High Resolution Characterization of Magnetic Materials for Spintronic Applications

DISSERTATION

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by

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ABSTRACT

Materials science encompasses a broad range of different materials and applications; however, at its core is the drive to understand structure-property relationships and exploit them to engineer new materials that out-perform current ones. A unifying theme in this is materials characterization: the study of material structure, properties, processing, and performance.

Next-generation electronic devices will likely exploit more than just charge transfer and bulk magnetism to compute and store data. Instead, they will also make use of the inherent spin of the electron in so-called spintronic devices. These devices promise higher densities and lower operating power demands, thus significantly increasing performance. Using electron microscopy, the structures of novel magnetic materials are characterized across many length scales, as well as their electronic and magnetic properties using spectroscopy and theory.

Advances in aberration corrected scanning transmission electron microscopy (STEM) make it possible to investigate materials’ structures at the atomic level on a routine basis. The growth of high quality magnetic thin films is essential to their application in future devices. Characterization of the growth mechanism of pyrochlore Nd$_2$Ir$_2$O$_7$ thin films, as well as their structure and composition is presented, with a thermodynamic explanation of the observed phenomena. In
addition, atomic-scale defects and ordering in double perovskite Sr$_2$CrReO$_6$ thin films were studied both experimentally, as well as via a quantum mechanical electron scattering model. It is found that three-dimensional ordering information can be extracted from two-dimensional high-angle annular dark field STEM images. This is due to the fact that as the electron travels through the specimen, it is encoded with such information before being collected to form the image. Using certain sample- and experiment-specific parameters, the experimental data can be compared to simulated results to access the three-dimensional ordering data.

In addition to thin films, the electronic properties of bulk double perovskite $A_2BOsO_6$ ($A$=Ca, Sr; $B$=Cr, Fe, Co) are studied using electron energy-loss spectroscopy. The results are explained through the use of first principles calculations. Studying electronic structure in the electron microscope allows for high spatial resolution investigations into the effect of interfaces and other defects on electronic structure and their implications in magnetic properties.

Finally, magnetic skyrmion materials are studied in situ using Lorentz TEM and Lorentz differential phase contrast (DPC) STEM as a function of applied magnetic field and temperature. These materials may allow for ultra-high-density storage requiring orders of magnitude less energy. Skyrmions are studied in both bulk and thin film geometries. The size, temperature range, and field stability of skyrmions are investigated in two main classes of materials: B20 thin films and heterostructures, as well as perovskite bilayers. Progress is made on the development of zero- and low-field Lorentz DPC-STEM and its application to imaging different skyrmion types with improved spatial resolution and sensitivity.
To my parents, Martin and Michelle,

for their unwavering support of everything I do.
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CHAPTER 1
INTRODUCTION

The work presented in this dissertation is separated into two main parts. Chapters 2-7 will focus on high spatial resolution characterization of oxide thin films and powders using electron microscopy, spectroscopy, and simulation. The second part, Chapters 8 and 9, will highlight current and ongoing results characterizing topological spin structures in bulk and thin film geometries using magnetic imaging in the electron microscope. A comprehensive conclusion is included in Chapter 10.

Chapter 2 will provide an overview of the materials of interest and a review of the state of research in the field. In Chapter 3, a detailed explanation of the experimental methods will be discussed, including applications, limitations, and practical considerations. Electron scattering theory and image simulation will be explained in Chapter 4, with a comparison between the two main models and motivation for the quantum excitation of phonons model.

Experimental characterization of electronic structure in a family of osmium-based double perovskites using electron energy-loss spectroscopy discussed in Chapter 6 will be compared with and more fully understood through the use of first principles calculations. Peer reviewed publications on the growth of pyrochlore iridate thin films
and atomic-scale ordering phenomena in double perovskite thin films are reproduced in Chapters 5 and 7, respectively.

Part two begins with further explanation of experimental methods in Chapter 8, specifically \textit{in situ} electron microscopy and its relation to exploring the effects of temperature and magnetic field on magnetic materials. Finally, Chapter 9 covers progress made on such imaging of magnetic skyrmions in bulk and thin film systems with potential applications for next-generation spin-based devices, including a plan for future work on the subject.
CHAPTER 2

MOTIONATION AND BACKGROUND

Materials science and engineering is a wide-ranging, interdisciplinary field that touches every aspect of our lives: from the smart phones in our pockets to modern jet engines and artificial joint replacements. The fundamental goal of a materials scientist is to study the complex relationships between a material’s structure, the way in which it was processed, its physical properties, and ultimately its performance. Given the broad scope of engineered materials in use today, there are many ways in which these relationships can be studied. The ways in which materials scientists measure properties, model materials’ behavior, and examine their structures fall under the umbrella of materials characterization, which is at the heart of the field, as shown in Figure 2.1. Materials have driven most of the historic shifts in human civilization, with entire ages dedicated to such advances as the first uses of stone, bronze, iron, and now silicon. Historians never fail to recognize the importance of the development of new materials, and materials scientists are constantly striving to develop new materials that are stronger, lighter, smarter, and more environmentally friendly. Materials characterization across all of the length scales, under variable environments, and with a broad set of tools is critical to this development.
2.1 Materials characterization

The most basic description of a material starts with its composition and atomic structure. Do the atoms arrange themselves in a regular crystalline pattern or are they randomly arranged in an amorphous fashion? Are the different elements in the material confined to certain regions or do they diffuse throughout? These are just some of the questions that are probed when characterizing materials. There exist many different tools to answer such questions including various forms of microscopy (light, electron, ion), spectroscopy (electron, X-ray, optical), and diffraction-based techniques (electron, X-ray). The techniques range in spatial resolution from picometers ($10^{-12}$ meters) to millimeters, and can be used in correlative ways to study material structure at every level. Physical properties and material performance are
both significantly influenced by the other, as well as processing. Such properties as mechanical strength, electrical conductivity, magnetic behavior, bio-compatibility, and many more are all encompassed by materials characterization depending on the application.

One of the most versatile tools has been the electron microscope since its first practical demonstration nearly eight decades ago. Whereas a traditional light microscope uses visible light waves and glass lenses to form magnified images with spatial resolution on the order of $\sim 200 \text{ nm} \ (2 \times 10^{-7} \text{ m})$, electron microscopes use the wave-particle nature of electrons accelerated by a high voltage and magnetic lenses to form far higher magnification images with spatial resolution as high as $\sim 40 \text{ pm} \ (4 \times 10^{-11} \text{ m})$. In addition to high spatial resolution imaging, electron microscopes have been used to qualitatively and quantitatively characterize mechanical, electrical, electronic, and magnetic properties under various conditions including variable atmospheric pressures, applied electrical current, magnetic field, temperature, and more.

### 2.1.1 Quantitative Electron Microscopy

Over the course of their development, electron microscopes have seen significant improvements in spatial resolution, practicality, and analytical capabilities. Specifically, the transmission electron microscope, which forms an image by passing electrons through a very thin specimen, has become widely used in research labs because of its ability to routinely image the atomic structure of materials, while also providing chemical and compositional information. Such high resolution has
driven the characterization community to extract as much quantitative information as possible from microscopy and spectroscopy data. Most of the time, this also necessitates the incorporation of simulations to fully support such data. For example, LeBeau et al. showed that experimental images can be quantitatively compared with simulated data, as shown in Figure 2.2, and can also allow for three dimensional information to be quantified, even from a two dimensional image. [1, 2]

Similar investigations of material structure at the atomic scale using a combined experimental/theoretical approach have been used to locate individual dopant atoms three dimensions, [3] study atomic-scale ordering phenomena, [4] and quantify atomic resolution compositional maps on an absolute scale. [5] In order to make such
quantitative analyses, the experimental conditions must be very well characterized from the specimen to the microscope; however, modern computational capabilities also allow for a large number of simulations to be calculated with a range of experimental parameters to find the best agreement between the two. These techniques can be applied to most material systems to develop a far greater understanding of the material structure, composition, and properties. The research in this dissertation will focus specifically on materials that can be used for spin-based computing, or spintronics.

2.2 Spintronics

Current electronic devices store data in a couple of different ways depending on the frequency with which the data needs to be accessed. Long-term, low-frequency data is typically stored on hard disk drives in the form of non-volatile magnetic bits; whereas, short-term, high-frequency data usage is stored in volatile random access memory, usually in solid-state formats. [6] The former is far cheaper than the latter with the added benefit of being non-volatile (i.e. does not require power to retain data); however, solid-state memory typically has write speeds that are many times faster. While reducing the physical size of bits in either format can lead to increased capacity, newer designs that yield cheaper, faster, and more energy efficient designs are currently being developed.

One such design is the so-called “racetrack” memory shown in Figure 2.3. [7] In this new design, logic bits are stored in a long strip (the racetrack) and then moved along it via a current pulse such that the needed bit passes a read or write head.
By integrating large arrays of vertical racetracks, high-density storage devices can be fabricated. One of the possible ways in which the magnetic data can be encoded in each bit is through the use of magnetic skyrmions, which can be moved with $10^5$-$10^6$ times lower current density than moving magnetic domain walls. [8–10] The prospect of high-density storage arrays that require orders of magnitude lower current densities has driven a significant amount of research on the subject in the last 5-10 years, with a strong focus on skyrmion materials and dynamics.

Figure 2.3: Schematic of the racetrack memory geometry in (a) vertical and (b) horizontal configurations. Magnetic memory bits (*red and blue*) are stored along the racetrack and then moved via a current pulse for (c) reading and (d) writing allowing for (e) high-density storage device arrays. [7]
The research presented in the following chapters will set out to explore the underlying structure-property relationships in magnetic materials that are promising candidates for spin-based computing using high-resolution electron microscopy and spectroscopy. The instrumentation, techniques, and theory used will all be explained and put into context, while also presenting paths for future work.

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CHAPTER 3
EXPERIMENTAL TECHNIQUES

3.1 Background

As discussed in Chapter 2, materials characterization is central to our understanding of structure-property-processing relationships. While there is a wide range of instrumentation available for materials characterization, from electrical and magnetic measurements to thermal and mechanical measurements, few are as capable of simultaneously measuring several properties at scales across orders of magnitude as the electron microscope. Electron microscopes, including the scanning electron microscope and various forms of the transmission electron microscope, can be configured to make measurements either in situ or ex situ with control over parameters such as applied electric and magnetic fields, temperature, strain, gas pressure, and more, at spatial resolutions from millimeters to picometers. Such a broad scope makes electron microscopy a pivotal tool in further understanding fundamental materials properties.
3.2 Electron Microscopy

The following section will provide broader context for the instrumentation used over the course of this dissertation. In addition, it will describe both how they operate and their relation to the research described later, while pointing to well-established external sources for more detail where helpful.

3.2.1 DualBeam focused ion beam

The DualBeam focused ion beam (FIB) consists of two focused probes: an electron beam and an ion beam. The former is simply a scanning electron microscope that allows for direct surface imaging at medium to high magnifications. The latter has an ion source (typically Ga\(^+\), though also Xe\(^+\) in some cases) that is focused to a spot coincident with the electron beam and is used to remove material from a specific region of a sample to prepare thin specimens for imaging in the transmission electron microscope (TEM) or scanning TEM (STEM), as discussed in subsequent sections.

Sample preparation in the FIB has been used extensively over the course of this research. While an in-depth explanation of FIB instrumentation and techniques can be found in [1], only a brief explanation of the process and experimental considerations will be provided in this dissertation. Thin film specimens were typically provided in the form of a 5 mm by 5 mm wafer substrate with a thin film grown on top. In most cases, gold was sputter deposited on top of the thin film to protect against potential Ga\(^+\) implantation or damage in the FIB. The wafer was imaged in the DualBeam FIB using the electron beam and oriented with respect to a specific crystallographic direction using the cleavage planes of the wafer substrate. The ion mill was then
used to remove material leaving a rectangular specimen normal to the surface of the substrate with nominal dimensions of 1-2 \( \mu \text{m} \) thick by 30-40 \( \mu \text{m} \) wide, as shown with both the electron and ion beams in Figure 3.1.

Specimens are removed \textit{in situ} by first attaching a thin needle [seen in Figure 3.1(b)] using Pt deposition, then using the ion beam to cut around the sides and bottom of the specimen. Specimens are then transferred to a standard 3 mm TEM grid for further thinning to electron transparency. A high accelerating voltage of 30 kV is used for both milling and initial thinning at an incidence angle of approximately 2° off of parallel, with final thinning finishing at an accelerating voltage of 5 kV to reduce potential ion-induced damage. After thinning to electron transparency (generally < 50 nm), the specimen is transferred to a low energy Ar ion mill to further reduce sample preparation-induced damage.
3.2.1.1 Low energy ion milling

In order to ensure the highest quality specimens for high resolution imaging and spectroscopy, all specimens underwent final milling in a Fischione 1040 NanoMill at voltages of 900 and 500 V. Using such low voltages has been shown to drastically reduces any surface amorphization created by the high voltage Ga\(^+\) ion beam. [1, 2] This is especially critical when imaging in the TEM and STEM at atomic resolution, as well as when comparing experimental and simulated data, which often assumes a perfect structure with no amorphous surface layers.

3.2.2 Transmission electron microscope

Materials characterization has commonly been performed in the TEM because of its high spatial resolution - currently around 70 picometers with image aberration correction, as discussed below. The TEM has been a versatile tool use to investigate materials as diverse as classical metallurgical defects, 3D biological tomography, and nanoparticle catalysts. For an in-depth review of the TEM, including a historical perspective, basic operational procedures, and more specific imaging, spectroscopy, and diffraction techniques, refer to [3].

The TEM can be considered to be made up of three major systems: illumination, objective/specimen, and imaging. The illumination system is made up of an electron source and a set of lenses used to form a beam. The microscopes used in this research operate using Schottky field emission guns, which generate a high brightness, highly coherent electron beam with a small source size, which is beneficial for most applications. Electrons are emitted from the source and are accelerated via a large
potential, typically between 60 and 300 kV, though higher and lower accelerating voltages have been used for special applications. The electrons then travel through a set of condenser lenses (2 or 3 depending on the microscope) to form the beam for imaging. In the TEM, the condenser lenses operate such that a plane wave of electrons is focused onto the specimen, as shown in the left hand side of Figure 3.2. Conversely, in the STEM, a converged probe is focused at or near the plane of the specimen for imaging (as discussed in Section 3.2.3). In Figure 3.2, the lenses (C1, C2, C3, minicondenser, and objective) are all represented by double-headed black arrows. The C2 aperture, represented in blue, is used to define the area of parallel illumination in TEM, and probe convergence semi-angle in STEM.

