_2$O$_2$Fe$_2$O(S, Se)$_2$ undergo a magnetic transitions from paramagnetic (PM) phases to antiferromagnetic (AFM) phases at respective Néel temperatures $T_N$. Neutron powder diffraction (Fig. 3.6 and Table 3.1) showed that the thermal displacement parameter for the O(2) atom along the $c$-axis was larger than all the other thermal displacement parameters. This was the finding for both materials $M = S$ and Se.

In order to probe the local structure, we employed the neutron PDF technique to investigate the local changes in the atomic positions and $c$-axes of La$_2$O$_2$Fe$_2$O(S, Se)$_2$. The PDF analysis revealed similar thermal displacement behavior on short length scales. In addition, the temperature dependence of the $c$-lattice parameter showed a kink near the Néel temperature for $M = Se$ (see Fig. 4.4). However, no discontinuity was observed in the case of $M = S$. Such a finding is consistent with previous reports of $c$-lattice discontinuities in oxyselenides [183, 184, 57] and the less prominent occurrence of this behavior in the oxysulfides [56]. The discontinuities were attributed to magnetostrictive effects in the oxyselenides. In the case of oxysulfides, a relatively reduced amount of $c$-lattice discontinuity was argued to be due to shorter $c$-lattices [56]. According to Horigane et al. [166] deviations in the $c$-lattice parameter from the average crystallographic structure are due to the fact that the thermal displacement parameter $U_{33}$ for O(2) along the $c$-axis grows rapidly with the increase in temperature. A similar O(2) trend, in SrFeO$_2$ [185], was reported to be related to Fe$_2$O planar buckling.
For La$_2$O$_2$Fe$_2$O(S, Se)$_2$, the buckling of the Fe$_2$O plane may occur when there is distortion in either the Fe or O(2) sites. In the case of $M = \text{Se}$, a high $U_{33}$ value for O(2) (see Fig. 3.6) suggests that the largest distortions should occur for that site. A distortion in the Fe site can lead to two Fe-Se correlations since each Fe atom is surrounded by four Se atoms of the octahedra (see Fig. 3.7b). Therefore, the modification observed in Fe-Se correlation peak (the third peak of see Fig. 3.3a) might indicate a subtle distortion in the Fe site. Overall, these findings for $M = \text{Se}$ suggest that there is a distortion either in the Fe or O(2) sites, and both implicated as possible reasons for Fe$_2$O buckling.

Our analysis of the local structure of La$_2$O$_2$Fe$_2$O(S, Se)$_2$ reveals the presence of short-range orthorhombic distortions on a length scale of 1 - 2 nm over a temperature range from 2 - 300 K. These distortions are very similar to those found in FeSe [72, 164] and (Sr, Na)Fe$_2$As$_2$ [68, 69], which have been attributed to short-range nematic fluctuations that persist up to temperatures well above the magnetic and/or structural transition temperatures. Given the structural and magnetic similarities between these iron oxycalcogenides and the superconducting iron pnictides and chalcogenides, we suggest that the local orthorhombicity observed here is likewise related to fluctuating, short-range nematic distortions.

The occurrence of such fluctuations across a variety of pnictide superconductors and the incoherent electronic systems presented here raise the question of how critical nematic fluctuations are to the superconducting mechanism. This specific inquiry has become the key focal point of the field of iron-based high-$T_c$ superconductivity. In most FeSCs, superconductivity is found in close proximity to a magnetically ordered state. However, there is a nematic, non-superconducting state besides magnetism at a specific temperature $T_{\text{nem}}$. Nematic ordering has been systematically observed in iron pnictide and chalcoginide superconductors. The short-range nematic fluctuations, which are deviations from the average structure, may provide the informa-
ation about the origin of nematicity and its relation to superconductivity mechanism [186, 187, 188, 164, 72, 189, 190, 191]. In FeSCs and other related materials, significant information can be gained from the nematic phase which occurs near $T_s$ and from the nematic fluctuations that occur over a large range of temperatures.

The fact that nematic degrees of freedom appear to be active in these Mott insulating, non-superconducting iron oxychalcogenides highlights the ubiquity of nematicity for layered iron-based systems. It also suggests that active nematic degrees of freedom are not sufficient to guarantee superconductivity, although they may well be necessary. It may be the case that nematic fluctuations and another phase must conspire to produce high-temperature superconductivity in iron-based systems. The energy-integrated nature of the PDF measurements means we are probing fluctuations on a time scale of $10^{-13}$ s or slower. However, we were unable to extract any other temporal information using the PDF data alone. Complementary probes such as NMR or Mössbauer spectroscopy could help clarify the situation [192].

4 Conclusions

The local structure of Mott insulating iron oxychalcogenides was studied using neutron powder diffraction and pair distribution techniques. Neutron powder diffraction showed a similar nuclear structure of $M = \text{Se and S}$ with the only difference in the atomic radii of two chalcogens. Pair distribution function analysis indicated the presence of the local distortion between tetragonal and orthorhombic symmetry. These findings suggest the presence of short-range local distortion with a typical length scale of 1 - 2 nm in both of these materials.
Iron-chalcogenides \((\text{FeCh})\) \(\text{Fe}_{1+y}\text{Te}\) are promising candidates to understand the mechanism of superconductivity in the family of Fe-based superconductors. They exhibit the simplest structure and the highest \(T_c\) among the iron-based superconductors (FeSc). In contrast to the Fe\(Pn\), FeTe has unique properties such as the development of a monoclinic lattice distortion upon cooling. Such a distortion is uncommon among materials that are considered to be unconventional high-transition temperature superconductors. Furthermore, the magnetic order of \(\text{Fe}_{1.1}\text{Te}\) is unlike that of the Fe\(Pn\) since the high temperature paramagnetic (PM) state undergoes a transition to a long range bicollinear antiferromagnetic (AF) order (see Figure 4.1) \([193, 115]\).

The bicollinear AFM ordering structure factor shows peaks at \(Q = \pm(\pi/2, \pm\pi/2)\), which is not the nesting vector within FeTe’s Brillouin zone.

Iron telluride (FeTe) is known to display a bicollinear magnetic order at low temperatures together with a monoclinic lattice distortion. Coupling between the monoclinic lattice distortion and an orbital nematic parameter with \(B_{2g}\) symmetry will generate the novel bicollinear nematic state. Replacing Te with Se the bicollinear magnetic order is eventually lost, the material becomes superconducting, and it develops an orthorhombic nematic phase above its superconducting critical temperature. \(\text{Fe}_{1+y}\text{Te}\) exhibits antiferromagnetic order \([193]\), with a pattern that is distinct from that commonly found in the iron pnictides \([115]\). These two spinstructures, which are commonly labelled “bicollinear” and “stripe”, are illustrated in Figure 4.1. Also, the bicollinear
phase is argued to dominate the plaquette ordering because of ring exchange or spin-lattice interaction [193]. Tetragonal Fe$_{1+y}$Te shows a complex interplay between structural and magnetic phase transitions in the presence of excess amount of Fe. The onset of the bicollinear AFM order is concomitant with a structural phase transition from a tetragonal to a monoclinic symmetry. As such, Fe$_{1+y}$Te are found to be suitable candidate to better understand electronic nematicity.

![Figure 4.1. Bicollinear nematicity in Fe$_{1.1}$Te](image)

1 Experimental

The neutron powder diffraction measurements on Fe$_{1.1}$Te were collected at the Nanoscale Ordered Materials Diffractometer (NOMAD) beamline at the Spallation Neutron Source (SNS) of Oak Ridge National Laboratory (ORNL). Crystals of Fe$_{1.1}$Te were powderized and loaded in the vanadium can inside the argon-filled glove box. The data was collected at seventeen different temperatures, ranging from 5K to 300K,
with smaller steps around the phase transition temperature. In order to obtain the information purely from the samples, an identical empty vanadium can was measured for background subtraction. Data was Fourier transformed to obtain a real space representation of inter-atomic correlations using the pair distribution function (PDF) analysis. Since PDF analysis takes into account both Bragg and diffuse scattering and, therefore, is sensitive to studying atomic deviations from the average structure. Modeling of the experimental PDF data was carried out using the PDFGUI program and the DIFFPY-CMI Suite.

Magnetic Susceptibility and resistivity of a comparable sample were measured using the quantum design magnetic property measurement system. Fig.4.2 shows the magnetic susceptibility, $dM/dH$ as a function of temperature where $M$ is defined as the magnetization per unit volume and $H$ is the applied magnetic field. These measurements are carried out in order to understand the nature of the phase transitions in Fe$_{1.1}$Te. Data were collected using the magnetic field $H = 0.1$ T. The magnetic susceptibility of Fe$_{1.1}$Te grows steadily with decreasing temperature until it reaches 65 K, at which point it sharply decreases. The phase transition from the paramagnetic to the antiferromagnetically ordered state happens at this temperature. The Curie–Weiss law governs susceptibility at high temperatures.

2 Results

In this section, we present the experimental results of nuclear and magnetic structures. Atomic displacements, corresponding to the bond disparity of 0.1 Å have been observed in Fe$_{1+y}$Te, where they were attributed to a long-range ferro-orbital ordering [114].
Figure 4.2. a) Magnetic susceptibility and b) resistivity of Fe$_{1.1}$Te

2.1 Nuclear Structure

Local structure of Fe$_{1.1}$Te was studied through the pair distribution function analysis. Recently, it was found that the PDF technique is an effective probe to study the local structure. Fig. 4.3 shows the refined PDF plot of Fe$_{1.1}$Te measured at 300 K in the range of 1.0 - 20.0 Å. Observed and calculated data are shown in blue and red, while
the difference pattern is shown in green (see Fig. 4.3).

Figure 4.3. PDF refinement plot of Fe$_{1.1}$Te at a) 2 K and b) 300 K. Observed and calculated PDF patterns are represented by $G_{\text{obs}}$ (blue) and $G_{\text{calc}}$ (red), respectively, with the difference profile by $G_{\text{diff}}$ (green).

Fig. 4.4(a) shows the temperature dependence of lattice parameter $a$ and $b$ from the low temperature to room temperature. It clearly shows the first order structural phase transition from tetragonal to monoclinic crystal symmetry at the temperature of 70 K. Fig. 4.4(b) present the temperature dependence of $c$ lattice parameter which shows clear anomaly at 70 K. Temperature dependence of the monoclinicity parameter is shown in Fig. 4.4(c).
Figure 4.4. Lattice parameters as a function of temperature for Fe$_{1.1}$Te determined from temperature-series sequential PDF refinement. a) $a$, $b$ lattice parameter and b) $c$-lattice parameter c) Temperature dependence of orthorhombicity.

2.2 Magnetic Structure

We used the DiffPy-cmi program to refine mPDFs in order to examine the local magnetic structure in Fe$_{1.1}$Te. We performed atomic PDF fits using the known monoclinic structure at low temperature after producing the experimental PDF (which included contributions from both nuclear and magnetic scattering). Figure 4.3 shows the effect of this refining in the range of 1 – 25 Å. The strong peaks of the atomic PDF are properly captured by this model, but it is unable to capture the unnormalized mPDF signals at low temperature, resulting in a substantial fit residual, as shown
by the offset green curve in Figure 4.3 a). The oscillating nature of this difference curve, which consists of the unnormalized mPDF plus any residual errors in the fit to the atomic structure, exposes the antiferromagnetic structure of $\text{Fe}_{1.1}\text{Te}$. Antiferromagnetic order exist at low enough temperatures, but it disappears at and above the Néel point. Antiferromagnetism is divided into three types: A, C, and G. Antiferromagnetic superexchange interactions between nearest neighbors stabilize the G-type magnetic structure. Ferromagnetic planes connected antiferromagnetically along the c axis in an A-type antiferromagnetic order. The FMchains of the C-type AFM structure are parallel to the $a$-axis, which is longer than the $b$-axis, in the orthorhombic AFM phase. We have used G-type antiferromagnetic model to fit our short range pdf data.