After the beam is formed in the condenser system, it is further focused onto the specimen via the objective lens, which consists of two pole pieces (upper and lower) that surround the specimen, and in some cases, a minicondenser lens. The objective lens produces a large magnetic field at the plane of the specimen under normal imaging conditions (≈2-3 T), which will be a very important consideration in Chapter 8 when discussing in situ imaging modes for magnetic structures. The specimen itself sits in a holder at the end of a rod that is inserted into the microscope between the upper and lower objective pole pieces normal to the path of the electrons. Specimen holders typically have 4 or 5 degrees of freedom, including the $x$-, $y$-, and $z$-axes, $\alpha$-tilt (around the sample rod axis), and occasionally $\beta$-tilt (along the sample rod axis). By allowing 5 degrees of freedom, many different crystallographic directions can be aligned parallel to the beam direction, with typical restrictions on $\alpha$- and $\beta$-tilts being roughly $\pm 30^\circ$ depending on the holder and lens configurations.
Figure 3.2: Schematic ray diagram of (left) TEM and (right) STEM in a 3 condenser system, such as the FEI Titan microscopes. It can be seen from the diagram that the specimen, which sits between the upper and lower objective pole pieces, is imaged with a plane wave in TEM mode, and a converged probe in STEM. Adapted from [4].
Figure 3.3: Schematic ray diagram of electrons being focused by the lower objective pole piece (labeled “lens”), forming an image in the image plane, and a diffraction pattern in the back focal plane. The ratio of the object distance to image distance $d_o/d_i$ defines magnification, per Equation 3.1. [3]
In the TEM, the lower objective pole piece is set to strongly refocus the electrons after scattering through the specimen in the object plane, such that an image is formed on the camera or microscope viewing screen, as shown schematically in Figure 3.3. The ratio of the object and image distances, $d_o$ and $d_i$, respectively, define the image magnification, $M$, as seen in Equation 3.1.

$$ M = \frac{d_o}{d_i} $$

At the back focal plane noted in Figure 3.3, electrons are focused to form a diffraction pattern, which will be discussed in further detail in Section 3.2.3 in the context of scanning transmission electron microscopy and other related techniques.

Imaging in the TEM results in the image plane being projected onto the microscope viewing screen. While TEM images have historically been exposed on film, modern TEMs make use of charge-coupled diodes (CCDs). In most microscopes, electrons are not directly imaged using the CCD, but rather via a scintillator that converts the impact of an electron into photons that are then passed to the nearest pixel on the CCD to form an image. It should be noted, however, that high frame rate, high dynamic range, direct electron detectors are quickly being commercialized with significant impact for a broad range of fields including in situ experiments, magnetic imaging, and biological studies. [5–9]

### 3.2.2.1 High-resolution transmission electron microscopy

High-resolution TEM (HR-TEM), often performed at atomic resolution, yields results that require complex processing to fully understand. One of the major issues comes from the fact that image contrast is predominately due to phase shifts of the
plane wave of transmitted electrons, leading to reversals in contrast as a function of the focal length of the objective lens. [10] This means that depending on the imaging conditions, atomic columns may appear bright or dark. To account for this, HR-TEM imaging is typically performed as a through-focal image series (with the accompanying contrast reversals) that is then run through a reconstruction algorithm to extract the information of interest, referred to as an exit wave reconstruction. [11–13] An experimental imaging mode that does not suffer from such intricacies is generally more practical.

3.2.2.2 Reciprocity

In contrast to HR-TEM, STEM can be operated in such a way that it yields complementary results that are relatively straightforward to interpret, while still maintaining very high spatial resolution. It can be formally proven through the theory of reciprocity [14–16] that HR-TEM is inversely related to STEM. Whereas in TEM a plane wave of electrons is transmitted to the plane of the specimen, scattered through the specimen, and then focused to an image, in STEM the electron beam is focused to a point at the plane of the specimen and rastered in the x-y plane, then scattered through the specimen, and transmitted to a detector plane, as shown schematically in Figure 3.4. The theory of reciprocity can also be extended to include inelastically scattered electrons. [15, 16] This important relationship not only sets the stage for the use of STEM imaging, but also validates many of the fundamental theories upon which image simulation will be based, as discussed in Chapter 4.
Figure 3.4: Reciprocity in the transmission electron microscope. On the left is HR-TEM with a plane wave originating at point A, scattered through the specimen (P), and focused to an image at point B. On the right is STEM with a convergent beam focused from point $B'$ to the plane of the specimen (P), and transmitted to the detector at plane $A'$. The primes on the labels arbitrarily distinguish between HR-TEM and STEM. [16]

3.2.3 Scanning transmission electron microscope

The STEM has seen a significant rise in popularity over conventional TEM for many applications due to the relatively large number of possible configurations, many times allowing for quick switching between modes to gather complementary information with little to no additional alignment necessary. Most modern microscopes are built to switch between TEM and STEM modes, and as such most of the hardware is shared between the two with the main differences coming in the form of lens strengths, scan coils, and the types of detectors.

As shown on the right hand side Figure 3.2, there are significant similarities in the illumination setup between TEM and STEM. The first of which, in a three condenser
system, is the increased strength of the C3 lens, which allows the combination of the minicondenser and upper objective lens fields to converge the electron beam down to a point on the plane of the sample, rather than a plane wave as in TEM. Using scan coils (not pictured in Figure 3.2, but in Figure 8.7), the electron probe is rastered in the \(xy\)-plane across the specimen. The lower objective lens field is set far weaker than in TEM to allow the back focal plane, or diffraction pattern, to be projected onto the microscope viewing screen. Regardless of the STEM imaging mode, images are formed in series: signal is collected for each probe position as it is rastered in the \(xy\)-plane, and the image is constructed pixel-by-pixel.

There are many different imaging modes in which the STEM can be operated. Per the theory of reciprocity, HR-TEM is equivalent to operating the STEM in bright field mode, where a detector is placed directly on the optic axis, as shown in Figure 3.4 at point \(A'\). Bright field STEM suffers from many of the same issues as HR-TEM, including contrast reversals, rendering it generally less widely used than other STEM modes. The most commonly used STEM imaging mode is called annular dark field (ADF). Whereas bright field images include electrons that have not been scattered off the optic axis, dark field images are formed by electrons that have been scattered, excluding un-scattered electrons. The most apparent difference between bright and dark field images is essentially a contrast inversion, where regions in the image plane that do not scatter (i.e. vacuum) appear bright in bright field, and black in dark field. Scattered electrons are typically collected in the diffraction plane using an annular dark field detector, which allows the un-scattered electrons to be transmitted through the annulus of the detector. Using the optics below the specimen, the effective
distance between the specimen and the detector (known as camera length) can be
varied, affecting the angular range of scattered electrons that fall on the ADF detector
and enabling imaging conditions with different contrast modes.

3.2.3.1 Dark field STEM

At short camera lengths, the majority of low scattering angles in the diffraction
pattern fall within the detector annulus, resulting in an image formed with electrons
scattered through high angles, called high-angle ADF (HAADF) STEM. In this mode,
images have contrast that is strongly dependent on atomic number, called Z-contrast,
due to the Rutherford-like nature of scattering. Additional contrast is provided by
thermal diffuse scattering (TDS), which is due to phonon scattering and will be
critical in the discussion of image simulation theory in Chapter 4. Changing the
optics to produce intermediate or long camera lengths gives rise to medium- and
low-angle ADF (MAADF and LAADF, respectively). With lower angle scattering
included in the image, diffraction contrast can be used to highlight strain in the
specimen or defects such as dislocations. The average ADF detector works by simply
integrating the signal that falls on it as a function of probe position. This process,
however, gives no insight into variations in scattering either as a function of scattering
angle (radially from the center of the annulus) or azimuthally (around the annular
detector). More recently, ADF detectors have been segmented to separate out these
subtle differences. Segmented detectors will be discussed in Chapter 8 as they are
applied to in situ imaging of magnetic structures in the STEM.
3.2.3.2 The Ronchigram

Whereas in TEM, an image is formed all at once by illuminating a specific area with a plane wave of electrons, STEM images are formed incoherently by rastering a focused probe across the specimen. As mentioned in Section 3.2.3, the optics of a STEM are such that a diffraction pattern is projected onto the viewing screen and/or any detectors (BF, ADF, CCD). The zero-order transmitted beam in STEM, which contains electrons that have not been diffracted off-axis, is often referred to as the Ronchigram, named after the Italian physicist Ronchi who developed a lens test for light-optics that produced a similar feature. In ADF-STEM, the Ronchigram is by definition not used to form the image; however, in modern microscopes it is heavily used to align the microscope, as it can be used to measure aberrations, which will be discussed in Section 3.2.4. Not only can the Ronchigram be used to understand and correct imperfections in the microscope optics (aberrations), it can also be used to characterize a number of other experimental conditions such as probe diameter, specimen thickness, polarity, atomic arrangements, etc. [17, 18]

3.2.3.3 Position averaged convergent beam electron diffraction

For both TEM and STEM, it is often important to know with some certainty what the thickness of the specimen is along the beam path. Thickness can be used in a number of applications from estimating the volumetric density of features (i.e. precipitates or defects), quantifying compositional spectra, and simulating electron-beam interactions to calculate images, diffraction patterns, and ionization spectra. It was shown that specimen thickness, polarity, and specimen tilt can
all be experimentally determined using position averaged convergent beam electron
diffraction (PACBED) coupled with simulations. [18, 19]

PACBED is based on the fact that current STEM probe sizes have become smaller
than the unit cell of any crystalline specimen. This means that as the probe is
placed in different positions within the unit cell, different CBED patterns will form.
For example, a sub-Ångstrom probe typical in a modern state-of-the-art STEM will
give a different diffraction pattern on an atomic column versus between two atomic
columns. The technique requires that diffraction patterns from many probe positions
throughout the unit cell be incoherently averaged, resulting in a PACBED pattern.
Practically, this is done by rastering the beam over a defined area of the specimen,
which should include an integer number of unit cells, while exposing the CCD.
With CCD exposure time on the order of seconds, and probe dwell times on the
order of microseconds, the resultant image is an average of the CBED patterns as a
function of probe position. Using PACBED, it was shown that specimen thickness
can be experimentally determined to better than 10%, as shown in Figure 3.5. To
quantify the results, image matching is used with simulated data either manually or
by $\chi^2$ mapping to find the simulation with the smallest numerical difference from the
experimental data.

Hwang et al. showed that PACBED can be used to distinguish between
different types and magnitudes of octahedral tilting in perovskite thin films by
collecting experimental PACBED patterns from a LaNiO$_3$ thin film grown on a
(LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT) substrate. [19] The substrate lattice parameter
resulted in an in-plane tensile strain of 0.78% in the LaNiO$_3$ film. A systematic
Figure 3.5: Simulated PACBED patterns for different thicknesses of a SrTiO$_3$ crystal along [001] showing thickness sensitivity of at least 1 nm. [18]
set of LaNiO$_3$ structures was generated with varying degrees of octahedral tilting about two different orthogonal axes (in- and out-of-plane), $\alpha$ and $\gamma$, respectively. PACBED patterns were simulated for each structure holding the sample thickness and probe convergence semi-angle constant. When compared to the experimental data via an image correlation algorithm, a normalized $\chi^2$ map was generated, as shown in Figure 3.6, allowing for experimental determination of octahedral tilt angles to within 1°, demonstrating both the versatility and sensitivity of the technique.

### 3.2.4 Aberration correction

Advances in hardware design have led to significant increases in spatial resolution in the electron microscope; however, none have been as impactful as the aberration corrector. Early on, spatial resolution in the electron microscope was improved by
increasing the accelerating voltage (over 1 MeV in some cases), resulting in a smaller wavelength and better overall spatial resolution. This approach, however, was mainly used for special applications as it was expensive, cumbersome, and typically caused significant specimen damage. Instead, imperfections in the microscope optics called aberrations have been corrected by adding additional advanced lens systems.

Aberration correctors currently exist for two different aberrations: spherical and chromatic. Spherical aberrations naturally arise from imperfections in rotationally symmetric lenses, resulting in a spread of focal lengths for electrons as a function of radial distance from the optic axis of the lens. The effect of spherical aberrations can be minimized through careful lens design and smaller apertures, effectively limiting the angular range of electrons through the lens, as higher angle electrons will be focused more strongly by a lens than lower angle electrons. Chromatic aberrations, on the other hand, arise from variation in the inherent energy spread of the electron source, resulting in a spread of focal lengths for electrons of different energies focused by the same part of the lens.

For Schottky field emission guns, as were used in this work, the energy spread of the source is on the order of approximately 1 eV. This spread is objectively small when compared to the accelerating voltage of 300 kV used in this work; however, the spread contributes more strongly with decreasing accelerating voltage, as shown in Equation 3.2, which describes the relationship between minimum STEM probe diameter, $d_{0\ \text{chrom}}$, and energy spread, $\delta E/E_0$:

$$d_{0\ \text{chrom}} = \frac{1}{2} \left( \lambda C C \frac{\delta E}{E_0} \right)^{1/2},$$  \hspace{1cm} (3.2)
where \( \lambda \) is the electron wavelength, and \( C_C \) is the chromatic aberration coefficient. Chromatic aberration correctors have only been fitted to a small number of electron microscopes, but have been proven very useful in atomic resolution imaging of beam-sensitive materials with accelerative voltages as low as 20 kV. \([20]\)

Spherical aberration correction has been applied to both the image- and probe-forming systems in electron microscopes for improved spatial resolution in TEM and STEM, respectively, as well as jointly in some microscopes. While aberration correctors significantly increase the cost of the microscope, they improve spatial resolution to the sub-Ångstrom level, with ultimate TEM and STEM resolutions currently at 43 and 40.5 pm, respectively. \([21, 22]\)

Aberrations in the microscope can be represented mathematically in the form shown below in Equation 3.3. Generally, aberrations in the electron microscope, \( \chi \), vary with many parameters, including real space location (\( r, \phi \) in polar coordinates), reciprocal space vector (magnitude \( q \)), convergence semi-angle (\( \alpha \)), and electron wavelength (\( \lambda \)). \([16, 17, 23]\)

\[
\chi(r, \phi, q, \alpha, \lambda) = \sum_{C} \frac{1}{m+1} C^m,na_{m+1} r^u (\lambda q)^{m+1} \cos(n\alpha), \tag{3.3}
\]

where \( C^m,na_{m,na} \) is a given aberration coefficient, and a second, mutually orthogonal contribution can be formed by swapping the superscript \( a \) for \( b \) and changing \( \cos_1 \) to \( \sin_1 \), or the subscript \( a \) for \( b \) and changing \( \cos_2 \) to \( \sin_2 \). While Equation 3.3 is quite complex, it can be simplified by only considering rotationally invariant aberrations, yielding the more manageable form in Equation 3.4:

\[
\chi(q, \lambda) = \frac{1}{2} \Delta f(\lambda q)^2 + \frac{1}{4} C_s(\lambda q)^4 + \frac{1}{6} C_5(\lambda q)^6, \tag{3.4}
\]
where $\Delta f$ is defocus, $C_s$ is the 3rd order spherical aberration coefficient, and $C_5$ is the 5th order coefficient. The simplified form will be considered in the rest of the work presented here, and is especially important in Chapter 4 when discussing image simulation.

Most spherical aberration correctors on the market currently correct out to the 3rd order; however, 5th order aberration correctors are being commercialized and will likely be pervasive in the near future.

### 3.3 Spectroscopy

Imaging in the electron microscope can give powerful insight into materials’ structures, from atomic-scale ordering and displacements to defect complexes like antiphase domains and dislocations. In most cases, this level of characterization is significantly elevated with complementary chemical and compositional information. Two techniques stand out in TEM/STEM for their broad application at any length scale: electron energy-loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDX).