In order to better fit the mPDF signals, we have subtracted the 125 K fit residual from each of the lower-temperature fit residuals. This is intended to remove the temperature-independent features in the fit residual, such as systematic errors. The hope is that the mPDF signal is then prominent enough to make a meaningful fit. Next, we fit the magnetic model to this temperature-subtracted fit residual at each temperature (see Figure 4.5. We attempted mPDF fit at several $r$-ranges and discovered that the model agrees fairly well in this range (1.5 -25.0 Å). At larger ranges, fit quality was poor. Fitting parameters include scale factor, correlation length, and spin direction. After smoothing over the high-frequency noise (which can’t possibly be magnetic in origin), the mPDF signal becomes more apparent, although there is still significant interference in the signal. Still, the expected antiferromagnetic model matches the general features of the data and shows sensible trends with the temperature.
Figure 4.5. \(mPDF\) fit of \(\text{Fe}_{1.1}\text{Te}\) at different temperatures. a) 2K, b) 75 K, c) 90 K.

3 Discussion

We have performed extensive \(T\)- and \(r\)- series PDF fits to determine the atomic structure as a function of temperature and length scale [68]. The evolution of the
orthorhombicity of the local structure (short-range) to the average structure (long range) is presented in the color maps of Fig. 4.6. We did the $T$-series refinement by performing the PDF fits on low temperature data at first, then we run the sequential PDF fits for all of our data collected at various temperatures. For each temperature data, we have performed the $r$-series refinement in a sliding 20 Å data window from [1.5 - 21.5 Å] to [29.5 - 49.5 Å] in 1 Å steps, resulting in 29 fits per temperature. Figure 4.6 a) shows the orthorhombicity parameter vs $r_{mid}$ at three different temperatures 5 K, 114 K, 184 K. It was clearly seen that the orthorhombicity is high at the low temperatures.

**Figure 4.6.** Color map of local orthorhombicity
temperature. Next, Orthorhombicity ($\delta$) was extracted from all of these fits for all temperatures to produce the color maps. Color maps were made using the ORIGIN software [182]. In these color maps, the midpoint of the fitting range $r_{\text{mid}}$ is shown on the x-axis, the temperature is shown on the y-axis, and orthorhombicity is shown on the color bar as indicated by the brightness of the colors from blue to red (see Figure 4.6 b). The red color denotes high orthorhombicity, blue represents zero orthorhombicity, i.e., tetragonality. The maps indicate that at short ranges, over all temperatures, the presence of orthorhombicity is observed, but it diminishes over longer length scales. We can also observe the first order structural phase transition from the tetragonal to the monoclinic structure at around 70 K.

![Figure 4.7. Comparison of structural ($\delta^2$) and magnetic order parameter](image)

Figure 4.7 shows the comparative plot of structural and magnetic order parameter of Fe$_{1.1}$Te. Structural order parameter was calculated by squaring the local orthorhombicity, however, the magnetic order parameter was calculated by considering the intensity of magnetic peaks at different temperature. These data were fitted using the power law functional form $\phi^2(T/T_{S,N}) = (1 - T/T_{S,N})^{2\beta}$. $\beta$, the critical exponent, and $T_N$, the Néel temperature, $T_S$, the structural phase transition temperature, served as adjustable fit parameters. It can be observed that both structural
and magnetic phase transition temperatures are very close to each other, suggestive of a magneto-structural phase transition in this material system. Figure 4.8 shows the temperature dependence of ordered moment and correlation length extracted from mPDF fits. Both of these plot shows the long range magnetic ordering at low temperature and it undergoes the structural phase transition around 75 K and finally undergoes the short-range magnetic ordering at high temperature upto 100 K. These short range magnetic fluctuations are an indication of local magnetic fluctuations, suggestive of the presence of nematic fluctuations in this material.

4 Conclusion

We studied the local structure of Fe$_{1.1}$Te using the pair distribution function technique, which revealed the presence of short-range orthorhombicity suggestive of nematic fluctuations in a typical range of 2-3 nm. Susceptibility and resistivity measurements showed the first order magnetic phase transition from paramagnetic to the antiferromagnetic phase. A local structure study using mPDF analysis showed short-
range magnetic ordering at high temperatures of up to 100 K. These short-range magnetic fluctuations are indicative of local magnetic fluctuations in this material, implying the occurrence of nematic fluctuations. Thus, both structural and magnetic phases showed the short-range local distortion in this material system.
Because of its capacity to tolerate a high strain and the extensive theoretical research
done on strain-induced tuning of mechanical, electrical, and optical properties, black
phosphorus is an intriguing option for strain engineering [194, 195]. BP is a layered
structured material with van der Waals interactions stacking each atomic layer of
the puckered honeycomb lattices, giving it a wide range of anisotropic properties
[194, 196]. In many technologies, such as flexible electronics, a better knowledge
of the strain effects on the anisotropic characteristics of the phosphorene may be
advantageous. In order to develop new thermoelectric devices, the ability to modify
the electrical and thermal properties of 2D materials is highly desired. As a result,
strain engineering may be used to tune the electrical and thermal properties of 2D
materials [197]. E.g., a little amount of strain in borophene, for example, causes it
to tune its transport and I-V characteristics, implying that it could be used in future
electronic devices [198]. Strain causes changes in atomic bond configurations (bond
angles, bond lengths, and bond strength) in 2D materials, which leads to a significant
change in lattice vibration (phonon). Raman spectroscopy can detect these changes in
phonon frequency. In this work, we have used Raman spectroscopy to compare strain
dependent studies on several 2D materials, such as BP, 1T’-MoTe$_2$ and 2H-MoTe$_2$. 

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1 Experimental

BP crystals were synthesized via the short chemical vapor transport (CVT) method [199]. In short, crystals of pure black phosphorus were obtained by CVT method by annealing an evacuated quartz tube loaded with a mixture of red phosphorus, tin and tin (IV) iodide, where tin and tin (IV) iodide served as mineralization additives. An ampule with precursor powders was evacuated down to 106 Torr and sealed afterward using an oxy-acetylene flame torch. Sealed tubes were placed in a three-zone furnace (MTI OTF-1200X) for annealing in such a way that the hot end of the tube was placed toward the centre of the furnace. Sample was heated from room temperature to 650 °C in 3hr 10 min and left there for 20 mins and rapidly cooled back to 600 °C in 5 min and ramped down the temperature from 600 °C to 550 °C in 7hr 30 min and finally cooled back to room temperature in 5hr. Temperature gradient of 50 °C was maintained between hot end and cold end during the entire process. Crystals of 1T’- and 2H-MoTe$_2$ used in this study were purchased from hq graphene company.

The morphology, crystallinity and the details of the crystal structure of BP, 1T’-MoTe$_2$ and 2H-MoTe$_2$ samples were analysed using transmission electron microscopy (TEM). TEM specimens were prepared by drop-casting dispersions of samples onto commercial holey carbon-coated TEM grids. TEM measurements were performed using a 200 kV filed emission gun FEI Tecnai F20 instrument, equipped with a nanoprobe and scanning transmission electron microscopy (STEM) capabilities. The microscope was also equipped with analytical capabilities, including an EDAX TEAM™ Energy Dispersive X-ray Spectroscopy (EDX) analysis system with an Octane silicon drift detector.

Figure 5.1 shows TEM and high-resolution TEM (HRTEM) images of typical particles of the studied BP, 1T’-MoTe$_2$, and 2H-MoTe$_2$ samples. Typical selected area electron diffraction (SAED) ring patterns and corresponding radial intensity profiles obtained from these samples from regions containing several particles are also included.
Figure 5.1. TEM characterization of the BP (top row), 2H- MoTe$_2$ (middle row) and 1T’- MoTe$_2$ (bottom row). Low magnification TEM images (1st column from left), HRTEM images (2nd and 3rd columns from left) and SAED ring patterns (4th column from left) and radial intensity profiles (5th column from left). HRTEM images in the third column from the left are zoomed-in sections that are marked with dotted line boxes in images shown in the second column.

in Figure 5.1. For the BP sample, the particles had the form of multilayer flakes and in-plane diameter of around 10 μm, or more (Figure 5.1a). The flakes were mostly single-crystalline. HRTEM images of these flakes usually showed two sets of lattice fringes, characterized by the d-spacing values of either, both equal to 0.26 nm (Figure 5.1b) and (c) or one equal to 0.33 nm and the other one to 0.44 nm. These d-spacing values, were consistent with the structure of BP. Similarly, the electron diffraction ring pattern from this sample can be indexed to the phase of BP, described by the
Figure 5.2. Chemical composition analysis of BP (top row), 2H-MoTe$_2$ (middle row) and 1T'-MoTe$_2$ (bottom row). HAADF-STEM images (left panels), elemental maps (middle panels), and EDX spectra (right panels). The small concentration of oxygen detected in the spectrum of BP may originate from air exposure and residual surface contamination.

ICDD PDF 00-047-1626 (Figure 5.1(d) and (e)). The particles of the MoTe$_2$ samples were significantly smaller, typically with diameters of around 1 $\mu$m. In the case of 2H-MoTe$_2$, the particles had also a multilayer flake morphology. HRTEM images confirmed that they were primarily single crystals and showed a hexagonal Figure 5.2 (g) and (h)) which agrees with the structure of the 2H-MoTe$_2$. The SAED ring pattern for this sample can be indexed to the 2H-MoTe$_2$ phase, described by the ICDD PDF 00-015-0658 (Figure 5.1(i) and (j)). As expected, all strong diffraction rings observed for this sample are of the (hk0)-type (Figure 5.1 (i)). In the case of the 1T’-MoTe$_2$, 

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the particles did not show a clear flake morphology. Instead, they were rather heavily
distorted, defected flakes with their edges split into long fibber-like structures (Figure
5.1 (k)). HRTEM images of the flake-like sections showed d-spacing values and the
symmetry of the lattice fringes consistent with the crystal structure of 1T’-MoTe$_2$.
The SAED ring patterns of this sample showed predominantly polycrystalline nature,
in big part due to all those randomly oriented fibber-like segments, can be indexed
to the 1T’-MoTe$_2$ phase, described by the ICDD PDF 01-071-2157 (Figure 5.1 (n)
and (o)). This is consistent with previous reports concerning 1T’-MoTe$_2$ phase [200].
The chemical composition of all three samples was analysed using EDX. The EDX
spectra were continuously collected while the nanoprobe was scanned across selected
particle in each of the three samples. This allowed for the acquisition of representative
elemental maps. Figure 5.2 shows such example maps along with the corresponding
high-angle annular dark field scanning TEM (HAADF-STEM) images and EDX spec-
tra for all three samples. The analysis confirmed the nominal composition of these
samples and homogenous distribution of elements.

2 Results and Discussion

Here, we present strain dependent Raman spectra collected for BP, 1T’-MoTe$_2$, and
2H-MoTe$_2$. All the Raman measurements were done at the edge of each sample, since
dge was subjected to more stress compared to the middle regions.

2.1 Black Phosphorus under strain

We performed the strain dependent Raman experiment in order to investigate the
Raman shift as a function of uniaxial tensile strains. Figure 5.4(a) shows the Raman
spectra of few layer black phosphorus with different strain values ranging from 0.0 to
1.08%. We observed three active phonon modes $A^1_g$, $B_2g$ and $A^2_g$ at 365.4 cm$^{-1}$, 441.2
and 468.7 cm$^{-1}$, respectively for a as-prepared few-layer BP sample before the strain is applied. Here $A_{1g}$ mode corresponds to the vibration along the out-of-plane with the phosphorus atoms in the top and bottom sub-layers vibrating in opposite directions, whereas the $B_{2g}$ and $A_{2g}$ mode correspond to the vibration along the in-plane zigzag and armchair directions with adjacent atoms vibrating out of phase, respectively. As the strain was applied, all the three phonon modes were observed to red shift progressively up to the strain value of 1.0%. The phonon modes $A_{1g}$, $B_{2g}$ and $A_{2g}$ were red-shifted by 2.9 cm$^{-1}$, 4.1 cm$^{-1}$ and 4.3 cm$^{-1}$, respectively at the highest applied strain values. If a crystal is subjected to a tensile stress, the process can be envisioned that the atoms being pulled apart by lengthening the chemical bonds relative to their normal positions and lengths in the unstressed crystal. As the chemical bond length increases, the force constant decreases (for a given stress), hence the vibrational frequency decreases (frequency is proportional to the square root of the force constant). Hence shifts of the Raman peaks to lower frequencies are observed for materials that have been subjected to a tensile stress. Conversely, when a compressive stress is applied, the atoms in a crystal move closer to each other by shortening the chemical bonds, which leads to the Raman peaks shifting to higher frequencies [18, 201, 202, 203]. Hence, compressive and tensile strains induce corresponding stress in the crystal that can be observed as shifts of Raman peaks to higher or lower frequencies, respectively. The magnitude of the Raman peak shift depends on the stress and corresponding strain induced in the material. The degree to which the Raman band shifts depends on the elastic constants such as Young’s modulus of that material and the specific crystallographic axes being probed.

In order to avoid unreliable strain response measurements, we limited the Raman measurements to applied strains levels that produced a proportional response. At higher strain values however, we observed the peaks to be shifted back because of
Figure 5.3. a) Strain dependent Raman spectrum of black phosphorus. b) Raman shifts of the phosphorene sample with dashed line as a guide to an eye. The shaded region in b) shows the backward shifting of the peak position.

The relaxation of the stress (see Fig. 5.3). This behavior could be due to the poor adhesion of the sample to the tape or decoupling of the top layer from the lower layers within the few-layer BP.

We also noticed that these phonon modes ($A_1^g$, $B_{2g}$ and $A_2^g$) red-shifted at different rates with respect to the strain, i.e., they had different sensitivities, $\Delta \omega / \Delta \sigma$ where $\omega$ is the Raman shift and $\sigma$ is the strain. Our observation on the different shifting rates, $\Delta \omega / \Delta \sigma$ of $A_2^g$, $B_{2g}$ compared to $A_1^g$ is consistent with previously reported results on the comparison of polarization Raman spectroscopy between near armchair and near zigzag strain-red shift calculations [204, 194]. For any intermediate direction, it is also reported to have a red shift even though the in-plane modes are insensitive to near
Figure 5.4. (a) Strain dependent Raman spectrum of black phosphorus. (b) Raman shifts with quadratic fits of the phosphorene sample. (c) Unstrained Raman spectrum of BP with arrow showing the relative change in phonon modes. (d) Relative change in the Raman shift of phonon modes $A_{2g}^2$ and $B_{2g}$ with respect to $A_{1g}^1$.

Armchair strain while the zigzag strain has more prominent effect on these in-plane modes. The $A_{2g}^2$ and $B_{2g}$ modes show higher shifts in comparison to $A_{1g}^1$ mode presumably due to the Raman tensor element ratio $c/a$ [194]. Compared to our stretching experiment under tensile strain, a slightly more sensitive shift in $A_{1g}^1$ mode has been reported under bending condition. This results from the vibrations of the opposing P atoms of the top and bottom with respect to each other within the same layer.
Under stretching conditions this effect was not observed [18].

Figure 5.4(b) shows the peak position of all three phonon modes with respect to the strain where the blue line showing the quadratic fit of the measured data points. Figure 5.4(c) shows how the relative change in the peak position is defined. Figure 5.4(d) shows the relative change in the peak position of phonon modes $A^2_g$ and $B^2_g$ with respect to the relative change in phonon mode $A^1_g$. It was observed that rates of the change of phonon modes $A^2_g$ and $B^2_g$ against $A^1_g$, $\Delta\omega(A^2_g)/\delta\omega(A^1_g)$, $\Delta\omega(B^2_g)/\delta\omega(A^1_g)$ to be 1.40 and 1.38 respectively.

**Figure 5.5.** The changes in $A^2_g$ and $B^2_g$ Raman modes against the change in $A^1_g$ due to in-situ Li-intercalation as well as strain (shaded region) experiments.

Next, we compare the effect of tensile stress with the donor type intercalation (alkali metals, etc.) on the Raman shift of BP. Similar to tensile stress, donor type
intercalation leads to an increase in the electron density of a crystal and hence increase in the bond lengths eventually causing a decrease in the vibrational frequencies. Conversely, acceptor type intercalation leads to a decrease in the electron density causing a decrease in the bond length (increase in the force constant) and hence an increase of the vibrational frequencies [205]. In the case of intercalation, one can make a direct comparison between $\Delta \omega/\delta q$, where $\omega$ is the Raman shift and $q$ is the charge transfer, and $\Delta \omega/\Delta \sigma$ in the case of strain. Figure 5.5 shows the changes in $B_{2g}$ and $A_{2g}$ Raman modes against the change in $A_{1g}$ from in-situ Li-intercalation from our recent study [206] and strain (shaded region) experiments in this study. It is interesting to note that the Raman shifts of $B_{2g}$ and $A_{2g}$ against $A_{1g}$ due to the measurable strain values follow the same linear behaviour of the data resulting from much larger shifts due to Li+ intercalation. This is not surprising as both intercalation and strain effects cause bond length stretching of BP.

We have also performed first-principle calculation on the Raman shifts of black phosphorus and phosphorene (i.e., monolayer) under uniaxial strain along armchair and zigzag direction. As shown in Figure 5.6, the red shift of Raman spectra on both BP and phosphorene strongly depends on the direction of the strain exerted on the system even within the elastic deformation limit (i.e., strain 1%). In the case of black phosphorus, $A_{1g}$, $B_{2g}$ and $A_{2g}$ modes decrease slowly along the armchair direction with increasing strain with the slopes 3.3 cm$^{-1}$, 0.35 cm$^{-1}$, and 0.8 cm$^{-1}$, respectively (the left panel of Figure 5.6 (b)). While they decrease faster with increasing strain along the zigzag direction with the slopes 6.7 cm$^{-1}$, 8.5 cm$^{-1}$, and 1.2 cm$^{-1}$, respectively (the right panel of Figure 5.6 (b)), indicating the anisotropic behaviour of black phosphorus under strain. Such trend is also found in phosphorene under uniaxial strain (Figure 5.6 (c)). By comparing our theoretical calculations (open triangles in Figure 5.6 (d)) with our experimental results (solid circles in Figure 5.6 (d)), we found that the theoretical results for the strain along the armchair direction (left panels in
Figure 5.6. (a) Schematic illustration of the uniaxial strain exerted on the black phosphorus. (b) Calculated vibration modes of BP under uniaxial strain along the armchair direction (left panel) and zigzag direction (right panel), respectively. (c) Calculated vibration modes of phosphorene under uniaxial strain along the armchair direction (left panel) and zigzag direction (right panel), respectively. The corresponding number denotes the decreasing slope for each mode. (d) Comparison of uniaxial tensile strain experimental (open circle) and theoretical (closed stars) Raman shifts for three phonon modes of BP. Phonon modes $A_{1g}^1$, $B_{2g}$ and $A_{2g}^2$ are represented by blue, black and red colours.

Figure 5.6 (b) and (c)) are consistent with our experimental results (Figure 5.4 (b)) for the strain less than 1 %. This confirms that the strain applied to the sample acts effectively along the armchair direction.
In a comparative study, we have investigated the tensile strain effects of Raman spectra in two different phases of MoTe$_2$ as shown in Figure 5.7. Raman spectra of 2H-MoTe$_2$ shows one peak at 232 cm$^{-1}$ and we detected two peaks of 1T’- MoTe$_2$ at position 142 cm$^{-1}$ and 124 cm$^{-1}$. In both of these samples, upon increase of the strain from 0 to 5 %, we saw downshift in each peak position (as shown in Figure 5.7) by a peak shifting of 2.05 cm$^{-1}$ (first peak) and 1.15 cm$^{-1}$ (second peak) for 1T’- MoTe$_2$ and by 1.23 cm$^{-1}$ for 2H- MoTe$_2$, respectively at the highest strain value.
Finally, Figure 5.8 shows the comparison of phonon mode shifting of BP (3 modes), 1T’-MoTe$_2$ (2 modes) and 2H-MoTe$_2$ (1 mode). It is observed that peak shifting ratio, $\Delta \omega / \Delta \sigma$ of black phosphorus is much higher than that of MoTe$_2$. For BP, we observe that phonon mode $A^2_g$ and $B^2_g$ are downshifted by an amount that is 1.6 times larger than that of $A^1_g$ ($5.50$ cm$^{-1}$ vs $3.4$ cm$^{-1}$). For, 1T’-MoTe$_2$, $\Delta \omega / \Delta \sigma$ for the two phonon modes are $0.70$ cm$^{-1}$ and $0.40$ cm$^{-1}$ while 2H-MoTe$_2$ shows the smallest shift with strain with $\Delta \omega / \Delta \sigma \sim 0.25$ cm$^{-1}$.
3 Conclusions

In summary, we studied and compared the strain dependent Raman behaviour of black phosphorus and 2 phases of MoTe$_2$ crystals, 1T'-MoTe$_2$ and 2H-MoTe$_2$. We employed a custom strain mount which allowed variable reproducible strains to be applied to these materials. Our result shows that the strain induced Raman peak shifting of black phosphorus is more pronounced than that of both phases of MoTe$_2$, which can be understood as due to the lower Young’s modulus value of BP. We also see a resemblance between donor-type intercalation induced vibrational properties and tensile stress induced vibrational properties in BP as both mechanisms result in bond length increase in BP. Therefore, peak shifting of the phonon mode is a good means in understanding the strain behaviour of 2D materials. Such methods could be beneficial for manufacturing future flexible electronic devices.
CHAPTER 6

STRUCTURAL AND THERMEOLECTRIC PROPERTIES OF BLACK ARSENIC-PHOSPHORUS

Due to some unique features such as higher carrier mobility, thickness-dependent band gap tunability, and in-plane anisotropy of several thermal, optical, and electrical properties, two-dimensional (2D) materials have gotten a lot of attention in the hunt for these innovative TE materials [125, 207, 208, 209, 210, 211]. Since the advent of graphene, which is likely the most studied and recorded 2D material to date, an array of new 2D compounds have emerged, including transition-metal dichalcogenides (TMDs) and hexagonal boron nitride (h-BN), and the 2D material family is continually growing. Graphene and TMDs both offer exciting features, but their applicability in the electronics sector is limited by graphene’s zero bandgap and TMDs’ weak carrier mobility [120]. In the recent past, phosphorene, which is the 2D counterpart of black phosphorus (BP), has sparked researchers attention. The layer-dependent adjustable band gap [varying from 0.3 to 1.5 eV (from bulk to monolayer)] [212, 213] and higher field-effect hole mobility (1000 cm²V⁻¹S⁻¹) [212, 214, 215, 216] is one of the main reasons for this. As a result, phosphorene has been recognized as a promising material candidate for innovative electronics applications [217]. More crucially, phosphorene’s puckered layer structure renders it extremely anisotropic, with mutually orthogonal electrical and thermal transport routes, which is ideal for TE applications [125, 218, 219, 220, 221, 23]. We have used the chemical vapor transport approach to synthesize a series of AsₓP₁₋ₓ alloys in order to comprehensively study
their transport and thermal properties. The TEP and the resistance of the As$_x$P$_{1-x}$ ($x = 0, 0.2, 0.5, 0.83, 1$) alloys as prospective TE materials are compared in this work.