#### 3.3.1 Electron energy-loss spectroscopy

EELS can be performed in both the TEM and the STEM, most commonly with the addition of a post-specimen spectrometer that disperses and/or filters the transmitted electron beam as a function of energy. As the electron beam (either plane wave or convergent probe) transmits through a specimen, there is a probability that a fast electron in the beam will interact with the specimen in either an elastic or inelastic manner. The former includes electrons that lose no (or a negligible amount of) energy...
and generally refers to diffracted electrons. The latter, however, refers to a wide range of interactions in which the fast electron loses a measurable amount of energy. One such interaction was discussed in Section 3.2.3 with high-angle thermal diffuse scattering and Z-contrast imaging in STEM. Electrons, however, may be inelastically scattered through a range of different energy-losses and scattering angles depending on the type of scattering event. When collected by a spectrometer and dispersed, an EEL spectrum or image is formed. A comprehensive review of the physics, hardware, and techniques involved in EELS can be found in [24].

3.3.1.1 Plasmons, core excitations, ELNES

There are a number of different inelastic scattering events that may occur as a fast electron passes through the specimen; however, for thin specimens used in the TEM/STEM (typically less than 50 nm) the electron has the highest probability of passing through the specimen without losing a measurable amount of energy. These electrons, when put on an EEL spectrometer would have the same energy distribution with which they left the source, which in Schottky FEGs tends to be on the order of the primary energy $E_0$ with a FWHM of 1 eV, as mentioned in Section 3.2.4. The convention in EELS is to label this distribution the zero loss peak (ZLP), where the maximum of the peak is set to 0 eV on the spectrum, the full width at half maximum (FWHM) is considered the experimental energy resolution, and further energy-losses are labeled as positive energies, as seen in Figure 3.7.

When the fast electron interacts with the specimen, it can ionize an atom by exciting single inner- or outer-shell electrons, or by exciting many valence electrons.
Figure 3.7: Representative experimental EEL spectrum across a wide range of energy-losses. At E=0 is the zero loss peak (ZLP) with a FWHM of 0.3 eV, while at low energy-losses, the plasmon peak can be seen. At higher energy-losses, core-shell ionizations can be seen for N, Ti, O, Mn, and Ni, labeled with their respective ionized shells. The background in the core-loss region is denoted by the dashed line, with the background subtracted spectrum shown as a solid black line. Note the core-loss region has been significantly amplified with respect to the low-loss for clarity.
The latter is called a plasmon and is a collective oscillation of valence electrons forming a wave with energy \( E_p = \hbar \omega_p \), where \( \hbar \) is the reduced Planck’s constant and \( \omega_p \) is the plasmon frequency (in rad/s) and depends on the density of valence electrons. Plasmons can form in the bulk or at surfaces in thin specimens and can be used to probe optical properties in the microscope, including the specimen dielectric function, at high spatial resolution. While optical properties are not the focus of the research presented here, the low energy range of plasmon excitations (5-30 eV) make them an important consideration in EELS of specimens close to or greater than the mean free path length of the electron. With thicker specimens, the probability of a fast electron undergoing plural scattering increases, potentially showing features at energy-losses that correspond to the sum of the inelastic events, convoluting the spectrum. The effective mean free path, \( \lambda \), of a known material can be estimated using parameterizations reviewed in [24], as well as the program IMFP from the same reference. Typical values of \( \lambda \) tend to be on the order of 50-150 nm, demonstrating the usefulness of very thin specimens in EELS analysis. By comparing the integrated signal in the ZLP \( (I_0) \) to the total signal in the spectrum \( (I_t) \), a relative thickness measurement can be taken using Equation 3.5.

\[
\frac{t}{\lambda} = \ln \frac{I_t}{I_0},
\]

where \( t \) is the specimen thickness. While this value is simply a relative measure of thickness, and thus less accurate in most cases than PACBED (Section 3.2.3.3), it offers a quick way to characterize the thickness of a region of interest, and therefore its suitability for analysis using EELS.
Single electron ionization events can give rise to rich information about the composition of the specimen, valence states, and bonding environments to name a few. The EELS presented in Chapter 6 focuses on inner-shell ionization (core-losses) and the fine structure associated with such losses. Core-lose EELS is typically performed at energy-losses of 100s to 1000s of eV depending on the atomic number and core shell of interest. For example, Ti shows very prominent energy-losses called “white lines” starting around 456 eV related to the excitation of $2p$ electrons into unoccupied $3d$ states, seen in Figure 3.7. Excitations in EELS predominantly follow the dipole selection rule, in which transitions with $\Delta l = \pm 1$ occur, where $\Delta l$ is the change in angular momentum quantum number between the initial and final states. For core-loss spectroscopy, the EEL can be related to the density of unoccupied states above the Fermi energy. A more detailed description of core-loss spectroscopy, the interpretation of results, and comparison with first principles calculations will be given in Chapter 6.

Spatially resolved EELS maps can be acquired in TEM or STEM, with some differences between the operational modes. In TEM, an image is formed with a plane wave by selecting electrons of a certain energy-loss window using an energy filter, called energy filtered TEM (EFTEM). Benefits of EFTEM include fast parallel acquisition and lower electron dose rates than the comparable STEM techniques; however, multiple images must be taken at different energy-loss ranges to record maps for different elements, resulting in higher overall electron dose. The EELS data collected in subsequent chapters were collected in STEM, where a diffraction pattern is formed with the transmitted beam passed into the entrance aperture of the EEL.
spectrometer. In STEM, EEL spectra can be collected at specific points, averaged over a given area, or collected as a function of probe position to form a spectrum image, sometimes referred to as a 3D data cube ($x$, $y$, and energy-loss axes).

3.3.1.2 Detection

Energy-loss spectra in STEM mode are collected on a post-specimen spectrometer that disperses the transmitted beam as a function of energy via a magnetic prism. Typically the prism deflects electrons through a large angle ($\geq 90^\circ$), where electrons that have lost energy are more strongly deflected than electrons that have not. The strength of the magnetic prism determines the dispersion in the EEL spectrum, which is the distance in energy-loss between adjacent energy channels in the spectrum. Depending on the application, energy dispersions from to 0.01 to 1 eV/channel can be used. Large dispersions (small eV/channel) result in EEL spectra covering a small range of energy-losses, giving a detailed view of the fine structure across those energy-losses. On the other hand, small dispersions give EEL spectra covering a large range of energy-losses, which can be useful for identifying the presence of a number of elements simultaneously, without any fine structure information. The total energy-loss range is dictated by the dispersion multiplied by the number of channels in the spectrometer (typically 1024 or 2048 channels), where the starting energy-loss is set by applying an offset voltage to the drift tube.

3.3.1.3 Energy and spatial resolutions

Spatial resolution in STEM-EELS is strongly dependent on probe size, as the signal does not delocalize much in specimens of appropriate thinness for EELS.
In probe aberration corrected STEM, this means that atomically resolved spectral images can be acquired; however, TDS can contribute to artifacts in the maps. [25, 26] In many cases, the energy resolution of EELS is of higher priority than the spatial resolution. Energy resolution is dependent on a variety of factors including the inherent energy spread of the electron source, the dispersion of EEL spectrometer, aberrations in the spectrometer, and more. The design of modern spectrometers reduces many aberrations and also allows for the correction of first- and second-order aberrations to improve energy resolution. Most importantly, the electron source can be monochromated to reduce the inherent energy spread of the beam. Whereas a Schottky FEG starts with approximately 1 eV of energy spread, average monochromators can reduce this to \( \leq 100 \text{ meV} \), while state-of-the-art monochromators can reduce energy spread to \(< 10 \text{ meV}\). [27] Reduced energy spread (improved energy resolution) not only improves the quality of fine structure in the EEL spectra, it also serves to improve spatial resolution at lower accelerating voltages where chromatic aberration plays a more significant role in limiting spatial resolution, as in Equation 3.2. Monochromation is achieved in much the same way as the dispersion of electrons in an EEL spectrometer. Below the electron source, a monochromator disperses electrons which have an initial energy spread. The beam is then passed through an energy-selecting slit and then refocused using the lenses in the illumination system. With higher monochromator dispersion comes better energy resolution, usually at the expense of probe current. Field emission guns, however, have substantially higher brightnesses than thermionic sources, which allows for highly
monochromatic, Ångstrom-sized probes with enough beam current to do analytical spectroscopy (such as EELS or EDX).

3.3.2 Energy dispersive X-ray spectroscopy

While the ionization events discussed in EELS, as discussed above, are primary processes, they may result in secondary processes which can also be useful in characterization. The most ubiquitous of which is called energy dispersive X-ray spectroscopy (EDX). EDX has been a staple characterization technique across almost all material systems, across many length scales, from millimeters in the SEM to the atomic scale in STEM. The fundamentals of EDX, including hardware design, quantification, and processing are thoroughly reviewed by Williams and Carter in [3].

3.3.2.1 Ionization

After a fast electron in the beam ionizes an atom in the specimen, the atom is left in an excited state, which must decay to a lower, more energetically favorable ground state. This decay involves an electron from an outer shell (and thus higher energy) releasing energy to fill the electron hole left by the ionization event. The amount of energy released is characteristic of the difference in energy between the two shells, and for inner shell ionization events the energy released is typically such that an X-ray is emitted. For outer shell ionization events, the energy release is much lower and may generate a photon in the visible spectrum or may be released in the form of a phonon, neither of which will be observed in EDX spectra. Because the energy of the X-rays are characteristic of the transition made, they can be detected and used to provide compositional information about the specimen.
3.3.2.2 Detection

There are two major types of X-ray detectors commonly used in the electron microscope: Si(Li) and silicon drift. The Si(Li) detector has been largely replaced by the silicon drift detector (SDD) in favor of their higher count rates and a wider collection efficiency range. In a Si(Li) detector, Si is doped with Li to compensate for its natural p-type behavior, which would have deleterious effects on the detector efficiency, making the Si intrinsic. When an X-ray strikes the detector, its energy is transferred to the Si(Li) generating electron-hole pairs within the detector which can directly be linked to the energy of the incoming X-ray. The electrons and holes are separated by a reverse bias through the thickness of the detector, which generates a current pulse that can be processed to form the EDX spectrum. Steps in the current pulse are correlated back to the energy of the original incoming X-ray that generated the electron-hole pairs, which can then be ascribed to a given ionization event.

SDDs work in much the same way as Si(Li) detectors; however, they are based on a different geometry design. Using concentric rings of p- and n-type Si on the back side of the detector, a radial reverse bias is generated that facilitates the flow of electrons generated by incoming X-rays towards the center of the detector where an integrated transistor is used to send the electrical signal to be processed, as shown in Figure 3.8. The EDX data discussed later was all collected via SDD.

One of the limiting factors of EDX spectroscopy is the ability to collect enough X-rays to generate statistically meaningful spectra. The most straightforward way to do this is to collect for longer periods of time; however, this poses problems for materials that are beam sensitive, as well as at high magnifications, where specimen
drift can negatively affect spatial resolution. Count rates can also be improved with larger area EDX detectors. The solid angle subtended by the detector can be effectively increased by moving the detector closer to the specimen; however, this may be limited by the design of the objective lens pole pieces, especially in spherical aberration corrected STEMs, where the pole piece gap tends to be very small. While X-rays are generated in all directions from the specimen, most systems have just one detector above the specimen. Significant improvements in count rates and collection efficiency can be gained by using multiple SDD detectors located around the specimen, as seen in the right hand side of Figure 3.8 with the Super-X detector geometry used in this work. [28, 29]
3.3.2.3 Energy and spatial resolutions

While the energy resolution of EELS can be as good as 10 meV with monochromation, EDX offers relatively poor energy resolution typically in the range of 130-150 eV due to electronic noise. This can make quantification difficult in some cases as multiple ionization peaks overlap in a given spectrum, especially at lower energies where there are usually a large number of peaks. Spatial resolution in STEM-EDX is for the most part probe-limited, allowing for compositional analysis at the atomic scale using spherical aberration corrected electron microscopy. With many systems now having sub-Ångstrom-sized probes and SDDs, compositional maps that appear to be atomically resolved have become fairly common in a number of materials systems; however, as will be discussed below, caution must be taken when quantifying EDX data, and especially when interpreting data taken at the atomic scale. Specifically, channeling can result in the electrons from the probe being scattered and then coupling to nearest- and next-nearest-neighbor columns, convoluting the compositional information for that given probe position. When present in an EDX spectrum image, this convolution can be computationally expensive to remove, as discussed below.

3.3.2.4 Quantification

In general, qualitative EDX has been so useful in materials characterization because it is easily collected across many length scales, with fairly robust analytical software for processing the data. When performed in a qualitative manor, EDX can readily show compositional gradients at interfaces and grain boundaries, highlight
precipitates, prove the presence of solutes, and much more. Quantitative EDX, however, takes a great deal more effort to properly process and understand, and requires careful characterization of experimental parameters.

The most common method for quantifying EDX data is called the Cliff-Lorimer method, whereby the ratio of X-ray intensities in an EDX spectrum are related to composition via a scalar pre-factor, often called the Cliff-Lorimer k-factor. [30] As seen in Equation 3.6, for a simple A-B binary system the ratio of the composition of each element ($C_A$ and $C_B$, respectively) is related to the ratio of their integrated X-ray intensities ($I_A$ and $I_B$, respectively) by an experimentally determined k-factor ($k_{AB}$).

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \quad (3.6)$$

For more compositionally complex materials, a system of equations can be set up in the format of Equation 3.6 to quantify the EDX spectrum. This process requires that the k-factor be experimentally determined using a specimen of known composition under the same experimental conditions, which can be difficult in many cases. Additionally, the interaction of the electron beam with the specimen (especially probe channeling) may have an effect on the probability of ionization, and thus the specimen orientation is also a critical experimental consideration in crystalline materials. When possible, EDX should be performed away from strong probe channeling conditions (i.e. low index crystallographic zones) to avoid irreproducible experimental conditions. When this is not possible, experimental k-factors should be determined for a given zone axis.
Figure 3.9: (left) EDX spectrum image of a $Y_3Fe_5O_{12}$ (YIG) powder particle used as a standard. (center) Net counts (red, green, blue lines) and relative thickness (open circles) as a function of distance as indicated by the yellow line in the spectrum image. k-factors are calculated as a function of relative thickness for use in quantifying EDX spectra from a YIG thin film (right) from [31]. Inset shows high resolution HAADF-STEM image of the YIG lattice (field of view is 2 nm).

One example of quantitative EDX using a standard is shown in Figure 3.9. On the left is an EDX spectrum image of a known standard of $Y_3Fe_5O_{12}$ (YIG) powder where the stoichiometry can be assumed to be perfect. The particle was oriented along the same crystallographic zone axis as the specimen of interest - a thin film grown on (111) $Gd_5Ga_5O_{12}$ (GGG). Using relative thickness information ($t/\lambda$) from EELS and the relative X-ray count ratios of Fe, Y, and O (center of Figure 3.9), k-factors were generated as a function of relative thickness for YIG under the given microscope conditions. EDX was collected from the thin film YIG under the same experimental conditions and quantified using the calculated k-factors.