1 Experimental

A series of As$_x$P$_{1-x}$ compounds with different atomic compositions ($x = 0, 0.2, 0.5, 0.83$ and 1) were synthesized from red phosphorus and gray arsenic by chemical vapor transport growth method. Stoichiometric ratios of red phosphorus (Sigma, $> 97\%$) and gray arsenic (Sigma, 99.99\%) with a total weight of 500 mg were annealed inside evacuated (10$^{-6}$ Torr), sealed quartz ampoules at 650 $^\circ$C. Sn (20 mg, Alfa Aesar, 99.8\%) and SnI$_4$ (10 mg, Alfa Aesar, $> 95\%$) was added as the mineralization additive. A temperature gradient of 50 $^\circ$C was maintained between the hot and cold ends of the ampoule throughout the annealing process in order to facilitate vapor transport and resultant As$_x$P$_{1-x}$ alloy crystals were grown at the cold end. Previous works [128, 129] show similar synthesis approaches which have been used to synthesize As$_x$P$_{1-x}$ crystals with different compositions, and this technique is genuinely inspired by chemical vapor transport growth of BP itself [222, 199].

The As$_x$P$_{1-x}$ alloys were thoroughly characterized using several techniques. Raman spectra were measured to characterize vibrational modes using Renishaw inVia with 632 nm He-Ne laser. Transmission electron microscopy (TEM) was used to characterize the morphology, crystal structure, and chemical composition of selected As$_x$P$_{1-x}$ alloys, namely alloys with nominal compositions of As$_{0.8}$P$_{0.2}$ and As$_{0.5}$P$_{0.5}$. TEM specimens were prepared by pulverizing these materials and dispersing them onto holey carbon-coated TEM grids. A comprehensive TEM analysis, including TEM and high-resolution TEM (HRTEM) imaging, selected area electron diffraction (SAED), scanning TEM (STEM) high annular angle dark filed (HAADF) imaging, energy dispersive X-ray spectroscopy (EDX), and elemental mapping, was performed using a
200 kV field emission gun Tecnai F20 transmission electron microscope (FEI, Inc.), equipped with a 2048 x 2048 CCD camera (Gatan, Inc.), a HAADF detector (E.A. Fischione Instruments, Inc.), and TEAM EDX analysis system (EDAX, Inc.). The morphology and elemental composition of the alloy samples were also characterized using scanning electron microscopy (SEM) and SEM-based EDX, respectively. These measurements were performed using a Tescan Vega 3 system equipped with an EDAX EDX detector.

Transport properties of all samples were measured by anchoring two miniature thermocouples [Chromel (KP)/Au 7 at. % Fe (Au/Fe); 100 m diameter], two additional current leads, and a resistive heater (see the schematic diagram of the sample with the electrical contacts). Thicknesses of the AsP alloys used for the transport measurement were ~800 µm with lateral dimension of 2-3 mm. The DC resistance $R$ was measured with a standard four-probe technique and the thermopower $S$ was measured by the analog subtraction method. To measure $S$, a temperature difference ($\Delta T < 1$ K) was generated across the sample by applying a voltage pulse to the heater. The typical heating power was < 10 mW, and the pulse duration was 35 s. The slope of the TE voltage ($\Delta V$) versus temperature difference ($\Delta T$) due to the heat pulse was used to obtain $S$ at a given temperature. For $R$ measurement, an excitation current was applied through the two current leads and the voltage across the two thermocouple wires was measured in a van der Pauw configuration [223]. The excitation current level was kept extremely low to avoid Joule heating especially at low temperatures. Further experimental details are described in refs [224, 225, 226, 227]. The $S$ and $R$ of all samples were measured over a temperature range of 15300 K. A chip carrier supporting the sample was attached to the copper cold finger of a closed cycled refrigerator (Janis Research Co. CCS-350ST-H) which could be cooled down to a base temperature of ~ 10 K.
2 Results and discussion:

Raman spectra obtained for gray As, BP, and different As$_x$P$_{1-x}$ alloys are shown in Figure 6.1a. Pristine BP has three main Raman modes (labelled in pink in Figure 6.1a), $A_{1g}^1$, $B_{2g}$, and $A_{2g}^2$ which correspond to out-of-plane vibrations, in-plane vibrations along the zigzag direction, and in-plane vibrations along the armchair direction, respectively [199, 228]. However, for alloy samples which have both As and P atoms, it was observed that the Raman spectra consisted of peaks not only from P-P vibrations, but also from As-P and As-As (labeled in violet in Figure 6.1a) vibrations.

The spectral range of Raman spectra for a given As$_x$P$_{1-x}$ alloy can be split into three main frequency regimes. For the series of alloys, high-frequency region (> 350 cm$^{-1}$) contains peaks from P-P atomic vibrations, whereas low-frequency region (i.e. 270 cm$^{-1}$) contains peaks from As-As atomic vibrations. For each alloy sample, three peaks in the low frequency region can be identified as $A_{1g}^1$, $B_{2g}$ and $A_{2g}^2$ modes for As-As vibrations (labeled in violet in Figure 6.1a). The identification of As-As vibrational modes is analogous to the work reported by Liu et al [128] in 2015. Modes arising from heteroatomic As-P vibrations can be observed in the mid-frequency region (270 cm$^{-1}$ to 350 cm$^{-1}$). As arsenic concentration of the alloy increases, a decrease in peak intensities for P-P vibrational modes were observed, whereas peak intensities corresponding to As-As vibrations were increased. It is reasonable because P-P vibrations become less prominent when more P atoms are replaced by As atoms in the lattice. It is also observed that peaks of alloy samples are red shifted (w.r.t BP sample) with increasing arsenic concentration (Figure 6.1b).

Raman spectroscopic data shows that both As-As and P-P phonon modes undergo a red-shift with increasing As concentration. It was also observed that for P-P vibrations, modes $B_{2g}$ and $A_{2g}^2$ shift more than $A_{1g}^1$ with increasing As concentration, by factors of 2.2 and 2.4, respectively. This observation is noteworthy and intriguing as we observed similar trends in Li-intercalated BP with increasing Li concentration.
Figure 6.1. (a) Raman spectra for pristine BP, gray As, and As\textsubscript{x}P\textsubscript{1-x} alloys with different chemical compositions. (b) Raman shift vs arsenic concentration (x) for P-P (top) and As-As (bottom) vibrational modes. Dotted lines provide guide to the eye with linear fits.

(by a factor ~ 1.5) [206] as well as BP under increasing uniaxial strain (by a factor ~ 1.4) [229], which will be addressed in detail in a dedicated study.

Figure 6.2 shows the morphology and chemical composition of typical particles of As\textsubscript{x}P\textsubscript{1-x} alloys, as obtained from STEM HAADF and EDX analysis. It was observed that the particles were clusters of flakes in the size range from tens of nanometers to several micrometers. The phosphorus (P-K) and arsenic (As-K) elemental maps showed relatively homogenous distribution of both elements within the particles. However, for the As\textsubscript{0.2}P\textsubscript{0.8} sample, the intensity of the As-K map was much lower than that of the P-K map, while for the As\textsubscript{0.5}P\textsubscript{0.5} sample the intensities of both maps were comparable. This was consistent with the nominal composition of these alloys and it was further confirmed by the relative peak intensity of the P-K and As-K lines in corresponding EDX spectra.

The morphology and structure was further analyzed using (HR)TEM and SAED
Figure 6.2. (a, e) STEM-HAADF images, (b, f) P-K and (c, g) As-K elemental maps, and EDX spectra (right column) of (d) As$_{0.2}$P$_{0.8}$ and (h) As$_{0.5}$P$_{0.5}$ alloys.

and typical results obtained from this study are presented in Figure 6.3. First, the flake morphology was confirmed and HRTEM images of individual flakes showed large single-crystalline areas with lattice fringes, which corresponded to the orthorhombic puckered structure. SAED patterns of individual flakes were predominantly single
crystalline in nature and showed the symmetry consistent with the same type of crystal structure, that is, orthorhombic puckered structure with the \textit{Cmca} space group, which is characteristic for BP. However, these measurements showed a systematic expansion of the crystal structure with the increase of arsenic concentration, \( x \). This can be seen from HRTEM and SAED data summarized in Table 6.1, where \( d \)-spacing values of several low-index planes, their relative changes, and the measured \( c/a \) ratio of the in-plane lattice parameters are shown. Using this data, one can calculate
Figure 6.4. The relative lattice change with increase of arsenic concentration in As$_x$P$_{1-x}$ alloys as measured from HRTEM and SAED. For details please see Table 6.1

The average relative change of $d$-spacing and obtain values of 0, 0.011, and 0.033 for As$_0$P$_1$, As$_{0.2}$P$_{0.8}$, and As$_{0.5}$P$_{0.5}$, respectively. The dependence can be fitted well with a proportional function described by relative lattice expansion coefficient of 0.0645 (see Fig. 6.4). In addition, the data suggest some anisotropy of the crystal structure in-plane expansion. Specifically, the lattice increase along the $c$-axis was stronger than along the $a$-axis (see the last column in Table 6.1). This is consistent with the crystal structure and easy deformation direction of the orthorhombic puckered structure. Recently, we have seen similar behavior for the Li-intercalated BP [206].

At a larger scale, alloyed materials were found to be polycrystalline, as shown by HRTEM and SAED. In addition, domains of different orientations inside larger grains, extended structural defects, such as dislocations, and structural inhomogeneity, such
Table 6.1. Values of \(d\)-Spacing Measured from HRTEM and SAED, Their Relative Changes as Compared to BP, and the \(c/a\) Ratio of In-Plane Lattice Parameters

<table>
<thead>
<tr>
<th>(x)</th>
<th>(d_{111} [\text{Å}])</th>
<th>(d_{111}/d_{111,BP})</th>
<th>(d_{100} [\text{Å}])</th>
<th>(d_{100}/d_{100,BP})</th>
<th>(d_{001} [\text{Å}])</th>
<th>(d_{001}/d_{001,BP})</th>
<th>(c/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.54</td>
<td>1</td>
<td>3.31</td>
<td>1</td>
<td>4.37</td>
<td>1</td>
<td>1.32</td>
</tr>
<tr>
<td>0.2</td>
<td>2.56</td>
<td>1.010</td>
<td>3.35</td>
<td>1.012</td>
<td>4.42</td>
<td>1.011</td>
<td>1.32</td>
</tr>
<tr>
<td>0.5</td>
<td>2.63</td>
<td>1.035</td>
<td>3.38</td>
<td>1.021</td>
<td>4.55</td>
<td>1.041</td>
<td>1.35</td>
</tr>
</tbody>
</table>

as heavily distorted atomic planes, were often seen in HRTEM images. The high concentration of structural defects and lattice distortions was also reflected in the arcing of diffraction spots in SAED patterns recorded from larger sample areas. An example data showing all these features is included in Figure 6.5.

Typical results obtained from SEM and SEM-based EDX analysis are shown in Figures 6.6, 6.7 and 6.8. In brief, the layered morphology and relatively uniform elemental composition were confirmed for all alloyed materials. Besides, the average compositions, as measured by SEM-EDX, were in agreement with the nominal compositions. However, the composition distribution within different grains characterized by the standard deviation of about 0.05 was measured for these samples.

The temperature dependence of 4-probe resistance and thermopower of each sample are shown in Figure 6.9. As seen in Figure 6.9c, both pure arsenic and \(\text{As}_{0.83}\text{P}_{0.17}\) samples showed metallic temperature behavior with a decrease in resistance as the temperature decreased in the entire temperature range. As the arsenic concentration \((x\) in \(\text{As}_x\text{P}_{1-x}\)) decreased, the samples showed a transition to a semiconducting (activated) behavior with an increase in resistance for the temperature decrease, especially in the low-temperature regime. Moreover, as \(x\) changed from 0 to 1, the resistance was found to decrease by more than 3 orders of magnitude. Furthermore, as shown
Figure 6.5. TEM analysis of microstructure and defects in As$_{0.2}$P$_{0.8}$ (left panel) and As$_{0.5}$P$_{0.5}$ (right panel) alloys.

In Figure 6.9d, both pure arsenic and As$_{0.83}$P$_{0.17}$ samples showed very small TEP values ($\sim 7 \mu$V/K) at room temperature, consistent with their metallic nature. As the $x$ decreased to 0.5, TEP value increased to $\sim +550 \mu$V/K and eventually reached a value as high as $+803 \mu$V/K for $x=0.2$. However, when $x$ decreased to 0 (BP), TEP value decreased to $+323 \mu$V/K, consistent with the published literature values for BP [230, 231]. A comparison plot showing the loop used for calculating TEP of As$_x$P$_{1-x}$ alloys is shown in Figure 6.10. The thermopower remains positive in the entire temperature range for samples with $x = 0, 0.2,$ and 0.5. However, for samples with $x = 0.83$ and 1.0, the sign of the thermopower changes from positive to negative at low temperatures. An example plot showing the changes in the slope of the loop of $x = 0.83$ sample is shown in Figure 6.11.
Figure 6.6. Morphology and elemental composition analysis of $\text{As}_0.2\text{P}_{0.8}$: (a-d) SEM images, (a) arsenic and (f) phosphorus elemental maps of area shown in d, and (g) distribution of arsenic concentration (i.e., $x$ in $\text{As}_x\text{P}_{1-x}$) obtained from EDS quantification of 25 random grains.

The concentration dependence of both the TEP and the 4-probe resistance is plotted in Figure 6.12. The dotted lines are guides to the eye. It can be inferred from the plots that both the TEP and the resistance reach maximum values at an arsenic composition, $x \sim 0.2$.

In order to understand the transport mechanism, we developed a framework for the temperature dependence of both $R$ and $S$. In Figure 6.13, we have plotted the
Figure 6.7. Morphology and elemental composition analysis of $\text{As}_{0.5}\text{P}_{0.5}$: (a-d) SEM images, (a) arsenic and (f) phosphorus elemental maps of area shown in d, and (g) distribution of arsenic concentration (i.e., $x$ in $\text{As}_x\text{P}_{1-x}$) obtained from EDS quantification of 25 random grains.

The normalized resistance,

$$\Delta R/R = (R(T) - R(RT))/R(RT)$$

where $R(RT)$ is the resistance at room temperature. The solid lines are the fits to the appropriate theory. The electrical resistivity, $\rho$ of most pure metals/semimetals is predominantly due to electron-phonon scattering. The standard theory developed for scattering of charge carriers by acoustical phonons leads to the Bloch–Grüneisen
Figure 6.8. Morphology and elemental composition analysis of $\text{As}_{0.83}\text{P}_{0.17}$: (a-d) SEM images, (a) arsenic and (f) phosphorus elemental maps of area shown in d, and (g) distribution of arsenic concentration (i.e., $x$ in $\text{As}_x\text{P}_{1-x}$) obtained from EDS quantification of 25 random grains.

expression [232]:

$$\rho = \left( \frac{T}{T_R} \right)^5 \int_0^{T_R/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx,$$

(31)

where $T_R$ is the Bloch–Grüneisen (BG) temperature which is approximately equal to the Debye temperature ($\theta_D$). The BG theory predicts that $\rho \sim T^5$ for $T \ll T_R$ due to the dominant electron-phonon scattering but shows $T^3$ dependence if the ef-
Figure 6.9. (a) Schematic diagram of the sample holder with electrical contacts. (b) Detailed schematic circuit diagram of sample showing two thermocouples (Chromel (KP)/ Au:Fe), resistive heater and additional leads for thermopower and 4-probe resistance measurements. (c) Temperature dependence of the 4-probe resistance and (d) thermopower of As$_x$P$_{1-x}$ alloys.

The effect of density of phonon is considered. Furthermore, at low temperatures, the most energetic thermal phonons have the momentum, $k_B T/\nu_s < \hbar k_F$, which is the momentum of the conducting electrons at the Fermi surface, implying that the electrons undergo only small-angle scattering events, where $\nu_s$ is the velocity of sound and $k_F$ is the Fermi wave vector. This leads to $T^2$ dependence of $\rho$. At high temperatures ($T >> T_R$), because of the presence of thermal phonons with momenta $> \hbar k_F$, the electrons experience large-angle scattering [233], and the density of interacting...
Figure 6.10. Loop of the room temperature data of As$_x$P$_{1-x}$ alloys with the solid line showing the linear fit. Slope was used to calculate the respective room temperature thermopower values of each sample. $V_1$ corresponds to the thermoelectric voltage ($\Delta V$) and $V_2$ corresponds to the temperature difference ($\Delta T$).

Phonons varies as $T$ leading to linear $T$ dependence of $\rho$. For pure arsenic and As$_{0.83}$P$_{0.17}$ samples, resistance can be very well fitted with $R = aT + bT^3$ relationship, which accounts for linear temperature ($T$) dependence at high temperatures and $T^3$ dependence at low temperatures due to phonon scattering (lower two curves) [234].

The data for $x = 0$, 0.2, and 0.5 (top three curves in Figure 6.13a) samples are shown in Figure 6.13b in a blown-up scale for clarity. They show a rather anomalous behavior. Generally, for semiconductors, the band conduction governs the charge transport properties at high temperature. In band conduction, charge carriers from localized states are thermally activated and transported to the delocalized states [235]. However, in deformed or disordered materials at relatively low temperature, the charge carriers hop through localized states without excitation to the conduction band. Overall, there are mainly two types of conduction mechanisms in such materials, namely (a) band conduction or thermal activation and (b) hopping. This hopping mechanism can be further subdivided into two types: (i) nearest-neighbor-
Figure 6.11. Loop of the room temperature data of $\text{As}_{0.83}\text{P}_{0.17}$ ($x = 0.83$) sample with the solid black line showing the linear fit. Closed (open) triangle shows the loop of 295 K and 30 K, respectively. $V_1$ corresponds to the thermoelectric voltage ($\Delta V$) and $V_2$ corresponds to the temperature difference ($\Delta T$).

hopping (NNH) and (ii) variable-range-hopping (VRH) and the universal equation governing these conduction mechanisms in semiconductors is given by $\sigma \sim e^{-T^{-p}}$, where $p$ defines a specific mechanism based upon the density of states (DOS) at Fermi level. For band conduction $p = 1$, and for variable range hopping (VRH) $p$ lies between 0 and 1 and the transport of charge requires a conduction mechanism through localized states via nearest NNH and VRH. In general, VRH relationship between conductance and temperature can be expressed for various spatial dimensions as $\sigma \sim e^{-T^{[-1/(d+1)]}}$, where $d$ is the spatial dimension. As our sample thickness is $\sim 800 \, \mu\text{m}$, one would expect the electrical transport to be governed by 3D transport mechanism as the condition for 2D transport, $k_Fl < 1$ is no longer valid. However, the inter-layer hopping is assumed to be sufficiently weak compared to the in-plane hopping thereby confining the charge carriers in a quasi 2D plane so that 2D Mott VRH is applicable [236].
Based on 2D VRH mechanism, the resistance data were fitted with $\frac{\Delta R}{R} = aT + be^{T^{(-1/3)}}$ function. The linear $T$ dependence accounts for the metallic behavior at high temperatures, while exponential term stems from the Mott’s VRH with $R = R_0e^{(T_0/T)^{1/3}}$ in 2-dimension [237].

Figure 6.14a shows the temperature dependence of TEP with appropriate theoretical fits. The diffusion term of the thermopower is generally expressed as (Mott formula),

$$ S = \frac{\pi^2}{3e}K_B^2T\frac{\partial(\ln\sigma(E))}{\partial E} \bigg|_{E_F} $$

(32)

,where the thermopower is proportional to the energy derivative of the electronic density of states (DOS) at Fermi energy $E_F$ [238, 239, 240]. For conventional nondegenerate semiconductors, $S$ is inversely proportional to the temperature and expressed as

$$ S = \frac{K_B}{e}\left(\frac{E_C - E_F}{K_BT} + const\right) $$

(33)
where $E_C$ is the energy at the conduction band edge [241]. Various theoretical behaviors have been found for the thermopower in the variable range hopping regime. Cutler and Mott have predicted a linear variation with temperature $T$ of the thermopower: $S \sim T$ [242]. Zvyagin, Overhof and Mott [243, 244, 245] showed that $S \sim T^{1/2}$. Triberis and Friedman [246] have found $S \sim T^{-1/4}$. In general, using the Mott formula, and the general expression for the conductivity for a given spatial dimension, it can be shown that $S \sim T^{(d-1)/(d+1)}$ [247]. The $S(T)$ data for the samples with $x = 0$, 0.2, and 0.5 were fitted with $S(T) \sim aT^{1/3}$. Again, the $T^{1/3}$ dependence of the $S$ originates from the 2D Mott’s variable range hopping (VRH) mechanism [237]. The data at high temperatures can be fitted quite reasonably with the theory with $S \to 0$ as $T \to 0$. A blown-up view of the data for $x = 1$ and 0.83 is presented in Figure 6.14b. The temperature dependence of thermopower for both samples show a negative sign of the thermopower at low temperatures. This sign change in thermopower can be qualitatively explained within the framework of a two-band model facilitating two-carrier conduction allowing for the overlap of two types of carriers.

**Figure 6.13.** Plot of normalized resistance vs temperature with theoretical fits. (b) The right panel shows a blown-up view of the upper three curves.
with opposite sign (electrons and holes). At the compensation temperature, the Seebeck coefficient vanishes yielding intrinsic conduction. In that case, the electrical resistivity should display a maximum due to minimum carrier density. In this model, the total electrical conductivity ($\sigma_{\text{total}}$) and total thermopower ($S_{\text{total}}$) are given by $\sigma_{\text{total}} = \sigma_e + \sigma_h$ and $S_{\text{total}} = (\sigma_e S_e + \sigma_h S_h)/(\sigma_e + \sigma_h)$ where the subscripts $h$ and $e$ refer to holes and electrons, respectively. The total thermopower is determined by the compensation of partial thermopower weighted by the partial conductivity of holes and electrons. Modification of the Fermi surface when the Fermi level, $E_F$ lies deep in the band (metallic) or the change in the band structure at higher levels of As can also play a role in the reversal of the sign of the thermopower. The work by Jeavons et al. [248] shows the temperature dependence of the $S_{11}$ and $S_{33}$ components of the Seebeck coefficient tensor (only down to 77 K). According to them, $S_{11}$ shows a positive (linear dependence with temperature) values while $S_{33}$ shows negative values in the temperature region between 77K - 300 K. In a follow up work, Heremans et

**Figure 6.14.** (a) Plot of TEP vs temperature with theoretical fits. (b) The right panel shows the blown-up view of the results for the two samples with high Arsenic concentration ($x = 1$ and 0.83).
Table 6.2. Comparison of Room Temperature Electronic Transport Properties ($S$, $\rho$ and $PF$) of $As_xP_{1-x}$ alloys with Standard TE Materials.