With EDX taken under low channeling conditions, the Cliff-Lorimer method can be applied with relatively small error assuming a homogeneous standard of known
stoichiometry can be made. In the case of EDX taken under high probe channeling conditions, such as high spatial resolution EDX taken on a low-index crystallographic zone axis, results can only be fully quantified using rigorous simulations to deconvolve the effects of probe channeling and thermal diffuse scattering. In spite of the fact that channeling and TDS can contribute significantly to both EDX and EEL spectra when collected on a zone axis, [32] simulation of the electron-specimen interaction and ionization cross-sections, as well as subsequent inversion of the experimental data can retrieve the truly quantified spectra, though this is a non-trivial process both experimentally and computationally. [25, 26]

BIBLIOGRAPHY


CHAPTER 4
SIMULATION OF INELASTIC SCATTERING OF FAST ELECTRONS

As spatial resolution in the electron microscope has rapidly improved through better hardware design and aberration correctors, so too has our understanding of the physical phenomena that contribute to the many signals recorded in modern microscopes. The interactions between electrons traveling at relativistic speeds and condensed matter are certainly complex and require rigorous modeling to fully understand. Many imaging modes (especially HAADF-STEM) have been proclaimed to be easily understood to the point of triviality; however, emphasis has recently shifted towards coupling simulations with experimental imaging to confirm hypotheses, explain anomalous results, and/or fully quantify images and spectroscopic data. A number of books and articles have been written on the subject of simulating images and spectroscopy. [1–5]. A brief background and comparison between different methods, as well as more in-depth explanations where necessary will be presented below.

4.1 Background

Scattering theory has been applied to electron microscopy for many decades; though, it has never been more important than with atomically resolved imaging, where
even small instrumental artifacts can significantly hinder interpretation of results. There are two main methods for simulating the virtual microscope: Bloch wave and multislice. The former is well-suited for simulating images of perfectly crystalline specimens with small unit cells; however, computational times increase in an quadratic fashion ($\propto N^2$) with resolution, which makes it ill-suited for large simulations or aperiodic specimens. On the other hand, the multislice method approximates the 3D specimen as a series of 2D slices separated by vacuum, and typically makes use of fast Fourier transforms (FFTs), resulting in much slower growth of computational times ($\propto N \log_2 N$), making it much more convenient for simulation of large specimens, those with interfaces and defects, and/or amorphous specimens. For these reasons, Bloch wave simulations will not be addressed here; however, more information can be found in [6] and [7]. Many programs have been created to perform multislice simulations, arriving at essentially the same results with some major and some minor differences along the way depending on the intended use - usually calculation speed versus accuracy.

4.2 Multislice simulations

The first step in image simulation via any method is to generate a model of the structure of interest. This can be done using visualization software such as CrystalMaker or VESTA, [8, 9] first principles calculations, or simply by scripting (for crystalline or amorphous materials, interfaces, etc.). Specimens are generally made such that they closely resemble experimental specimens; however, image simulation allows for virtually unlimited flexibility in exploring unique specimen geometries.
Once a specimen has been generated, it is divided into a series of 2D slices normal to the direction of the electron probe. Depending on the geometry of the specimen and the number of slices chosen (typically limited by computational resources), this process can result in atomic translations along the beam path such that the atom sits in one of the 2D slices; however, the number and thickness of slices are usually chosen such that the spacing between slices is small, on the order of the interplanar spacing or a few Å.

The 2D slices, which at this point simply include information about the atomic species and their coordinates, are then used to make 2D projected potentials. Projected potentials are simply the atomic potential (including the positive point charge of the nucleus and shielding by negatively charged atomic electrons) integrated along the \( z \) direction. In most cases, electron scattering factors are converted from X-ray scattering factors, which are well parameterized. \[10\] This can be done via the Mott-Bette formula which also takes into account atomic number, the electron mass, and vacuum permittivity. \[6, 11–13\]

With calculated projected potentials, the wave function of the electron probe at a given plane \( z + \Delta z \) can be modeled as \( \psi(x, y, z + \Delta z) \), where the probe wave function has been modified by the projected potential in the previous plane, \( z \), through a convolution. \[1\] The multislice approach is made more efficient through the use of fast Fourier transformations (FFTs) in which the convolution becomes a simple multiplication in Fourier space, significantly reducing computational demands. The probe-potential convolution, often referred to as transmission, occurs at each slice position along with a step in which the wave function is allowed to propagate along
the $z$ direction a distance equal to the slice thickness, $\Delta z$. For crystalline materials oriented along a low index zone, slice thickness is usually intuitive (i.e. $\Delta z = a/2$ for face- or body-centered cubic materials oriented along the [001] direction, or $a/\sqrt{2}$ along the [110] direction). Potential slice thickness options are demonstrated in Figure 4.1 where three different projections of SrTiO$_3$ are shown ([001], [011], and [111]) with natural slice thicknesses indicated by the double headed arrows. Proper sampling of the structure is critical to avoid artifacts in the simulation, typically extraneous intensity in Fourier space (i.e. the diffraction pattern, $|\psi(k)|^2$). This can be challenging with amorphous materials, complex defect structures, or crystallographic directions that are not easily sliced normal to the beam direction. In such cases, a larger number of slices and/or non-uniformly thick slices can be used, though the amount of computational time and resources needed may limit the possible options. In most cases, projecting potentials at a frequency higher than the frequency of planes normal to the probe direction (i.e. more than twice along [001] in Figure 4.1) will result in nominally more accurate simulations at the expense of computational time, and thus it is not generally necessary.

In STEM, the image is formed by placing a detector in the diffraction plane and integrating the signal over a range of scattering angles (i.e., BF integrating from 0 mrad to some small angle, or ADF integrating over inner and outer collection angles, $\theta_i$ and $\theta_o$, respectively). In simulations, this is done by defining the detector integration range and applying a top-hat function to the diffraction pattern, allowing for unlimited virtual detector geometries to be explored in the same simulation without increasing computation time. Not only can this be used to compare
Figure 4.1: Three different crystallographic projections of SrTiO$_3$ showing natural choices of slice thickness, $\Delta z$, for each projection. *left to right*: [001], [011], and [111] views of SrTiO$_3$. Different values of $\Delta z$ can be chosen depending on computational resources, though under-sampling the number of projected potentials will likely cause artifacts in the simulated data.

with experimental data, which sometimes includes the use of multiple detectors simultaneously, it can also allow for better experimental setup with foresight towards which detector geometry best suits the problem.

There are two main ways in which scattering is mathematically modeled in simulation packages: semi-classically or quantum mechanically. An overview of both methods and the major differences between them, as well as a motivation for the latter is provided below; however, more in-depth mathematical formalisms can be found in [1, 14–16], as well as a comparison between the two in [17, 18]. While the fundamental difference between the two models lies in the way in which they treat thermal scattering, both reliably produce results that agree closely with experiment. The latter, however, will be shown to be beneficial in that it can separate the two
scattering phenomena (elastic and inelastic), providing far greater insight into electron scattering physics.

### 4.2.1 Semi-classical

Electron scattering in the electron microscope can be successfully simulated under certain conditions using a semi-classical approach called the frozen phonon model.\[15, 16, 19, 20\] The premise of the frozen phonon model is based on the idea that the interaction time of a fast electron with atoms in the specimen is much shorter than the vibrational time of the atom. Because of this, the simulation can be simplified by creating a number of projected potentials for each slice where the atoms are randomly displaced from their equilibrium lattice positions along vectors defined by their mean-squared displacements, \(<u^2>\), or the Debye-Waller temperature factor, which depends on \(<u^2>\), to represent phonons, as shown in Figure 4.2. In practice, this Einstein model of atomic oscillation is performed by using a random number generator with an isotropic Gaussian distribution, thus rendering the atomic displacements uncorrelated. While this might not be the most physically correct representation of phonons in crystalline materials, which are certainly directionally anisotropic, the resultant simulated images are in sufficient agreement with experiment when a large enough number of phonon displacements are used. One reason for this is due to the contribution of other instrument-related factors such as finite-source size, which is the size of the probe at the plane of the specimen as it is demagnified by the condenser system. In spherical aberration corrected STEM, the source is generally Gaussian in shape with a size on the order of 0.7 Å; whereas, atomic displacements are typically an
Figure 4.2: Projected potentials along the [001] direction of SrTiO$_3$ with slice thickness of $\Delta z = a/2 = 1.9525$ Å. (top) SrO layer with Sr at the top left corner, O at the center. (middle) TiO$_2$ layer with Ti at the center and O on the edge centers. (left to right) The effect of phonon displacements in the projected potentials with 0, 3, and 20 phonons. Potentials are sharp and localized without phonons, and become more diffuse with the addition of many phonons, as shown in the line trace across the middle of the TiO$_3$ layer. All intensities are arbitrary, but shown on the same intensity scale. Each projected potential is $a = 3.905$ Å wide.
order of magnitude lower in crystalline materials at room temperature. Additionally, the typical experimental dwell time of the probe in STEM at any given position is typically on the order of $\mu$s. This means that while any single electron in the probe only sees a “snapshot” of the specimen mid-vibration, there will usually be a large number of electrons contributing to the image at a given probe position (pixel).

In the frozen phonon model, electrons in the probe are convolved with a phonon-modified projected potentials many times and summed incoherently via a Monte Carlo integration. In this way, each electron only interacts with one single frozen phonon lattice in some vibrational configuration; however, quantum mechanically, the electron should be aware of all possible vibrational configurations. This motivates the approach discussed below in Section 4.2.2. Interestingly, though, the frozen phonon model replicates the effect of thermal diffuse scattering in the diffraction plane under most conditions, again assuming a sufficiently large number of phonon configurations are simulated. In a simple example, if a crystalline structure is left undistorted by phonons (i.e. $T = 0K$), the atomic positions would all be exactly their symmetry defined lattice positions, and the TEM diffraction pattern would only have intensity at exactly the Bragg diffraction angles. With the addition of atomic displacements in the frozen phonon model, the symmetry of the specimen is broken locally as atoms shift off of their equilibrium lattice sites, which allows for diffuse background between Bragg peaks. This process, however, is not physically representative of the actual inelastic scattering events taking place in the specimen because it implies that TDS results from elastic interactions with a distorted lattice and cannot occur at absolute zero temperature. In actuality,
regardless of temperature, inelastic scattering events can occur as a fast electron transmits through a thin specimen, namely the excitation of phonons through an energy and/or momentum transfer from the fast electron to the specimen.

### 4.2.2 Quantum mechanical

The shortcomings of the physical framework of a semi-classical approach such as the frozen phonon model have been overcome via the implementation of a quantum mechanical approach called the quantum excitation of phonons model (QEP). \[14\]

As mentioned above, the two approaches arrive at the same mathematical result for a single scattering case, in spite of the fact that they are based on fundamentally different physics. The QEP model proposed by Forbes et al. also makes use of the same process for atomic displacements; however, the quantum mechanical nature of the simulation accounts for energy losses, especially through phonon excitation (on the order of meV). While the QEP model yields results that are functionally the same as those calculated using a semi-classical approach, the inclusion of inelastic transitions is more physically correct and enables separate tracking of elastic and inelastic scattering events, as shown in Figure 4.3, where a TEM diffraction pattern of SrTiO$_3$ is shown next to its inelastic and elastic components. In STEM, these two different channels can also be tracked as a function of probe position in the $xy$-plane and depth, $z$. The ability to track such scattering provides significant insight into electron-solid scattering and helps to explain contrast in experimental images, which will be put to use and explained in greater detail in Chapter 7.
CHAPTER 4  SECTION 4.2

Figure 4.3: *(left)* Simulated TEM diffraction pattern, $|\psi(k)|^2$, for a 200 Å-thick SrTiO$_3$ specimen oriented along [001], with its *(middle)* inelastic and *(right)* elastic components. Bragg peaks can be seen in the elastic channel, while Kikuchi lines and thermal diffuse scattering can be seen in the inelastic channel. All three images are shown on the same $\ln |\psi(k)|^2$ scale to enhance contrast.

4.2.3 Practical considerations

*Structural modeling*

Image simulation has become an integral part of advanced characterization using electron microscopy. Great care must be taken to ensure that the simulated result is not subject to significant errors or artifacts. The most critical of these considerations will be discussed here; however, different systems and types of simulations may come with additional challenges.

As mentioned above, the first step of any simulation is to form a model of the specimen of interest. For crystalline materials, this tends to be a trivial process given any background in crystallography. For a perfect crystalline material like SrTiO$_3$, most simulations (image, diffraction, ionization) will be performed along a low index crystallographic zone axis like those shown in Figure 4.1. Additionally, in most
experimental imaging the specimen is typically assumed to be flat with entrance and exit surfaces normal to the direction of the electron beam. In this case, a unit cell must be projected along the direction of interest in such a way that the new unit cell has orthogonal sides (i.e. $\alpha = \beta = \gamma = 90^\circ$) and one of the sides is normal to the chosen direction. As an example, the matrix transformations for SrTiO$_3$ from its cubic form (*space group: Pm\overline{3}m*) to both the [110] and [111] projections are included in Equations 4.1 and 4.2, respectively. The new unit cell projections are also displayed in Figure 4.4 along their respective directions. For reference, the new projections in Figure 4.4 can be compared to those in Figure 4.1 to confirm that while the unit cell definition changes, the crystal remains unchanged, as it should.

\[
\begin{bmatrix}
x \\
y \\
z
\end{bmatrix}
\begin{bmatrix}
1 & 1 & 0 \\
0 & 0 & 1 \\
1 & 1 & 0
\end{bmatrix}
= 
\begin{bmatrix}
x' \\
y' \\
z'
\end{bmatrix}
\] (4.1)

\[
\begin{bmatrix}
x \\
y \\
z
\end{bmatrix}
\begin{bmatrix}
1 & 0 & 1 \\
1 & 2 & 1 \\
1 & 1 & 1
\end{bmatrix}
= 
\begin{bmatrix}
x' \\
y' \\
z'
\end{bmatrix}
\] (4.2)

With lower symmetry space groups and/or higher index viewing directions, the unit cell transformations can become much more complex, in which case it can be more straightforward to manually select the volume of interest. In either case, a volume with periodic boundary conditions must be chosen to avoid edge effects. Additionally, shared atoms on unit cell faces, edges, and corners should only be included once based on the symmetry of the position (i.e. only one Sr atom should be included on a corner site of SrTiO$_3$). In the simulation, the unit cell provided will typically be repeated in the $x$ and $y$ directions to avoid artificial beam interactions (discussed later), and in the $z$ direction to the desired specimen thickness.
Figure 4.4: Possible unit cells of SrTiO$_3$ including the (left) reference cubic primitive cell, (middle) tetragonal unit cell projected onto the (110) plane using Equation 4.1, and (right) orthorhombic unit cell projected onto the (111) plane using Equation 4.2. The bottom row shows each of the unit cells slightly rotated off of its axis for perspective.
With extended structures (amorphous materials, dislocation structures, interfaces, disordered materials, etc.), a unit cell may not exist, and instead a supercell that is not repeated may be necessary. From a research point of view, these tend to be the more interesting materials to study as they are more realistic than perfect crystals; however, they are also more challenging. For example, to study a 200 Å thick specimen of pure Al would require just two projected potentials that are then repeated approximately 50 times in the \( z \) direction; whereas, a disordered Al alloy of the same thickness would require projected potentials for each plane along the entire thickness (\( \sim 100 \) planes), which is considerably more computationally intensive. Computational resources and experimental conditions should always be considered, but with access to supercomputer facilities and/or modern graphics processing units (GPUs), computational restrictions are quickly fading.

As a final note, with structures that do not or cannot reasonably have periodic boundaries, the model can be padded with vacuum in the \( xy \)-plane to minimize edge effects, though this will typically only work for image not diffraction simulations as it artificially adds periodicity to the structure when repeated.

**Projected potentials and slicing**

As was discussed earlier in this chapter, the projected potentials and slice thickness, \( \Delta z \), are critical to the accuracy of the simulation. Slice thickness was already addressed; however, it is important to note that under certain imaging conditions some liberty can be taken with slice thickness when balancing computational resources. For example, [110]-oriented SrTiO\(_3\) in Figure 4.4 has a density of 4 distinct planes, where half of them exclusively contain O atoms. A
HAADF-STEM image simulation of that structure should be sliced at $\Delta z = 1.381$, but would see very little difference if sliced at half the frequency ($\Delta z' = 2\Delta z$). Effectively what this does is shift the 2 O atoms toward the SrTiO plane. In that example, no atoms were shifted in such a way that they overlapped in the projected potential and it was only lighter atoms that do not heavily influence contrast in the given imaging mode. This is certainly not always the case and should be avoided, especially if multiple atoms are involved that are strong contributors to the contrast mode. Additionally, as was already noted, slicing in any way that does not follow the natural symmetry of the specimen along the beam direction will likely lead to incorrect contrast in the diffraction plane, especially at higher scattering angles.

The atomic potential is a very sharp function, which requires high pixel densities in the projected potentials. Additionally, when using the QEP model the unit cell must be tiled in the $x$ and $y$ directions a number of times to ensure that the probe wave function does not extend beyond the boundary of the simulation, as that will cause it to re-enter the simulation at the opposite edge since periodic boundary conditions are used. This effect, usually called “wrap around,” can lead to significant edge effects and incorrect intensities in the simulation. A tiling that results in a supercell with side lengths of approximately 30 Å will fully contain an Ångstrom-sized probe used in most modern STEM simulations. [21] Tiling need not be the same in the $x$ and $y$ directions and in many simulations should not be. For specimens that are not square in the $xy$-plane, tiling should be chosen to yield a supercell that is square (or close to it), as will be made more obvious below.
Because FFTs are used in most multislice calculations, the number of pixels in
the projected potentials are usually chosen to be square and powers of small prime
numbers, usually 2, for the highest efficiency of the FFT routines. The number of
pixels and the unit cell tiling together determine the resolution of the simulation (even
before experimental microscope parameters are considered). A real space resolution
can easily be calculated by dividing the number of pixels by the length of the supercell
in the x and y directions, as shown in Equation 4.3.

\[ R_x = \frac{\#\text{pixels}_x}{n_{\text{tile}_x} \|[a00]\|}, \quad R_y = \frac{\#\text{pixels}_y}{n_{\text{tile}_y} \|[00]\|} \]  (4.3)

Where \(\|[a00]\|\) and \(\|[00]\|\) are the magnitudes of the unit cell vectors in the x and
y directions, respectively. Resolution is determined in reciprocal space by Fourier
transforming the real space potential, as shown in Figure 4.5. The reciprocal space
potentials are bandwidth limited by inscribing the largest possible circle into the
potential (whether or not the potential is square) and applying a top-hat function
that removes any frequencies beyond the radius of the circle, \(k_{\text{max}}\), which has units of
Å\(^{-1}\) or mrad. This ensures that the scattering in the simulation is equally represented
in all directions.

To make sure that the simulation includes all of the relevant scattering events, the
value of \(k_{\text{max}}\) should be checked with respect to the mode of interest. For example,
HAADF-STEM imaging should use a value of \(k_{\text{max}}\) that is either greater than the
outer collection angle of the ADF detector, \(\theta_o\), or a large portion thereof. The value of
\(k_{\text{max}}\) is usually increased by putting more pixels into the projected potential; though,
this will strongly influence the calculation time (i.e. going from 512x512 pixels to
Figure 4.5: Schematic representation of the effect of bandwidth limiting on projected potentials, especially non-square ones. The real space potential (left) with coordinates in the $xy$-plane is Fourier transformed ($\mathcal{F}$) to get the reciprocal space representation of the potential with coordinates in $k$ space (middle). Because the spatial frequencies in $k$ space are radial, the reciprocal space potential is bandwidth limited by the largest inscribed circle (right), giving a maximum scattering magnitude of $\|k_{\text{max}}\|$ in all scattering directions.

1024x1024 pixels is 4 times more pixels). Finally, calculation speed is generally fastest when there is an integer number of pixels in the unit cell. For example, SrTiO$_3$ can be simulated with a 1024x1024 pixel projected potential and a tiling of 8x8, giving a value of $k_{\text{max}} = 211.9$ mrad at 300keV. Both inelastic and elastic current at scattering angles greater than 200 mrad are typically many orders of magnitude less than even 100 mrad, making this a valid $k_{\text{max}}$ for most systems; however, this should be tested for convergence on a case-by-case basis by increasing the value of $k_{\text{max}}$. Likewise, smaller values may be acceptable depending on the type of simulation.

**Microscope parameters**

Finally, it is important to make sure that experimental conditions are well characterized before running a simulation. The number of experimental parameters
can be quite large depending on the experiment, the goal of the simulation, and/or the specimen. Generally, the most important values to characterize experimentally are specimen thickness and microscope aberrations (see Chapter 3). One of the major benefits, however, of simulations is that many different parameters can be explored far more easily than in an actual experiment, which can either be used to guide future experiments or to precisely characterize the original experimental conditions by comparing simulated and experimental data. When using simulations to guide experimental design, it is critical that details of the microscope be known, such as accelerating voltage, aperture sizes, aberrations (usually to the 3\textsuperscript{rd} order, but sometimes out to the 5\textsuperscript{th}), camera lengths, and detector geometries.

BIBLIOGRAPHY


CHAPTER 5

EPITAXIAL GROWTH OF IRIDATE PYROCHLORE Nd₂Ir₂O₇ FILMS

This chapter is presented in the form of a peer-reviewed journal article titled “Epitaxial growth of iridate pyrochlore Nd₂Ir₂O₇ films,” published 29 February 2016 in *Scientific Reports* 6, 22282. The co-authors include James Gallagher¹, Bryan Esser¹, Ryan Morrow, Sarah Dunsiger, Robert Williams, Patrick Woodward, David McComb, and Fengyuan Yang. The supplementary information is included in Appendix A.

5.1 Abstract

Epitaxial films of the pyrochlore Nd₂Ir₂O₇ have been grown on (111)-oriented yttria-stabilized zirconia (YSZ) substrates by off-axis sputtering followed by post-growth annealing. X-ray diffraction (XRD) results demonstrate phase-pure epitaxial growth of the pyrochlore films on YSZ. Scanning transmission electron microscopy (STEM) investigation of an Nd₂Ir₂O₇ film with a short post-annealing provides insight into the mechanism for crystallization of Nd₂Ir₂O₇ during the post-annealing process. STEM images reveal clear pyrochlore ordering of Nd and Ir in the films. The epitaxial relationship between the YSZ and Nd₂Ir₂O₇ is observed

¹These authors contributed equally to this work
clearly while some interfacial regions show a thin region with polycrystalline Ir nanocrystals.

5.2 Introduction

The 5d transition metal oxides have attracted much attention due to their strong spin-orbit coupling (SOC), which scales with $Z^4$, where $Z$ is the atomic number. Given such strong SOC, exotic phases of matter are predicted to occur, including the topological insulator, Weyl semimetal, and chiral spin liquid. [1–4] Such materials have potential applications in quantum computing and spintronics. [5] The family of pyrochlore iridate compounds ($A_2\text{Ir}_2\text{O}_7$) are proving to be a promising arena within which to investigate these interesting phases. In some cases, the materials are geometrically frustrated, as the magnetic species occupy a network of corner sharing tetrahedra. The spin liquid phase has been observed in Pr$_2$Ir$_2$O$_7$ down to 0.3 K, [6] and there is evidence for the Weyl semimetal phase in Rh-doped Nd$_2$Ir$_2$O$_7$ [7] and Eu$_2$Ir$_2$O$_7$. [8] Theoretical studies have shown that the predicted topological insulator and Weyl semimetal phases can be induced by an all-in all-out spin structure of the rare earth (RE) pyrochlore iridates. [9, 10] In addition, there has been experimental observation of metal-to-insulator transitions in some RE pyrochlore iridates ($A = \text{Y}, \text{Nd}, \text{Sm}, \text{or Eu}$) at the same temperature as the magnetic ordering temperature. [9, 11–13]

Theoretical studies of the pyrochlore iridate thin films predict that the topological insulator and Weyl semimetal phases can be induced in the pyrochlores from epitaxial strain and finite size effects [9, 14] providing motivation to synthesize pyrochlore thin
films. Previous research reports the synthesis of Bi$_2$Ir$_2$O$_7$ [15] and Eu$_2$Ir$_2$O$_7$ [16] thin films by pulsed laser deposition. In this paper, we report the synthesis of Nd$_2$Ir$_2$O$_7$ using off-axis magnetron sputtering with ex situ post-annealing.

5.3 Synthesis

5.3.1 Sputter Target Synthesis

Nd$_2$O$_3$ and IrO$_2$ powders were thoroughly mixed then ground for at least 2 hours in stoichiometric ratios with an excess of 5 mol% IrO$_2$. The samples were pressed into a pellet, and placed in an alumina tube, which was sealed in an evacuated silica tube to prevent the iridium from volatilizing as the IrO$_3$ phase [17] during heating before forming the ternary pyrochlore Nd$_2$Ir$_2$O$_7$ phase. This would cause the powder to be neodymium rich and lead to the formation of Nd$_3$IrO$_7$ or Nd$_6$Ir$_2$O$_{13}$ impurity phases (depending on the oxygen level). [18, 19] After sealing in a silica tube, samples were heated for 160 hours at a temperature T = 950 °C with a ramping rate of 1 °C/min. Afterwards, the samples were taken out of the silica tubes and heated at T = 1125 °C in pure O$_2$ at atmospheric pressure in a tube furnace for several days to volatilize the excess iridium away, leaving stoichiometric pyrochlore powders with a lattice constant of 10.373 Å (see [APPENDIX] information for further analysis of the powder).

5.3.2 Thin Film Synthesis

The Nd$_2$Ir$_2$O$_7$ powder was pressed into a 2-inch sputtering target and used for ultra-high vacuum, off-axis magnetron sputtering. Nd$_2$Ir$_2$O$_7$ films were deposited on (111)-oriented 8 mol% yttria-stabilized zirconia (YSZ) substrates in 12.5 mTorr of Ar + 1% O$_2$ atmosphere at room temperature. DC sputtering with a constant current
of 60 mA was used, resulting in a deposition rate of 2 nm/minute. After the sputter deposition, the films were crystallized by annealing in atmospheric pressure N$_2$/O$_2$ mixture with oxygen partial pressures ranging from 30 mbar to 200 bar at 750 °C for times ranging from 5 min to 50 hr with ramping rates of 0.5-1 °C/min above 500 °C. Results showed that changing the oxygen partial pressure does not have an obvious effect on the crystal quality; however, annealing at higher temperatures (≥ 775 °C) results in the formation of the possible Nd$_3$IrO$_7$ or Nd$_6$Ir$_2$O$_{13}$ impurity phases. A summary of the effect of annealing under different conditions is shown in Table 5.1. Each film was analyzed with a Bruker D8 Discover triple-axis X-ray diffractometer. Figure 5.1(a) shows the synchrotron XRD scan of the Nd$_2$Ir$_2$O$_7$ powder converted to the Cu K$_{\alpha 1}$ wavelength for comparison with Figure 5.1(b,c) showing the 2θ-ω XRD scans of a Nd$_2$Ir$_2$O$_7$ film, which only exhibit the (111)-series of the pyrochlore peaks, indicating a phase-pure, (111)-oriented pyrochlore film on YSZ. The out-of-plane lattice constant was calculated to be 10.387 Å for the Nd$_2$Ir$_2$O$_7$ film, which is close to the bulk value of 10.373 Å obtained from the synchrotron XRD data. The inset to Figure 5.1(c) shows a rocking curve of the Nd$_2$Ir$_2$O$_7$ (222) peak which reveals a narrow peak with a full-width-at-half-maximum of 0.006° and a broad baseline possibly caused by inhomogeneity in the Nd$_2$Ir$_2$O$_7$ film.

5.4 Microscopy Analysis and Discussion

In order to study the early stages of the growth mechanism of Nd$_2$Ir$_2$O$_7$, an 800 nm Nd$_2$Ir$_2$O$_7$ film was deposited, followed by a 5-minute post-growth annealing at 750 °C (with the same ramp rate specified above). High-angle annular dark
### O₂ partial pressure effect (12 hour anneal at T=750 °C)

<table>
<thead>
<tr>
<th>O₂ pressure</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03 bar to 200 bar O₂</td>
<td>Pure phase epitaxial pyrochlore Nd₂Ir₂O₇ films</td>
</tr>
<tr>
<td>No O₂ (Pure N₂ or vacuum)</td>
<td>No Nd₂Ir₂O₇ phase detected</td>
</tr>
</tbody>
</table>

### Temperature effects (12 hour anneal at 1 bar of pure O₂)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>T ≥ 775 °C</td>
<td>Epitaxial Nd₂Ir₂O₇ forms, but with an impurity phase at 2θ ≈ 29° in XRD (possibly Nd₃IrO₇ or Nd₆Ir₂O₁₃)</td>
</tr>
<tr>
<td>T = 750 °C</td>
<td>Pure phase epitaxial pyrochlore Nd₂Ir₂O₇ films</td>
</tr>
<tr>
<td>T = 700 °C</td>
<td>Pure phase epitaxial pyrochlore Nd₂Ir₂O₇ films, though intensities of the pyrochlore XRD peaks are weaker and can be enhanced by further heating at 750 °C</td>
</tr>
</tbody>
</table>

### Annealing Time Effects (750 °C in air)

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 minutes</td>
<td>Nucleation of epitaxial Nd₂Ir₂O₇ crystallites of ~100 nm observed at YSZ interface [see Figure 5.2(a)].</td>
</tr>
<tr>
<td>≥ 6 hours</td>
<td>Nd₂Ir₂O₇ films are fully crystalized</td>
</tr>
</tbody>
</table>

**Table 5.1:** Summary of results of annealing amorphous Nd₂Ir₂O₇ films.
field scanning transmission electron microscopy (HAADF-STEM) of the pyrochlore film was performed using an FEI probe-corrected Titan$^3$ 80-300 S/TEM at 300 kV with a detector collection range of 55-375 mrad. Figure 5.2(a) shows a low magnification HAADF-STEM image of a cross-section of the annealed film. The film was predominantly amorphous with crystallites nucleated at the YSZ interface. Close examination reveals {111} and {001} faceted crystallites [Figure 5.2(b)] surrounded by regions exhibiting dark contrast [Figure 5.2(c)] in the HAADF image.