Table 6.2. Comparison of Room Temperature Electronic Transport Properties ($S$, $\rho$ and $PF$) of $As_xP_{1-x}$ alloys with Standard TE Materials.

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Compound</th>
<th>TEP ($S$)</th>
<th>Resistivity ($\rho$)</th>
<th>PF ($S^2\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$As_0P_1$</td>
<td>323.0</td>
<td>$4.66 \times 10^{-03}$</td>
<td>22.38</td>
</tr>
<tr>
<td>2</td>
<td>$As_{0.2}P_{0.8}$</td>
<td>803.0</td>
<td>$5.85 \times 10^{-03}$</td>
<td>110.26</td>
</tr>
<tr>
<td>3</td>
<td>$As_{0.5}P_{0.5}$</td>
<td>550.9</td>
<td>$9.59 \times 10^{-04}$</td>
<td>316.54</td>
</tr>
<tr>
<td>4</td>
<td>$As_{0.83}P_{0.17}$</td>
<td>7.4</td>
<td>$8.34 \times 10^{-06}$</td>
<td>6.57</td>
</tr>
<tr>
<td>5</td>
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<td>5.2</td>
<td>$5.22 \times 10^{-06}$</td>
<td>5.18</td>
</tr>
<tr>
<td>6</td>
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<td>-105.0</td>
<td>$6.3 \times 10^{-04}$</td>
<td>17.5</td>
</tr>
<tr>
<td>7</td>
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<td>575.0</td>
</tr>
<tr>
<td>8</td>
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<td>$4.34 \times 10^{-04}$</td>
<td>4.68</td>
</tr>
<tr>
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<tr>
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<td>Sb$_2Te_3[253]$</td>
<td>129.3</td>
<td>$4.68 \times 10^{-04}$</td>
<td>357.0</td>
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</table>

al. [234] show the temperature dependence of $S_{11}$ down to $\sim 2.5$ K. They show that $S_{11}$ has a small negative value at low temperatures; undergoes a change of sign at $\sim 16$ K; exhibits a positive maximum at $\sim 30$ K; decreases towards a minimum at $\sim 60$ K; and finally rises smoothly to a positive value at higher temperatures. Uher has measured $S_{11}$ of arsenic down to 0.3 K and shown that below 2 K the thermopower is due to carrier diffusion and follows a linear temperature dependence while phonon drag is important at higher temperatures [233]. Our results for $x = 1$ and 0.83 are somewhat closer to the results by Heremans et al. except for the positive hump. This may be because our thermopower measurement is not in a specific crystalline direction (random).
resistivity $\rho$ and power factor (PF) of the $\text{As}_x\text{P}_{1-x}$ alloys and other thermoelectric materials. Room temperature transport results for BP ($x = 0$) shows the Seebeck coefficient $S$ to be $323 \, \mu\text{V/K}$ and electrical resistivity $4.66 \times 10^{-03} \, \Omega\text{m}$, which result in the power factor (PF) of $22.38 \, \mu\text{Wm}^{-1}\text{K}^{-2}$. Moreover, at room temperature, the large power factor of $316.54 \, \mu\text{Wm}^{-1}\text{K}^{-2}$ was reached for $\text{As}_{0.5}\text{P}_{0.5}$ sample. Plot of effect of As concentration on the Residual-resistance ratio (RRR) of the AsP alloys (see Figure 6.15) and the temperature dependence of power factor of $\text{As}_{0.5}\text{P}_{0.5}$ benchmarked with $\text{Bi}_2\text{Se}_3$ [250] is presented in Figure 6.16. This suggest that the thermoelectric properties of the BP can be improved by doping, resulting in comparable or even better performance than some of the reported outstanding thermoelectric materials. However, it should be pointed out that extended defects present inside the measured polycrystalline alloy samples (Figure 6.5) could contribute to the thermopower [254]. Therefore, a follow up transport study using single crystalline samples may be needed to determine the intrinsic alloy contributions in the thermopower.

Figure 6.15. Effect of As concentration on the Residual-resistance ratio (RRR) of the AsP alloys.
In summary, we have synthesized and conducted the comparative study of structural and transport properties of series of As$_x$P$_{1-x}$ alloys. Raman spectroscopy demonstrated the existence of 3 types of atomic vibrational (phonon) modes arising from As-As bonding ($< 270$ cm$^{-1}$), As-P bonding ($270$ cm$^{-1}$ - $350$ cm$^{-1}$) and P-P bonding ($> 350$ cm$^{-1}$). Phonon modes found to be red shifted with increasing As concentration. This is due to the changes in bond strengths and bond lengths occurring when P atoms are being substituted by As atoms. TEM characterization shows that these alloys consist with clusters of flakes ranging from few tens of nanometers to few micrometers in size. The alloyed samples showed the layered morphology and relatively uniform composition. They were found to crystallize in the orthorhombic puckered structure and the systematic expansion of the lattice structure with the increase of arsenic concentration was observed. At a smaller scale, individual flakes showed a mono-crystalline orthorhombic crystal structure analogous to BP, but at a larger
scale it was found to be more polycrystalline in nature. Formations of differently oriented domains were found even within the grains of a specific orientation. Furthermore, high resolution imaging reveals an abundant presence of structural defects and lattice distortions in the alloys, and the relationship between these defects and composition of alloys is yet to be studied differently. Transport studies have shown that samples with the higher concentrations of arsenic \((x = 0.83 \text{ and } 1)\) exhibited an anomalous temperature dependence at low temperature and a metallic behavior with negligible thermopower at room temperature. On the other hand, room temperature thermopower measurement of the samples with lower As concentration \((x = 0, 0.2 \text{ and } 0.5)\) showed the very high thermopower (as high as \(803 \mu V/K\) for \(x = 0.2\)). The temperature dependence of the thermopower also can be fitted with 2D VRH mechanism, \(S \sim T^{1/3}\). It was observed that the 4-probe resistance decreased by more than 3 orders of magnitude as As concentration increases. The lower As concentration samples was fitted well with 2D VRH mechanism, \(R \sim e^{T^{-1/3}}\) whereas the higher As concentration samples showed low 4-probe resistance values and displayed metallic behavior with almost linear temperature dependence.
The discovery of ferromagnetic order in monolayer 2D crystals has ushered in a new era for two-dimensional (2D) materials. 2D magnets are fascinating on their own, but when combined with van der Waals heterostructures, new and novel behaviors can be observed at the ultrathin limit. F. M. Haldane showed that a two-dimensional electron gas existing on a honeycomb lattice should exhibit a quantum Hall state without the presence of an external field [255]. This is based on the inherent topological nature of the bandstructure of low-dimensional systems. Since then, a diverse range of electronic and magnetic behaviors has been observed in hexagonal layered 2D materials: graphene is the most famous of such systems. Topological band structures do not only exist in $\frac{1}{2}$-integer spin materials like graphene. In fact, many materials show topological behavior. 2D ferromagnets, which exhibit magnetic analogs of the Dirac particles found in topological electron bands (e.g. graphene or MoTe$_2$), are a tantalizing area of materials.

The Cr$_X$$_3$ ($X =$ Cl, Br, I) families of chromium trihalides have been the most investigated among magnetic 2D crystals to date. The ferromagnetism in these Cr$_X$$_3$ compounds may possess potential for adding magnetic species into devices based on van der Waals heterostructures. Chromium trihalides (Cr$_X$$_3$, $X =$ Cl, Br, and I), despite being heavily studied more than half a century ago, have recently attracted much attentions due to their unique low temperature magnetic orders in the monolayer and few-layer forms. In the monolayer, all Cr$_X$$_3$ display the in-plane ferromagnetic (FM)
order. The out-of-plane spin coupling becomes antiferromagnetic (AF) in the bilayer, which changes to FM for trilayer/bulk for CrI$_3$ and CrBr$_3$ but CrCl$_3$ remains AF. Thin Cr$_X$$_3$ also exhibit novel properties such as giant magnetic anisotropy, strong magneto-electric (ME) effect, large magneto-optical Kerr effect (MOKE), switchable magnetic bulk photovoltaic effect (BPVE), etc [141, 256, 257]. Because of the strong spin-lattice interaction and the hexagonal stacking order, the magnetic properties of Cr$_X$$_3$ depend sensitively on the number of layers and can be manipulated by electric field, magnetic field, pressure, and strain, making these trihalides the prime candidates for spintronics and magnetoresistive memory applications [258, 259]. In this work, we have studied the phonon modes of these trihalides.

1 Experimental

1.1 Synthesis

Single crystals of Cr$_X$$_3$ ($X =$ Cl, Br, I) were obtained by short chemical vapor transport (CVT) method. CrI$_3$ crystals were obtained by annealing mixture of chromium (Cr, Alfa Aesar 99.995 %) and iodine (Alfa Aesar 99.9 %) powders in a molar ratio of 1:3 in argon atmosphere. The well-mixed powder was sealed in an evacuated quartz tube and placed inside a gradient furnace at 750/600 °C for a period of 7 days. Single crystals of CrI$_3$ were formed at the cold end of the tube. CrBr$_3$ crystals were obtained by annealing an evacuated quartz tube loaded with mixture of chromium (Cr, Alfa Aesar 99 %) and tellurium bromide (TeBr$_4$, Alfa Aesar 99.9 %) powders at temperature gradient of 750/450 °C for 72 h. The single crystals of pure CrCl$_3$ were synthesized by vacuum sublimation of commercially available CrCl$_3$ powder (Alfa Aesar 99.9 %) at a temperature gradient of 700/550 °C for 72 h. Ampule with precursors was evacuated down to 10E-6 Torr and sealed afterward using an oxy-acetylene flame torch. Sealed tubes are placed in a three zone furnace (MTI OTF-1200X) for annealing in such a way that the hot end of the tube is placed toward the center of the furnace.
Evacuated ampule with precursor were heated at 3 °C/min to 700-750 °C, annealed for 72 h, and cooled down to room temperature at 5 °C/min. Several thin flakes of CrX₃ (X = Cl, Br, I) single crystals were formed at the cold end of the quartz tube [260]. We handled the sample in an argon gas atmosphere in a glove box to avoid any reactions with air, and the crystals were freshly cleaved before characterizations and measurements.

1.2 Material Characterization

As-synthesized crystals of CrX₃ were characterized using Raman, XRD, TEM, XAS and RIXS measurements.

1.2.1 Raman, XRD and TEM measurements

![Figure 7.1](image.png)

**Figure 7.1.** a) Raman spectra and b) XRD of Chromium halides.

In order to study the vibrational modes of these crystals, Raman spectra were collected using Raman spectroscopy stage (Renishaw inVia™ micro-Raman/PL
Figure 7.2. a) High-resolution transmission electron microscopy (HRTEM) image of the CrI$_3$ single crystal. (b) Selected area electron diffraction pattern obtained from a single grain. (c) Elemental mapping of a randomly chosen grain demonstrating the elemental uniformity in the sample. (d) Energy-dispersive x-ray (EDX) spectrum of the CrI$_3$ crystal with an table showing the elemental composition of the sample.

spectrometer with a 632 nm He-Ne laser) with a 50x objective lens and an exposure time of 10 sec with accumulations of 10 times. Figure 7.1a shows the raman spectra of CrX$_3$ which indicates our materials are of high quality. Phase purity and the structural analysis of the samples were characterized by X-ray diffraction using a Bruker D8 Discover diffractometer. A CuK$_\alpha$(\(\lambda = 1.541\) Å) radiation tube was used and the diffraction pattern were recorded using a scan speed of 0.02° s$^{-1}$, in the range of 2θ from 10° to 80°. CrI$_3$ crystallizes as a monoclinic AlCl$_3$ structure with
$C_2/m$ space group symmetry, then transitions to a rhombohedral BiI$_3$ form with $R_3$ symmetry at roughly $T_s$ 210-220 K [261]. At ambient temperature, CrCl$_3$ has the monoclinic AlCl$_3$ structure (space group $C_2/m$), whereas below 240 K, it has the rhombohedral BiI$_3$ structure (space group $R3$) [140]. CrBr$_3$ undergoes the same crystallographic phase transition, but at 420 K [140], resulting in a rhombohedral form at ambient temperature.

TEM specimens were prepared by drop-casting dispersions of samples onto commercial holey carbon-coated TEM grids. TEM measurements were performed using a 200 kV field emission gun FEI Tecnai F20 instrument, equipped with a nanoprobe and scanning transmission electron microscopy (STEM) capabilities. The microscope was also equipped with analytical capabilities, including an EDAX TEAM™ Energy Dispersive X-ray Spectroscopy (EDX) analysis system with an Octane silicon drift detector. In Figure 7.2 a), the HRTEM image of a representative CrI$_3$ single crystal has been exhibited, revealing the outstanding crystalline quality on a macroscopic length scale. Figure 7.2 b) shows the electron diffraction pattern formed by the crystallographic planes in a certain location. The EDX spectroscopy data obtained from various randomly selected parts of the developed crystals indicates the elements’ homogenous distribution, and the chemical composition of the crystal is extremely similar to the starting stoichiometry Cr:I=1:3. [see Figure 7.2 c)]. In Figure 7.2 d), we have shown the EDX spectrum and the elemental composition table obtained on one such small area, as a representative.

1.2.2 XAS and RIXS measurement

XAS by total fluorescence yield (TFY) mode and RIXS were probed in the qRIXS endstation at Beamline 8.0.1 at Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL) [262]. We cleave the air- and light-sensitive CrI$_3$ ex-situ in the dark Ar environment before mounting all Cr$X_3$ samples into the experimental
load-lock chamber to reduce the degeneration of quality. The measurement chamber was in ultrahigh vacuum ($5 \times 10^{-9}$ torr) and dark condition during the measurement. The x-ray photo polarization was in the horizontal plane ($\pi$-polarization) and the combined (Beamline and Spectrometer) energy resolution was set to 0.3eV (0.35eV) for CrCl$_3$ and CrBr$_3$ (CrI$_3$) at Cr $L$-edge. The open cycle cryostat with LN2 flow was used to cool down the Cr$X_3$ samples to 100K (80K) for CrCl$_3$ and CrBr$_3$ (CrI$_3$) measurement in the rhombohedral structural phase. The experimental geometry was set as the plot in figure 7.4(b). A rotatable GaAsP photodiode with a front aluminum window was used to detect TFY mode XAS and a modular x-ray spectrometer with a CCD detector was used to collect the emission signal of RIXS, respectively. Besides the general normalization with photon flux from an upstream Au mesh, the XAS spectra were further normalized to make the pre- and post-edge spectral weight to be 0. We used the elastic peak of carbon tape to convert the pixel number of the 2D CCD detector on the spectrometer to the emission energy in eV. For RIXS in figure 7.4(d), the collection time of each spectrum was fixed and preliminarily normalized by the total count on the CCD detector.

2 Results and Discussion

2.1 Cr$X_3$ ($X =$ Cl, Br) under strain:

In order to conduct strain dependent Raman studies, strain mount setup with sample mounted was placed in a Raman spectroscopy stage (Renishaw inVia$^{TM}$ micro-Raman/PL spectrometer with a 632 nm He-Ne laser) as discussed in Chapter 5. Raman spectra at various strain values were recorded in-situ using a 50x objective lens with an exposure time of 10 sec and an accumulation of 10 times. With increasing strain, we observed a systematic redshift of Cr$X_3$ ($X =$ Cl, Br) phonon modes (see Figure 7.3). This makes sense since when a crystal is subjected to tensile stress, the atoms are driven apart by lengthening chemical bonds in comparison to their
typical locations and lengths in the unstressed crystal. The force constant reduces (for a given stress) as the chemical bond length rises, and hence the vibrational frequency drops (frequency is proportional to the square root of the force constant). As a result, for materials that have been subjected to tensile stress, Raman peaks shift to lower frequencies. Conversely, when compressive stress is applied, the atoms in a crystal move closer to each other by shortening the chemical bonds, which leads to the Raman peaks shifting to higher frequencies. The peak shifting ratio for CrX$_3$ ($X = \text{Cl, Br}$) was observed to be smaller in comparison to BP and MoTe$_2$, most probably due to larger Young’s modulus.

Figure 7.3. a) Strain dependent Raman spectrum of CrBr$_3$ and CrCl$_3$ (b) Raman shifts with respect to strain. The fits are just a guide to an eye.
2.2 XAS and RIXS Results:

Figure 7.4. (a) Rhombohedral structure of Cr$X_3$. (b) The geometry of experimental setup. (c) X-ray absorption at Cr $L_{3,2}$-edge of CrCl$_3$, CrBr$_3$, and CrI$_3$ in rhombohedral structure phase. There is an obvious absorption edge shift between these three Cr trihalides. The photon energy locations at a, b or b’, and c are for the RIXS excitations. (d) The RIXS at excitations a (blue solid line), b or b’ (green solid line), and c (red solid line). The peaks in region I are $d - d$ transitions and region II are charge transfers. The energy shift on these peaks with different degree is observed.

The Cr$X_3$ consists of layer by layer stacking with the separation of vdW gaps. Every layer is formed by tilted octahedrons having central Cr$^{3+}$ ion coordination with six X- ions. The Cr$^{3+}$ ions in each layer connect to construct the honeycomb structure through the edge-sharing octahedral coordination as shown in Figure 7.4 (a). There is a crystallography phase transition from monoclinic (higher temperature) to rhombohedral (lower temperature) structure in CrCl$_3$, CrBr$_3$, and CrI$_3$ at 240K,
Figure 7.5. Chromium trihalide XAS spectra at Cr $L_{3,2}$-edge in the monoclinic (red) and rhombohedral (blue) structural phase. The monotonic energy shift of XAS spectra can be seen in both structural phases.

420K, and 200K, respectively [144, 140]. The magnetic orders of these three Cr$X_3$ emerge at further lower temperatures in the rhombohedral structure [263, 145, 264].

Therefore, we focused on the XAS and RIXS measurements in the rhombohedral structure. The tilted octahedrons and vdW separated layer can be observed in Figure 7.4(a) which exhibits the rhombohedral unit cell of the Cr$X_3$. Figure 7.4(b) shows the experimental setup. The angle between the incident x-ray beam and the detector is 40°, and the samples face towards the detectors of the XAS and RIXS. We do not align the orientation of the samples to specific order states. The Cr $L_{3,2}$-edge XAS in Figure 7.4(c) exhibits that the different halogen substitutes make the change in energy locations of the XAS edge jump. The energy locations with a, b/b’ and c labels are for the RIXS excitation energies. The XAS in the monoclinic structure is similar to the rhombohedral one (See Figure 7.5 ). This apparent shift suggests the significant evolution of electronic structure via the replacement of halogen substitutes, i.e., with different ligand effects. However, it’s difficult to determine the key energy scales.
reliably by only XAS. The Cr$_3$ RIXS spectra at various excitation energies in figure 7.4(d) preliminarily resemble the XAS result. The $d - d$ excitations in the region I and the LMCT features in region II both shift with the replacement of halogen substitutes. The shifting trend is consistent with Raman spectroscopy.

3 Conclusions

In conclusion, we have synthesized high quality crytals of Cr$_X$$_3$ and studied their strain dependent vibrational properties using Raman spectroscopy. We saw the systematic shifting of phonon modes with respect to strain. Furthermore, we present the result of the second-order RIXS process to determine the key energy scales that are fundamental to theoretically predict the basic properties and applications in such a 2D vdW magnetic orders material, Cr$_X$$_3$. It’s capable of capturing the reliable and closely real parameters of Cr 3$d$ orbit in Cr$_X$$_3$ compared to XAS and Raman spectroscopy. Determining these parameters by RIXS can significantly avoid the forbiddance of $d - d$ transition in Raman spectroscopy, moreover, we prove that RIXS is much more accurate to these energy scales than XAS despite insufficient energy resolution. The high energy resolution RIXS will be necessary for the future to further fine-correct these parameters and investigate these interactions in magnetic orders of Cr$_X$$_3$ at low temperatures.
Despite the fact that this thesis is made up of two separate projects - x-ray/neutron diffraction techniques were used to understand the nuclear and magnetic structure, and the second project was focused on studying the vibrational and transport properties of these layered materials – common themes bind them together. We have presented a comparison of the structural and magnetic properties of the homologs \( \text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2 \) based on susceptibility and neutron powder diffraction data. Our motivation was to present a comparison of the structural and magnetic details of \( \text{M} = \text{S and Se} \) as there had been no previously published, explicit comparison of these compounds. Neutron powder diffraction indicates that the nuclear structures of \( \text{La}_2\text{O}_2\text{Fe}_2\text{O}(\text{S, Se})_2 \) are similar to the structural characteristics found in other oxy-chalcogenides, with the main distinction being the difference in lattice size based on the atomic radii of the two chalcogens. In both of these materials, we observed the magnetic phase transition from paramagnetic to the antiferromagnetic phase. However, we didn’t see any indication of structural phase transition, which motivates us to study the local structure in these systems. The local structure of these systems was studied using the pair distribution function technique, which indicates the presence of short-range orthorhombicity suggestive of nematic fluctuations in a typical range of 1-2 nm. Furthermore, total scattering data analysis shows that the \( \text{Fe}_2\text{O} \) plane buckles below 100 K. The buckling may occur concomitantly with a change in octahedral height. We observed similar behavior in iron tellurides. In the case of \( \text{Fe}_{1.1}\text{Te} \), even
though the average structure suggests the structural phase transition from tetrago-
nal to the orthorhombic structure at around 75 K, total scattering analysis suggests
that there is the presence of local distortion between these two phases up to 100 K.
We have performed mPDF analysis which shows the presence of local distortion in
the magnetic moment. Overall, it was found that this material system shows the
presence of short-range nematic fluctuations which have been observed previously on
other FeSCs.
Next, we have designed a custom-made strain device which can be used for strain-
ing 2D crystals. Our device allows variable strain to be applied to these materials.
The strain dependent Raman behavior of black phosphorus and MoTe$_2$ crystals was
studied and compared using this device. Our findings show that the strain-induced
Raman peak shifting of black phosphorus is more pronounced than that of both
phases of MoTe$_2$, which can be explained by the lower Young’s modulus value of
BP. Both donor-type intercalation induced vibrational properties and tensile stress
driven vibrational properties in BP result in an increase in bond length. As a result,
peak shifting of the phonon mode is a useful tool for analyzing the strain behavior
of two-dimensional materials. Such techniques could be useful in the development of
future flexible electronic devices. Even though black phosphorus has various unique
properties, its industrial application is still limited because phosphorene is highly
unstable and tends to degrade under ambient conditions. Different surface passiva-
tion techniques have been utilized. However, just covering the surface may not be
the solution for practical application. In order to address this issue, we have alloyed
black phosphorus with arsenic. The structural and temperature-dependent transport
properties of As$_x$P$_{1-x}$ ($x = 0, 0.2, 0.5, 0.83$, and $1$) alloys have been synthesized and
reported. Samples with higher arsenic contents ($x = 0.83$ and $1$) had an abnormal
temperature dependence at low temperatures and a metallic behavior with negligible
thermopower at room temperature. Room temperature thermopower measurements
of samples with lower As concentrations ($x = 0, 0.2, \text{ and } 0.5$) revealed extremely high thermopower (as high as $803 \, \mu V/K$ for $x = 0.2$). Furthermore, as the arsenic content $x$ increases from 0 to 1, the 4-probe resistance of the $\text{As}_x\text{P}_{1-x}$ decreases by more than 3 orders of magnitude. This study reveals that black arsenic phosphorus is an excellent thermoelectric material for thermoelectric devices.