To fully understand the nature of the faceted crystals and Nd$_2$Ir$_2$O$_7$/YSZ interface, elemental analysis was performed by energy-dispersive X-ray (EDX) spectroscopy using the FEI Super-X quad-silicon drift detector system. An EDX profile across the crystalline/amorphous Nd$_2$Ir$_2$O$_7$ interface [Figure 5.2(d)] was quantified using experimental Cliff-Lorimer k-factors obtained from the Nd$_2$Ir$_2$O$_7$ crystal assuming perfect 2:2:7 stoichiometry. This demonstrates that the as-deposited (amorphous) material was stoichiometric, which implies that the nanocrystals formed during the post-anneal. Note that spectra were collected at specimen orientations far from major crystallographic zone axes to minimize probe-channeling effects that could differ significantly between the amorphous and crystalline materials.

Films that had been post-annealed for significantly longer times (approximately 12 hours) were observed to be completely crystalline. Higher magnification HAADF-STEM images of the Nd$_2$Ir$_2$O$_7$/YSZ interface in these films [Figure 5.3(a)] reveals an epitaxial relationship: $<111>_{\text{Nd}_2\text{Ir}_2\text{O}_7} \parallel <111>_{\text{YSZ}}$ and $<110>_{\text{Nd}_2\text{Ir}_2\text{O}_7} \parallel <110>_{\text{YSZ}}$. In HAADF-STEM or “Z-contrast” imaging, the intensity of an atomic column is approximately proportional to $Z^{1.8}$. As shown in Figure 5.3(b,c), this
Figure 5.1: (a) $\theta/2\theta$ XRD scan of Nd$_2$Ir$_2$O$_7$ powders (taken at Argonne National Lab Advanced Photon Source using an X-ray wavelength of 0.413191 Å), which was converted to the Cu K$_{\alpha1}$ wavelength of 1.5405 Å for comparison. (b) $2\theta$-ω XRD scan of a 200-nm thick Nd$_2$Ir$_2$O$_7$ film grown on YSZ (111). The sample was post-growth annealed at 750 °C in pure O$_2$ at atmospheric pressure with a ramp rate of 0.5 °C/min. (c) High resolution XRD scan of the same film around the YSZ (111) and Nd$_2$Ir$_2$O$_7$ (222) peaks. The inset is the rocking curve of the Nd$_2$Ir$_2$O$_7$ (222) peak, which consists of a narrow peak with full-width-at-half-maximum of 0.006° and a broad baseline.
contrast in the images of the Nd$_2$Ir$_2$O$_7$ film is characteristic of a high degree of pyrochlore ordering. The most intense atomic columns contain only Ir atoms ($Z = 77$), while the least intense contain only Nd ($Z = 60$), and the columns of intermediate contrast are alternating Nd and Ir atoms with 1:1 ratio.

In some regions of the Nd$_2$Ir$_2$O$_7$/YSZ interface, a thin “cloudy” layer was observed in the HAADF-STEM images, as shown in Figure 5.4(a). This observation might be mis-interpreted as an amorphous layer at the interface between the YSZ and the Nd$_2$Ir$_2$O$_7$, but this would be inconsistent with the epitaxial relationship described above. In order to demonstrate that this epitaxial relationship remains despite the presence of the “cloudy” layer, the image in Figure 5.4(a) was Fourier filtered to enhance the contrast from the crystalline materials. In the Fourier filtered image, the epitaxial relationship is clear [Figure 5.4(b)], although the filtering process does reduce the $Z$-contrast and introduces mathematical artifacts around the edges of the image. HAADF-STEM images acquired from thinner TEM foils, Figure 5.5(a), revealed nanocrystals, approximately 1-2 nm in diameter in the interfacial region. The nanocrystals exhibit a cubic crystal structure, with spatial frequencies in the fast Fourier Transform (FFT) that match the lattice parameter of metallic Ir [Figure 5.5(b)] and are distinctly different from those of the Nd$_2$Ir$_2$O$_7$ film [Figure 5.5(c)]. When the dark contrast observed at the triple junction of the YSZ substrate, amorphous Nd$_2$Ir$_2$O$_7$ and crystalline faceted Nd$_2$Ir$_2$O$_7$ noted in Figure 5.2(b), is examined at higher magnification [Figure 5.5(d)], it is observed that the Ir nanoparticles are also present [Figure 5.5(e)]. The accumulation of Ir nanocrystals, specifically at the triple junction, can help explain the appearance
Figure 5.2: (a) STEM image of a Nd$_2$Ir$_2$O$_7$ film with 5 minute post-growth annealing reveals several Nd$_2$Ir$_2$O$_7$ crystallites nucleated at the YSZ interface. (b) STEM image of the left-most crystallite in (a) with facets along the \{111\} and \{001\} planes. (c) High magnification STEM image near the top of the crystallite in (b). The decrease in volume from the crystallization causes void regions to appear around the crystallite. (d) EDX spectra across the amorphous to crystalline transition region with the crystalline region on the right. There is no detected difference in stoichiometry between the regions.
Figure 5.3: (a) STEM image of a Nd$_2$Ir$_2$O$_7$ film grown on YSZ (111) looking down the $<$110$>$ axis. The Nd$_2$Ir$_2$O$_7$ film is ordered in pyrochlore structure and has an epitaxial relationship with the YSZ substrate. (b) High resolution STEM image of the Nd$_2$Ir$_2$O$_7$ film away from the interface shows the pyrochlore ordering of the Nd and Ir sublattices as schematically shown in (c).

- Ir ($Z = 77$)
- Nd ($Z = 60$)
- Alternating Ir/Nd
of Ir metal in some regions of the interface but not others due to projection considerations in STEM imaging. It is reasonable to believe that the dark triple junction seen in Figure 5.5(d) completely surrounds the base of the crystalline Nd$_2$Ir$_2$O$_7$ island [Figure 5.6(a)]. Consequently, some areas of the TEM specimen near the interface may include partially the dark disordered region and partially crystalline Nd$_2$Ir$_2$O$_7$ along the electron beam path, resulting in a “cloudy” interface, as shown in Figure 5.6(a-c).

It is clear that the nucleation and growth of crystalline Nd$_2$Ir$_2$O$_7$ films is influenced by multiple factors. During the annealing process, it is common in some systems for
Figure 5.5: (a) High magnification STEM image of nanoparticles at the Nd$_2$Ir$_2$O$_7$/YSZ interface. (b) FFT of the nanoparticle indicated by red arrow in (a) clearly indicates a cubic structure, with spatial frequencies matching the lattice parameter of metallic Ir, which is distinct from (c) the FFT of the pyrochlore Nd$_2$Ir$_2$O$_7$. (d) HAADF-STEM image of the bottom-left corner of the island marked by the green box in Figure 5.2(b), (e) A saturated image of (d) shows metallic Ir nanoparticles filling the void space at the island growth front. Scale bars on all images are 5 nm.
nucleation sites to form at all edges of the film and not exclusively at the interface, resulting in the formation of a polycrystalline thin film, such as the case for YSZ grown on sapphire. [20] In other systems, nucleation sites at the interface grow epitaxially accompanied by the formation of a random polycrystalline film far from the interface, such as the case for YBa$_2$Cu$_3$O$_7$ films grown on SrTiO$_3$ with \textit{ex situ} annealing. [21] YSZ is well lattice matched to Nd$_2$Ir$_2$O$_7$ and its cubic fluorite structure is a variant of the pyrochlore structure favoring the formation of nucleation sites exclusively at the interface with an epitaxial orientation. This potentially enables the entire film to be epitaxial as the nucleation sites grow by consuming the surrounding materials until the film is fully crystallized and the epitaxial orientation is well preserved.

The curved surfaces that are apparent at the triple junctions [Figure 5.2(b) and Figure 5.5(e)] are consistent with wetting phenomena suggesting liquid- or glassy-like behavior at the amorphous-crystalline interface at elevated temperatures. This is worth considering further as the nominal annealing temperature is well below the melting temperature of Nd$_2$Ir$_2$O$_7$. We note that the crystallization of the pyrochlore phase is an exothermic reaction with an enthalpy of formation of 88.7 kJ/mol. [19] According to the Neumann-Kopp rule [22] the heat capacity of Nd$_2$Ir$_2$O$_7$ is

$$C_p(Nd_2Ir_2O_7) = 2C_p(IrO_2) + C_p(Nd_2O_3)$$

Previous research [23] has determined the heat capacity of IrO$_2$ to be

$$C_p(J k^{-1} mol^{-1}) = 87.6 + 6.20 \times 10^{-3}T - 7.80 \times 10^5T^{-2} - 433T^{-1/2},$$

and Nd$_2$O$_3$ has been determined [24] to be

$$C_p(J k^{-1} mol^{-1}) = 117 + 28.1 \times 10^{-3}T - 1.26 \times 10^6T^{-2}.$$
Eqs. (5.1-5.3) predict that the energy released from the crystallization could raise the temperature in the vicinity of the interface from 750 °C to about 1030 °C. This is above the decomposition temperature of IrO$_2$ of 1020 °C, [19] thus causing the formation of metallic Ir nanoparticles near the crystalline/amorphous interface. The high oxygen ion conductivity of YSZ, which peaks at 8 mol% Y$_2$O$_3$, [25] may enhance the formation of Ir nanoparticles by creating an oxygen deficient interfacial layer. It may be possible to prevent such an interfacial layer by using a buffer material to block the oxygen flow to the substrate. In addition, it may be possible to prevent IrO$_2$ decomposition by annealing at lower temperatures; however, crystallizing Nd$_2$Ir$_2$O$_7$ at temperatures below 750 °C is challenging.

5.5 Conclusions

In summary, Nd$_2$Ir$_2$O$_7$ powders were synthesized in an evacuated silica tube and their structural properties were analyzed using laboratory as well as synchrotron X-ray diffraction. We report growth of Nd$_2$Ir$_2$O$_7$ epitaxial films using off-axis magnetron sputtering followed by post-annealing. XRD results demonstrate phase-pure epitaxial films grown on YSZ (111). HAADF-STEM images reveal clear pyrochlore ordering. Additionally, Nd$_2$Ir$_2$O$_7$ grows by the formation of epitaxial nucleation sites exclusively at the YSZ interface that slowly absorb the surrounding amorphous material forming a (111)-oriented crystalline film.

5.6 Acknowledgments

Funding for this research was provided by the Center for Emergent Materials at the Ohio State University, an NSF MRSEC (Award Number DMR-1420451). Use of the
Figure 5.6: (a) Schematic of the crystallite shown in Figure 5.2(b) assuming the crystallite forms facets primarily along \{111\} and \{001\} planes. Features at the Nd$_2$Ir$_2$O$_7$/YSZ/amorphous triple junction represent Ir nanocrystals. (b) Schematic of the sample after being sliced into a <110> TEM foil with Ir nanocrystals visible only at the edges. (c) STEM image of crystallite with a schematic of the pyrochlore structure overlaid on the crystallite and the miller indices of the facets labeled. This confirms the crystal facets primarily on \{111\} planes, but also on \{001\} planes.
Advanced Photon Source at Argonne National Laboratory was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. Thin film X-ray diffraction measurements were provided through The Ohio State University’s NanoSystems Laboratory. BDE would like to acknowledge Lee Casalena for his help in constructing Figure 5.6.

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CHAPTER 6

ELECTRON ENERGY-LOSS SPECTROSCOPY OF OSMATE DOUBLE PEROVSKITES

The variety of signals available in the electron microscope, as well as the high spatial resolution makes it possible to correlate magnetic, electronic, and mechanical properties across a variety of length scales. As discussed in Chapter 5, atomic resolution imaging and compositional mapping using EDX can elucidate many of the nano- and atomic-scale phenomena that affect material performance. In this chapter, electron energy-loss spectroscopy (EELS) is employed to study the electronic structure of Os-based double perovskites. First principles calculations are used to help interpret fine structure in the spectroscopic data. Ultimately, the ability to study electronic structure with an Ångstrom-sized probe could be a very powerful way to understand the effect of interfaces and other defects on electronic and magnetic properties that is simply not possible with other techniques.

6.1 Background

Perovskites have been widely studied and used in applications from spintronic devices to photovoltaic cells and lasers. The family of materials demonstrates a broad range of physical properties including piezoelectricity, superconductivity, all types of
magnetism, ion conductivity, and much more. [1–3] These interesting properties are derived from the underlying crystallographic structure. The prototypical perovskite, $ABX_3$, is cubic with cations ($A, B$) at the corners and body center and anions ($X$) at the edge centers octahedrally coordinating the corner atom. Typically, $A$-site atoms are alkaline or rare-earth elements, with transition metal $B$-site atoms. $X$ is most often oxygen. (There are plenty of examples where $X$ is not oxygen, but this work is focused on oxides perovskites.)

The properties of perovskites can be heavily influenced through chemical pressure by swapping out cations for ones of a different size or valence or doping. [4] These changes can affect the crystal structure by introducing distortions or necessitating vacancies to maintain charge balance. The extent to which different elements can be stably interchanged within the ideal perovskite structure is dictated by the Goldschmidt criterion (Equation 6.1) that is used as a tolerance factor based on the ionic radii of the three elements ($r_A, r_B,$ and $r_O$): [5]

$$ t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}} \quad (6.1) $$

SrTiO$_3$ has a tolerance factor very close to unity, which represents the ideal perovskite structure. Compounds with tolerance factors greater than 1 will form a hexagonal variant of the perovskite structure where the $BO_6$ octahedra shift from corner to face sharing. A tolerance factor of less than approximately 0.9 will lead to the formation of an orthorhombic variant, with much smaller tolerance factors unable to form a perovskite structure. As the tolerance factor deviates from unity, the $BO_6$ octahedra tilt to accommodate the imperfect packing, which breaks the cubic symmetry and
Figure 6.1: Structural model of (left) $ABO_3$ and (right) $A_2BB'O_6$, where the $B$ and $B'$ cations order in a rock-salt structure on the $B$-site sublattice.

can significantly alter the electronic and magnetic properties of the system. [6] This effect can be leveraged by strategically engineering the composition of a material to tune functional properties. By expanding from a simple $ABO_3$ perovskite to one with two different transition metal cations on the $B$-site ($B$ and $B'$), the ability to tune such properties is greatly expanded.

In the presence of two transition metal cations on the $B$-site, the system may find it more energetically favorable to allow the $B$ and $B'$ atoms to randomly disperse on the $B$-site sublattice as an alloy, or they may order to form a double perovskite of the form $A_2BB'O_6$. In such a double perovskite, the $B$ and $B'$ atoms order in a rock-salt pattern on the $B$-site sublattice, as seen in Figure 6.1.
Table 6.1: Crystallographic information for the Os-based double perovskites studied.