Finally, we have synthesized magnetic topological materials $\text{CrX}_3$ ($x = \text{Cl, Br, I}$), which shows layer dependent magnetic properties. We have performed strain dependent studies and spectroscopic measurements (XAS and RIXS) in order to study their phonon modes. This study concluded that RIXS spectra is a much more accurate approach in obtaining the energy scales, which are needed to construct the base Hamiltonian than XAS, despite its relatively lower energy resolution.

1 Outlook

Weyl semimetals are crystals whose low-energy excitation is a Weyl fermion, a particle that has played an important role in the development of quantum field theory and the standard model. These Weyl fermions can emerge in systems where either time-reversal symmetry or inversion symmetry is broken. Moreover, they are known as quasiparticles in low-energy condensed matter systems. Traditional electronic devices suffer from severe heating problems as a result of structural or chemical flaws, which cause additional scattering and reduce carrier transmission. Therefore, understanding topological phase transitions is an increasing interest for many novel low-power and low-dissipation electronic applications.

Transition metal dichalcogenides (TMDs) $\text{MM'Te}_4$ ($\text{M} = \text{Ta, Nb}; \text{M'} = \text{Ir, Rh}$) have recently received a lot of attention due to their interesting physics and promising potential applications. $\text{NbIrTe}_3$ is a bulk ternary transition metal dichalcogenide with a structure similar to $\text{WTe}_2$ and $1\text{T'}-\text{MoTe}_2$. This material has four chalcogen layers unlike the more famous two layer MoS$_2$. It consists of Nb and Ir atoms
octahedrally coordinated by Te atoms. Tellurium has a greater tendency to show a wide range of Te...Te interactions though it has less ionic character. NbIrTe$_4$ is a Weyl semimetal even in the absence of Spin-orbit coupling (SOC), and the Weyl points are very well separated from each other in momentum space, implying a robust Weyl phase. The monolayer (ML) version is predicted to display quantum spin Hall QSH behavior, while in the bulk, it adopts WSM characters. The topological phase transition from the stacked topological insulators (TIs) to the bulk WSM is argued to result from a breaking of inversion symmetry which progresses as layer thickness increases. Therefore, this system represents an exciting opportunity to explore the presence of topological phase transitions as a function of sample thickness and temperature. The ability to carefully control MM'IrTe$_4$ thickness in a controlled manner would be valuable. Materials growth techniques that allow atomic layer-by-layer control would be ideal as an experimental basis for investigating topological ordering. Magneto-resistivity and other transport measurements will provide significant insight regarding the link between electronic ordering and the topologically protected surface states in 2D materials.

To gain a better understanding of CrX$_3$, it is critical to conduct experiments on both atomically thin and bulk 2D crystals, which shows emerging physical properties. Atomically thin chromium trihalides can be prepared by CVD or thermal evaporation method. However, bulk 2D crystals can be prepared using chemical vapor transport (CVT) method. Local atomic structures, such as surfaces, interfaces and defects, are also my field of interest. In addition, exploring novel electrical and magnetic properties hosted in these monolayer to bulk 2D crystals would be beneficial. It is beneficial to investigate tunneling magneto-resistance by encapsulating these insulators between graphene layers.

In addition, recently, we have reconstructed our cryogenic system for performing strain dependent electrical transport properties measurement. To make this system
to function, I had to fix the leaks in the helium compressor and CCR, calibrate the temperature and properly wire the system with electrical connections. Also, I was able to install the CS100 Razorbill strain device in our system and connect the wires of the strain cell from the CCR through a vacuum feedthrough, which will be connected to the measuring instrument. This setup will be helpful for studying the electrical transport properties of various single crystals under external stimuli such as temperature and strain.
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APPENDIX A: COMMONLY USED ACRONYMS

AFM - Antiferromagnetic
CIF - Crystallographic information file
DFT - Density functional theory
FM - Ferromagnetic
PM - Paramagnetic
GGA - Generalised gradient approximation
PDF - Pair distribution function
FC - Field cooled
GSAS - General structure analysis system
HRPD - High resolution powder diffraction
ICSD - Inorganic crystal structure database
irrep - Irreducible representation
MPMS - Magnetic properties measurement system
NN - Nearest-neighbour
NNN - Next-nearest-neighbour
R_{wp} - Weighted R-factor
SARAh - Simulated annealing and representational analysis
SQUID - Superconducting quantum interference device
TOF - Time-of-flight
XRD - X-ray diffraction
NPD - Neutron powder diffraction
ZFC - Zero-field cooled
2D - Two dimensional
VRH - Variable range hopping
PF - Power factor
TE - Thermoelectric TEP - Thermoelectric power
h-BN - Hexagonal boron nitride
MIT - Metal-insulator transition
1ML - Single monolayer
ME - Magneto-electric
MOKE - Magneto-optical Kerr effect
BPVE - Bulk photovoltaic effect
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SUMMARY OF QUALIFICATIONS

⇒ 4+ years of working experience in studying strongly correlated electron systems using X-ray and Neutron diffraction techniques.

⇒ Expertise in measuring transport properties of 2D materials and their applications in Li-ion battery and supercapacitors.
⇒ Extensive research experience in Scanning Electron microscopy (SEM), UV-vis Spectroscopy and Raman Spectroscopy.

⇒ Expertise in writing and editing of scientific documents and communications for peer-reviewed research journals, conference symposia and departmental seminars.

⇒ Experienced in writing and submitting beamtime proposals in various national and international laboratories.

EXPERIENCE

RESEARCH EXPERIENCE

- Employed X-ray and Neutron diffraction techniques in order to study properties such as phase transition, high temperature superconductivity, nematicity and topological quantum phase behavior.

- Extensive research experience in studying average structure by Rietveld Refinement and local structure by pair distribution function techniques of various inorganic materials.

- Experienced in preparing NMC electrode materials for Lithium/Sodium-ion batteries.

- Fabricated Graphene/h-BN/Graphene tunnel junctions using lithography free technique and measured it’s electrical properties.

- Studied electrical and thermal properties of 2D materials including thermoelectric power, 4-probe resistance, thermal conductivity and hall effect.

- Designed custom-made strain device and studied strain-induced vibrational properties of Black Phosphorus and MoTe$_2$ via Raman spectroscopic techniques.
• Experienced in operating and troubleshooting using helium leak detecting system, high voltage electrospinning system, uniaxial strain cell, high temperature torch glass sealing, two and three-zone furnaces, ultra high vacuum systems, and cryogenic systems.

TEACHING EXPERIENCE

• Supervised undergraduate student on the summer project entitled *Synthesis and Characterization of a Novel 2D Materials- Chromium Tri-iodide.*

• Managed and taught introductory physics labs. Instructed 500+ students to perform experiments up to 25 students per section.

• Worked with lab supervisor to develop new lab experiments and modify the content of the current lab experiments.

TECHNICAL SKILLS

• CAD Software: SolidWorks, Fusion-360.

• Programming Languages: Python, C++, LabVIEW, LATEX.

• Data Visualization & Analysis: ORIGIN, IGOR, MATLAB, MATHEMATICA, MAPLE, Fullprof, SarahRefine, GSAS-II, PDFgui, Diffrpy-ctxi Software.

• Material Characterization: Raman Spectroscopy, XRD, TEM, SEM, PPMS, UV-Vis.

AWARDS & SCHOLASTIC ACHIEVEMENTS

• Outstanding Graduate Performance in Physics, The Manuel Schwartz Award, 2021.

• 2019 American Crystallographic Association (ACA) Annual Meeting in Covington, KY, *Best Poster Prize Winner.*

• Journal of Structural Dynamics Poster Award, ACA, July 2019.
• Graduate Network in Arts & Sciences (GNAS) Travel Award, UofL, Spring 2020.
• Graduate Network in Arts & Sciences (GNAS) Travel Award, UofL, Fall 2019.
• Graduate Student Council Travel Award, June 2019.
• Graduate Student Awards for Undergraduate Research and Creative Activities, May 2019.
• ICDD 2018-2019 Cycle II Grant-in-Aid Award, October 2018.
• Graduate Network in Arts & Sciences (GNAS) Research Award, UofL, September 2018.
• American Conference of Neutron Scattering (ACNS) Travel Award, June 2018.
• Arts & Sciences Research & Creative Activities Grant, UofL, April 2018.
• Graduate Student Council (GSC) Research Award, UofL, February 2018.
• Graduate Network in Arts & Sciences (GNAS) Research Award, UofL, January 2018.
• Topper of institution, Highest Scorer in MSc Physics in St. Xavier’s College, 2012.
• Merit Scholarship, St. Xavier’s College, Maitighar, Kathmandu, Nepal, 2012.
• Merit Scholarship, Tri-Chandra Multiple Campus, Kathmandu, Nepal, 2010.

SCHOOL & CONFERENCES ATTENDED

• 2019 ACA Annual Meeting in Covington, KY.
• Magnetic Structure Determination from Neutron Diffraction Data School (Magstr), ORNL, Oct 2019.
• 2019 Neutron Scattering User Meeting in ORNL, June 2019 (Poster).
• Workshop on Neutron Sciences in support of Nuclear Power, ORNL, May 2019.
• 2nd US School on Total Scattering Analysis, July 2018.
• 2018 American Conference of Neutron Scattering, June 2018 (Poster).
• Modern Methods in Rietveld Refinement for Structural Analysis at Advanced Photon Source, Argonne National Laboratory, June 2018.
• Joint Nanoscience and Neutron Scattering user meeting at Oak Ridge National Laboratory, July 2017.

LICENSE & CERTIFICATIONS

• Learn Python 2 and 3 Side by Side.
• Linux Command Line Basics.
• Create Simple GUI Applications with Python and QT.

PATENTS


PUBLICATIONS


3. B. Freelon, R. Sarkar, S. Kamusella, F. Brückner, V. Grinenko, Swagata Acharya, Mukul Laad, Luis Craco, Zahra Yamani, Roxana Flacau, Ian Swainson, Ben-


9. B. Freelon, Z. Yamani, Ian Swainson, R. Flacau, Bhupendra Karki, Yu Hao Liu, L. Craco, M. S. Laad, Meng Wang, Jiaqi Chen, R. J. Birgeneau, and Minghu Fang,


11. Manthila Rajapakse, Rajiv Musa, Usman Abu, Bhupendra Karki, Ming Yu, Gamini Sumanasekera, Jacek B. Jasinski, Comparison of Vibrational Properties of Pristine and Lithium-Intercalated Black Phosphorous Under High-Pressure Conditions. *Accepted Annalen der Physik*.


14. A. Alfailakawi, B. Karki, Z. Yamani, Ovidu Garlea, B. Freelon, Structural Study of Ca$_2$O$_2$Fe$_{2.6}$OS$_{2-x}$Se$_x$ Novel Iron Oxychalcogenides (In preparation for J. Material Chemistry).


**EXTRA CURRICULAR ACTIVITIES**

- Member of American Crystallography Association (ACA).
- American Physical Society (APS).
• Member of Students Physics Society (SPS), University of Louisville.

• Former President of Nepalese Student Association (NSA), University of Louisville,

• Member of Club Programming Committee (CPC), University of Louisville.

• Former Executive Member of Nepal America Society of Kentucky (NASK), Louisville