<table>
<thead>
<tr>
<th>Material</th>
<th>Space Group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_2$CrOsO$_6$</td>
<td>$P2_1/n$</td>
<td>5.3826</td>
<td>5.5076</td>
<td>7.6971</td>
<td>90.0016°</td>
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<tr>
<td>Ca$_2$FeOsO$_6$</td>
<td>$P2_1/n$</td>
<td>5.4001</td>
<td>5.5467</td>
<td>7.7359</td>
<td>90.0052°</td>
</tr>
<tr>
<td>Ca$_2$CoOsO$_6$</td>
<td>$P2_1/n$</td>
<td>5.4051</td>
<td>5.6279</td>
<td>7.7908</td>
<td>90.0229°</td>
</tr>
<tr>
<td>Sr$_2$CrOsO$_6$</td>
<td>$I4/m$</td>
<td>5.5650</td>
<td>–</td>
<td>7.8758</td>
<td>–</td>
</tr>
<tr>
<td>Sr$_2$FeOsO$_6$</td>
<td>$I4/m$</td>
<td>5.5862</td>
<td>–</td>
<td>7.9458</td>
<td>–</td>
</tr>
<tr>
<td>Sr$_2$CoOsO$_6$</td>
<td>$I4/m$</td>
<td>5.6686</td>
<td>–</td>
<td>8.257</td>
<td>–</td>
</tr>
</tbody>
</table>

The materials studied in this work were a family of double perovskites where $A = (\text{Ca},\text{Sr}), B = (\text{Cr},\text{Fe},\text{Co})$, and $B' = \text{Os}$. The space group information and lattice parameters for all six compounds in Table 6.1 were calculated from first principles using the Vienna ab initio Simulation Package (VASP). [7, 8] It can immediately be seen that just from changing the $A$-site cation from Ca to Sr the space group changes from $P2_1/n$ to $I4/m$. More subtle changes can also be noted from the lattice parameters for a given cation (say Sr), the $a$ and $c$ lattice parameters increase with the atomic number from Cr to Fe to Co.

As the $BO_6$ and $B'O_6$ octahedra rotate to accommodate the different cation sizes, they do so in different ways, hence the difference in space groups between the Sr- and Ca-bearing compounds. There exists a notation for such octahedral tilts called Glazer notation [9] whereby the degree and phase of the tilt is listed in a concise manner for each of the three axes ($x$, $y$, and $z$). Using Glazer notation, the letters a,
CHAPTER 6  
SECTION 6.1

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Glazer Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fm3m</td>
<td>a^0a^0a^0</td>
</tr>
<tr>
<td>I4/m</td>
<td>a^0a^0c^-</td>
</tr>
<tr>
<td>R3</td>
<td>a^-a^-a^-</td>
</tr>
<tr>
<td>I2/m</td>
<td>a^0b^-b^-</td>
</tr>
<tr>
<td>P2_1/n</td>
<td>a^-a^-b^+</td>
</tr>
</tbody>
</table>

Table 6.2: Glazer notation for common $A_2BB'O_6$ double perovskites. [10]

b, and c are used to denote the degree of tilting, where tilts denoted by the same letter have tilts of the same magnitude (not to be confused with the crystallographic lattice parameters of the same symbols). To specify whether octahedra in successive planes rotate in- or out-of-phase, the superscripts $^+$ and $^-$ are used, respectively, or the superscript $^0$ if no rotations happen along the given axis. The Ca-bearing compounds take a Glazer notation of $a^-a^-b^+$ meaning that the rotations along the $x$ and $y$ axes have the same magnitude and rotate out-of-phase along their respective axes, while they rotate in-phase along the $z$ axis with a different magnitude. The Sr-bearing compounds have a Glazer notation of $a^0a^0c^-$, meaning that the octahedra only rotate along the $z$ axis in an out-of-phase manner. This is all shown in Figure 6.2 where an example from both systems is shown from both the [010] and [001] directions. The 5 most common double perovskite space groups can be categorized via Glazer notation as described in Table 6.2.
Figure 6.2: Example of the different Glazer notations for the Ca- and Sr-bearing double perovskites. The rotations are emphasized with arrows while the Glazer term is highlighted.
When a metal cation is octahedrally coordinated by anions as the $B$ and $B'$ atoms are in perovskites and double perovskites, the $d$ orbitals lose their degeneracy due to the fact that certain orbitals point towards the negatively charged $O^{2-}$ anions, while others point between them. For this reason, the $d_{xy}$, $d_{xz}$, and $d_{yz}$, orbitals move to a lower energy degenerate state, while the $d_{x^2-y^2}$ and $d_{z^2}$ move to a higher energy degenerate state, where the energy between the two states is called the octahedral crystal field splitting energy, $\Delta_{oct}$. The three lower energy orbitals are called $t_{2g}$ orbitals, while the two higher energy orbitals are referred to as $e_g$ orbitals.

From a functional perspective, such rotations are exciting because they give rise to rich physics that will most certainly affect the electronic and magnetic properties of the material. While techniques such as X-ray diffraction and PACBED are capable
of detecting octahedral rotations on large and local length scales, respectively, they
do not provide any information about the consequences of such rotations on the
electronic structure. To do just that, core-loss EELS was performed at the oxygen $K$
edge, which is sensitive to changes in the orbital overlap between the $B$ or $B'$ cation
and the oxygen anion, specifically the $O\,p$ and metal $d$ orbitals.

6.2 Experimental Work

As described in Section 3.3.1, core-loss EELS directly probes the site and symmetry
projected density of unoccupied states as the fast electron excites core electrons
from the specimen into different unoccupied states pursuant to the dipole selection
rule. Using an image aberration corrected FEI Titan$^3$ G2 60-300 S/TEM with
the gun monochromator excited such that a nominal energy resolution of $\leq0.2$ eV
FWHM, dual EEL spectra were collected including the ZLP region and the O $K$
edge from powders of each of the six compounds listed in Table 6.1. The low-loss
region was collected to ensure that the effects of plural scattering could be removed
using the Fourier Ratio method, [11] which allows spectra from different specimens
to be compared without thickness effects. Experimentally, the low- and core-loss
spectra are not collected simultaneously, but rather sequentially in rapid succession
by collecting the first spectrum (usually the core-loss) and then changing the energy
offset voltage on the spectrometer to collect the second spectrum (low-loss, in this
case).

The core-loss spectra for the six compounds are shown in Figure 6.4 after removing
plural scattering and ensuring that all of the spectra are aligned in energy using the
ZLP. Vertical lines at the peak position of the first three peaks guide the eye. (Note: in the spectra for the Cr-bearing specimens, the Cr $L_{2,3}$ white lines are visible at 575 eV energy loss.) First, it can be seen that there is a shift in the energy of the 3rd peak for both of the Co-bearing specimens. There are also prominent changes in the peak-to-valley ratios, most notably the valley just after the first peak at 535 eV energy loss. The valley is very well-defined for the Co-bearing specimens indicating a very small number of available transitions to unoccupied states at that energy (approximately 2.8 eV above the edge onset). As the $d$ electron count decreases to Fe and then Cr, the valley becomes far less pronounced, indicating an increase in unoccupied states at that energy in those specimens, most likely attributable to the electron configuration and structural distortions, as listed in Table 6.3. Finally there are a number of differences at higher energy losses away from the $K$ edge onset. These qualitative assessments of the core-loss data, while interesting, do not necessarily give much insight into the changes in electronic structure. For that, we must make comparisons with first principles calculations of the density of unoccupied states.

6.3 Comparison with First Principles Calculations

As mentioned earlier in the chapter, first principles calculations were performed in VASP. [7, 8] The unit cell was first relaxed to find the most energetically favorable lattice parameters (listed in Table 6.1), and then the spin polarized density of states were calculated. By taking into account spin polarization ($spin = \pm \frac{1}{2}$), a far more
Figure 6.4: Core-loss EEL spectra of the O K edge for the six osmate double perovskites listed in Table 6.1 after removing plural scattering and alignment.
realistic representation of the density of states is calculated, with the added benefit that it also gives greater insight into the fine structure of the EELS data.

The spin polarized density of states for Ca$_2$CrOsO$_6$, Ca$_2$FeOsO$_6$, Ca$_2$CoOsO$_6$, and Sr$_2$CrOsO$_6$, are shown in Figure 6.5. The O $p$ states in Figure 6.5 (thick red line) give insight into the experimental EEL spectra, which were taken at the O $K$ edge because this involves excitation of O 1$s$ electrons into $p$-like states ($\Delta l = +1$). From the calculated density of states, specifically the unoccupied density of states (above the Fermi energy), the cation states that most strongly overlap with the O $p$ states at a given energy can be attributed to that portion of the experimental EEL signal. For example, in the Ca$_2$FeOsO$_6$ density of states, the first large number of O states above the Fermi energy is in the spin up portion between approximately 0.4 and 1 eV. Over the same energy window, there is a very large number of Os $t_{2g}$ states (blue dotted line), and they closely trend with the O $p$ states. Similarly, there are Fe $t_{2g}$ and $e_g$ states that trend with the O $p$ states over the next 2 eV. When comparing this to the experimental data, the first major peak in the EELS (532-535 eV) can then

<table>
<thead>
<tr>
<th>Material</th>
<th>$B$-site</th>
<th>Os</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>valence</td>
<td>configuration</td>
</tr>
<tr>
<td>$A_2$CrOsO$_6$</td>
<td>3+</td>
<td>$3d^3$</td>
</tr>
<tr>
<td>$A_2$FeOsO$_6$</td>
<td>3+</td>
<td>$3d^5$</td>
</tr>
<tr>
<td>$A_2$CoOsO$_6$</td>
<td>2+</td>
<td>$3d^7$</td>
</tr>
</tbody>
</table>

Table 6.3: Electronic configuration for the osmates based on the $B$-site cation.
be attributed to mixing of the wave functions between these unoccupied states and those of O.

The site-specific, spin polarized density of states provides a vast amount of information about the electronic structure of the specimen with far greater energy resolution than is experimentally possible (or physically possible at these energy losses, for that matter). It is, however, useful to sum the calculated density of unoccupied O $p$ states and convolve it with the ZLP to account for experimental energy resolution. Assuming the transition matrix element is slowly varying with energy and excluding lifetime broadening, the density of unoccupied O $p$ states is a close approximation of the EEL spectrum for the oxygen K edge. [11] This is shown in Figure 6.6 for the same data presented in Figure 6.5.

It should be noted that density functional theory (which was employed here) is not the most physically representative model to use for trying to understand EELS data. This is because by definition calculated density functionals do not allow for the direct representation of the excitation of a single core shell electron to an unoccupied state, which would then have an effect on the electronic screening of the core hole. This type of calculation can be performed; however, it is far more computationally expensive to calculate such a many-body problem than it is to calculate a density functional. In spite of this, the number of peaks in the calculated unoccupied densities of states and their relative intensities still provide a better understanding of the electronic structure of the material, and thus the fine structure in the experimental EELS. As additional support, for the Ca$_2$CoOsO$_6$ specimen, X-ray absorption near edge structure (XANES) data (shown in green, Figure 6.6) is in very good agreement
Figure 6.5: Spin polarized density of states for some of the compounds investigated with EELS. The Fermi energy is set to 0 eV, which corresponds to the O K edge onset of 532 eV energy loss.
Figure 6.6: Summed density of unoccupied O p states from Figure 6.5 after convolution with the energy resolution of the experiment overlaid with the experimental EELS.

with EELS data for the same compound. As XANES and EELS are complementary techniques, the agreement between the two is a good confirmation of the quality of the data, both experimental and calculated.

6.4 Future work and conclusions

It proved more challenging for the first principles calculation to get sensible results for Sr$_2$FeOsO$_6$ and Sr$_2$CoOsO$_6$, which is why those data are not shown here. As future
work, understanding why those materials gave issues would be a good first step. The most important way in which this type of work can be applied in future projects is to collect similar data on known reference specimens (such as powder) and then use it to track changes in electronic structure in systems such as thin films, where interfaces, structural defects, grain boundaries, etc. can all significantly impact electronic and magnetic properties.

Monochromated dual EELS can be used probe densities of states to more fully understand electronic and magnetic properties in oxide materials when paired with first principles calculations. While this work was not done at high spatial resolution, the ultimate goal is to understand these phenomena in the bulk as was done here, and then to investigate defects and interfaces to probe such properties at the nano- or atomic-scale.

6.5 Acknowledgements

Thanks goes out to Dr. Molly Ball and Professor Wolfgang Windl for running the first principles calculations and insights into their interpretation. Additional thanks to Dr. Ryan Morrow and Professor Patrick Woodward for providing the materials and the XANES data.

BIBLIOGRAPHY


CHAPTER 7
QUANTITATIVE STEM IMAGING OF ORDER/DISORDER
PHENOMENA IN DOUBLE PEROVSKITE THIN FILMS

7.1 Introduction

This chapter is presented in the form of a peer-reviewed journal article titled “Quantitative STEM Imaging of Order/Disorder Phenomena in Double Perovskite Thin Films,” published 20 October 2016 in Physical Review Letters 117, 176101. The co-authors include Adam Hauser, Robert Williams, Les Allen, Patrick Woodward, Fengyuan Yang, and David McComb. Additional information about the simulations is presented in Appendix C.

7.2 Abstract

Using aberration corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), we investigate ordering phenomena in epitaxial thin films of the double perovskite Sr$_2$CrReO$_6$. Experimental and simulated imaging and diffraction are used to identify antiphase domains in the films. Image simulation provides insight into the effects of atomic-scale ordering along the beam direction on HAADF-STEM intensity. We show that probe channeling results in
±20% variation in intensity for a given composition, allowing 3D ordering information to be probed using quantitative STEM.

7.3 Background

Half-metallic double perovskites of the general formula $A_2BB'O_6$ are of great interest for their possible application in spintronic devices because they exhibit ferrimagnetism with high Curie temperatures ($T_C$) and a high degree of spin polarization. [1, 2] One current obstacle to their use is the ability to grow the materials in the form of high quality films with minimal antisite disorder. [3] Many factors can influence and modify the properties of double perovskites in thin film form, including lattice strain, [4] degree of chemical ordering, [5] the presence of defects, [6] etc. Further investigation into these phenomena is necessary to fully realize thin film double perovskites and the next generation of electronic devices.

The $B$ and $B'$ cations can be distributed in an ordered array or randomly on the B-site sub-lattice of the perovskite structure. The degree of $B/B'$ ordering is important due to the effect that it can have on the electronic and magnetic properties of double perovskites. [3, 7–13] In general, double perovskites must exhibit a high degree of $B/B'$ ordering in order to achieve their high $T_C$ and high spin polarization. [3] Thus, it is important to quantify the degree of $B/B'$ ordering in thin films at the atomic scale. This can be achieved through the use of quantitative aberration-corrected scanning transmission electron microscopy (STEM).

By carefully controlling experimental factors such as sample preparation and microscope conditions, quantitative comparisons have been made possible between
experiment and simulation. Quantitative STEM has been used to achieve atom counting in the beam direction, \[14\] location of individual dopant atoms in three-dimensions, \[15, 16\] and characterization of chemical ordering on the atomic scale. \[17–20\] All of these methods have relied on the intensity of atomic columns in high-angle annular dark field (HAADF) STEM images. In this letter, we will show that additional parameters, including specimen thickness and atomic-scale compositional analysis are necessary in combination with simulations to characterize atomic-scale ordering along the path of the electron beam.

### 7.4 Thin Film Sr\(_2\)CrReO\(_6\)

It was previously reported through Rietveld refinement of X-ray diffraction (XRD) data that thin films of the double perovskite Sr\(_2\)CrReO\(_6\) (SCRO) grown on (001)-oriented SrTiO\(_3\) (STO) with a 50 nm buffer layer of relaxed SrCr\(_{0.5}\)Nb\(_{0.5}\)O\(_3\) showed an exceptionally high ordering parameter \(\eta = 0.99 \pm 0.01\). \[21\] An ordering parameter this close to unity indicates that nearly all of the Cr and Re atoms are perfectly ordered on the \(B/B'\) sites - leading to a superlattice of (111) planes of \(B\) and \(B'\) ions that is equivalent to a rock-salt structure. At room temperature, the stable SCRO structure is tetragonal (I4/m, \(a = 5.569\ \text{Å}, c = 7.804\ \text{Å}\) \[4\] and has a well-defined orientation relation to the STO substrate, namely SCRO\(_{<100>}\) \parallel STO\(_{<\overline{110}>}\) and SCRO\(_{<001>}\) \parallel STO\(_{<001>}\). \[21\]

#### 7.4.1 Sample Preparation and Imaging

As reported in our previous studies, epitaxial SCRO(001) films were grown on STO(001) by ultrahigh vacuum off-axis sputtering. \[4, 21\] In the current study we
prepared cross-sectional TEM samples of the 190 nm thick SCRO film from Reference [21] using an FEI Helios NanoLab 600 DualBeam focused ion beam (FIB) with 30 kV then 5 kV Ga ions. Final cleaning passes were performed in a Fischione Nanomill with 900 V then 500 V Ar ions to remove any amorphous damage layers created in the FIB. The thickness of the specimen in the electron beam direction was measured to be approximately 8 nm by position averaged convergent beam electron diffraction. [22] Imaging was performed on an FEI Titan³ 80-300 probe corrected STEM at 300 kV. The use of a probe corrector limits the size of the electron probe to less than 100 pm, resulting in high-quality, high spatial resolution STEM images. When imaged in the HAADF-STEM condition with a collection range of approximately 55-375 mrad, the fully ordered double perovskite structure of SCRO should exhibit clear intensity variations when viewed along the [100] direction due to the individual columns of Cr, Sr/O, and Re. HAADF-STEM imaging provides Z-contrast, where Z is the atomic number, such that the Cr columns exhibit the lowest intensity while the Re columns show the highest. It was noteworthy that some regions in the SCRO films, mostly near the interface, exhibited contrast that did not appear to be well ordered in spite of the previously published XRD data of Hauser et al. which indicated that these same films were highly ordered over the entire sample. [21] Additionally, overall contrast was lower in these regions, as seen in the lower right hand portion of Figure 7.1(a). This STEM observation would suggest that there is a much lower degree of Cr/Re ordering within the films than previously reported, which would have significant (negative) implications for their properties.
After careful examination of many different regions within the SCRO thin films, it was concluded that the decrease in overall contrast within these seemingly disordered regions was unlikely to be a consequence of chemical disorder given the facetted/linear nature of the boundaries between what appeared to be ordered and disordered regions, as shown in Figure 7.1(a). The most likely reason for the observed structure was that the overall reduction in contrast was due to antiphase domains in the SCRO thin films, leading to a misregistry of the Cr and Re columns, as shown in Figure 7.2, leaving both Sr and O on equivalent sites. This misregistry is the proposed reason for the reduction in contrast in some regions of the thin films because it would result in columns of Sr/O and mixed Cr/Re. The average atomic weight of the mixed Cr/Re
columns would then be a weighted average based on the location of the antiphase boundary within the thickness of the TEM foil.

### 7.5 Image Simulation

In order to understand the observed contrast variation in both the ordered and antiphase domains, HAADF-STEM image simulations were performed using the quantum excitation of phonons model. [23, 24] A crystal model was prepared using a supercell of SCRO in which a $\frac{1}{2}[001]$ on (100) antiphase domain was created midway through the thickness normal to the viewing direction to simulate the lower contrast region, as shown in Figure 7.2(a). To match the observed experimental images there must also be a second antiphase boundary parallel to the viewing direction that forms a boundary between the high and low contrast regions, as seen in Figure 7.2(b). Thus, the supercell contained a region where clear $B/B'$ ordering led to distinct contrast variation, and a region where the intensity from the $B/B'$ columns due to antiphase domains was less distinct. Since the supercell was not periodic in nature, it was simulated with 5 Å of vacuum around it in the plane normal to the viewing direction. The supercell was made to be approximately 55 Å thick to simulate a thin STEM specimen and sliced such that each projected potential contained a single plane of atoms - approximately 1.4 Å in thickness. Imaging conditions similar to those used in the probe corrected Titan were used, specifically 300 kV accelerating voltage, a beam convergence semi-angle of 20 mrad, and aberration coefficients obtained from the microscope corrector software [$C_3$ and $C_5$ of 2 μm and 1 mm, respectively]. Further information about microscope details can be found in reference [25]. Finite source size
with a 0.8 Å full-width at half-maximum Gaussian, as well as detector shot noise of approximately 2% were incorporated in simulated image at zero defocus, [26] showing very good qualitative agreement with contrast observed in experimental images of the films, as seen in Figure 7.1(b).

To further confirm the hypothesis that the observed contrast is due to antiphase domains, not random $B/B'$ disorder, electron diffraction patterns were simulated using multislice simulations for the fully ordered SCRO structure and for a supercell containing an antiphase domain. The results showed that in perfectly ordered SCRO ($\eta = 1$), {101}-type superlattice reflections should be clearly visible in the diffraction
pattern. Conversely, in the supercell containing an antiphase domain, the intensity of the superlattice reflections is significantly reduced. For reference, the SCRO structure where Cr and Re are fully disordered (randomly distributed amongst the $B$ and $B'$ sites) results in a diffraction pattern with no $\{101\}$-type superlattice reflections due to structure factor considerations.

The simulation of diffraction patterns for SCRO with different ordering parameters illustrates that using experimental diffraction patterns it is possible to differentiate between low contrast regions in the HAADF-STEM image exhibiting high degrees of disorder and those that are a consequence of antiphase domains. Diffraction work was attempted on TEM samples prepared using a dual beam FIB; however, small variations in tilt across the sample due to the thin foil geometry and FIB process resulted in subtle changes in contrast in the diffracted beams, making any definitive analysis of the superlattice reflections very difficult. Instead, fast Fourier transformations (FFTs) of different regions within the HAADF images were taken (ordered, high contrast; “disordered”, low contrast). These yield similar results to diffraction patterns without the strong tilt dependence. In the FFTs, spatial frequencies consistent with $\{101\}$ superlattice reflections are visible in the high contrast ordered regions of the HAADF images, as expected, while weak reflections are visible in the low contrast regions, as seen in Figure 7.1(c) and 7.1(d), respectively. This indicates that the regions exhibiting low contrast in the HAADF images were not regions of highly disordered Cr and Re sites, but actually well ordered regions separated by an antiphase boundary. This is an important distinction because it helps to explain why the magnetic properties of the thin film SCRO were as notable
as they were, [21] in spite of seeing what appeared to be high degrees of $B/B'$ disorder in HAADF images like Figure 1(a). This shows that through direct interpretation of HAADF-STEM images of these films, information about the degree of $B/B'$ ordering can be deduced at the extremes of ordering: fully ordered, completely disordered, and fully ordered domains separated by one or more antiphase boundaries.

### 7.5.1 Probe Channeling

To show how channeling allows one to distinguish between structures with different ordering and demonstrate what is possible we have calculated the (integrated) HAADF signal on columns containing ten atoms in total (approximately 55 Å thick) for various compositions of Cr and Re atoms. Additionally, we have considered all the various possible orderings along the beam path, which is expected to further affect probe channeling. These results are shown in Figure 7.3.

There is a clear and unambiguous distinction between the case where there is only a single Re or Cr atom in the specimen. Also where that single atom is placed is in principle measurable, provided that an accurate measurement of image contrast can be made (i.e. the bit depth of the image). Contrast this with the case where there are five Re atoms and five Cr atoms in the column: now there are 252 possible permutations and, although there is still a one-to-one relationship between a given arrangement of atoms and the measured signal, considerably more accuracy would be required to distinguish between the different configurations. It is also evident that as, say, the composition of the column changes and the number of Cr atoms increase there are ambiguities between the case of one and two atoms (10 and 20 at% Cr,
respectively), but not between one and three atoms. Nevertheless, by measuring the thickness of the specimen via position averaged convergent beam electron diffraction [22] and the ratio of the two atomic species (using electron energy-loss spectroscopy and/or energy dispersive X-ray spectroscopy), [27] it is clear that, as we have done in this letter, useful information can be garnered by comparing theory and experiment. The key point to realize is that the differences in Figure 7.3 are due to differences in the channeling of the probe for different configurations and it is this fact that provides useful information about the structure, in particular between the different configurations for a given Cr to Re ratio. In a naïve model that ignores channeling Figure 7.3 would simply consist of a series of horizontal lines.

In Figure 7.4 the calculated probe channeling profiles from the entrance surface (top) to the exit surface (bottom) for three different columns with identical compositions - 50 Cr : 50 Re - are displayed to show how atomic-scale ordering along the path of the beam affects probe channeling within the specimen, and thus the observed HAADF-STEM intensities. Figure 7.4(a) shows that for a column with all Cr near the entrance and Re near the exit surface, there is enhanced probe channeling. Figure 7.4(b) and 7.4(c) show the channeling for a column with alternating Cr and Re atoms and for one with all Re near the entrance surface and Cr near the exit surface, respectively. The column in Figure 7.4(a) resulted in 15.9% and 21.7% higher HAADF intensity than that of Figure 7.4(b) and 7.4(c), respectively. This can be attributed to a “pre-focusing” effect that the lighter atoms near the entrance surface have on the probe. Due to this effect, the electron beam more strongly couples to the column, the second half of which has heavier Re atoms with larger scattering cross-sections,
Figure 7.3: Integrated HAADF intensity for different ratios (compositions) of Cr and Re atoms in a column of ten atoms taking into account the possible permutations of atoms in each case. Results have been ordered from the smallest to the largest cross section for each composition.
resulting in higher HAADF intensity on such columns. The results in Figure 7.4(a) and 7.4(c) are possible configurations that could be found in an antiphase domain such as that of Figure 7.1, further demonstrating that quantitative STEM imaging is able resolve the difference between the two scenarios specifically due to the differences in probe channeling.

In order to fully quantify the experimental data, potential sources of error must be taken into account. One of the largest sources of error can be signal coming from neighboring columns due to thermally scattered electrons. [28] Thermal diffuse scattering can result in off-column contributions of signal that can affect not only HAADF-STEM images, but also elemental maps. These effects can be accounted for by first quantifying experimental compositional maps in the manner of Chen et al. [27] together with simulations as described by Forbes et al. [28] The resultant compositional maps can then be used to simulate HAADF-STEM intensities using larger cells with nearest and even next-nearest neighboring columns to include the contribution of thermally scattered electrons. Additionally, specimen preparation-induced amorphization or oxidation layers can increase the mean error in quantification by a few percent depending on the composition and thickness of the layer. [29] These effects can be minimized by mechanical wedge polishing and/or low energy Ar ion milling to reduce/remove surface layers.

7.6 Conclusions

Fully quantitative HAADF-STEM imaging and spectroscopy has been demonstrated for sufficiently thin specimens, monoatomic systems, and highly ordered compounds.
Figure 7.4: Calculated scattering for a probe placed on three different 390 Å thick columns with identical compositions (Cr$_{0.5}$Re$_{0.5}$), where the top half of a) is Cr with the bottom half Re atoms; b) has Cr and Re atoms alternating; and the top half of c) is Re with the bottom half Cr atoms. Over-sized schematic structures are included in each panel to demonstrate the different types of ordering. Horizontal scale expanded 50x that of vertical scale for clarity. Color scale in % probe current.
In particular it has been successfully applied to locate impurity atoms in STO [15] for thin specimens of only a few layers thickness, yet is a challenging proposition for thicker samples (greater than a few nanometers), especially if the material does not exhibit well characterized ordering. Nevertheless, we have shown that using atomic resolution HAADF-STEM imaging, variations in column intensity can be used to distinguish the presence of random antisite disorder from that of antiphase boundaries in an otherwise highly ordered sample. Through the use of electron diffraction and image simulation, the low contrast regions in Sr$_2$CrReO$_6$ thin films can clearly be shown to be antiphase domain-like in nature. The identification of antiphase domains within double perovskite thin films is pivotal in explaining differences in electronic and magnetic properties from their bulk values through the disruption of periodic superexchange couplings necessary for ferrimagnetism.

7.7 Acknowledgments

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CHAPTER 7

SECTION 7.7

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The research contained in the previous chapters has thus far focused on characterizing thin films using high-spatial resolution electron microscopy and spectroscopy along with quantum mechanical simulations. The remainder of this document will focus on work that is ongoing related to in situ characterization of magnetic structures and ex situ structural characterization of the same at medium and high resolutions. The former is achieved using two imaging modes that are sensitive to in-plane magnetic induction in the specimen called Lorentz TEM and Lorentz differential phase contrast STEM (DPC-STEM). The latter chiefly employs HAADF-STEM and EDX. In this chapter, the experimental methods will be described in detail, while Chapter 9 will motivate the materials systems and physical phenomena, present current results, and lay out future work.

8.1 Background

Magnetic materials are ubiquitous in modern electronics and studying their behavior under a range of experimental conditions has enormous effect on our understanding of physical properties and their relation to crystallographic structure. There are myriad techniques for studying magnetic properties at various length scales, from
bulk property measurements like neutron scattering \cite{1} and the Hall effect, \cite{2} to
local microscopy methods like magnetic force microscopy, \cite{3} spin-polarized scanning
tunneling microscopy, \cite{4} and electron microscopy. \cite{5-8} The high spatial resolution of
electron microscopy has made magnetic imaging in the electron microscope a popular
technique for decades. While it is possible to image magnetic structures in the SEM, this chapter will focus on TEM- and STEM-based modes.

As described in Chapter 3, the electron microscope is capable of characterizing
materials across many length scales and versatile enough to study a diverse set of
physical properties. Over the last 6 decades, the most widely utilized imaging mode
for studying magnetic materials in the electron microscope has been Lorentz TEM.
Recently, a STEM-based technique called DPC-STEM has become more widespread
and has been shown to be complementary to Lorentz TEM, and in some cases even
more capable. The fundamentals behind both techniques, their applications, and
limits will be discussed below.

8.2 Lorentz TEM

In the TEM and STEM, the specimen typically sits in the middle of the objective lens
field (see Figure 3.2), which is the strongest lens of the microscope and is used to form
the image in conventional TEM. The challenge when studying magnetic specimens
is that the lens field is on the order of 2-3 T, which is high enough to saturate
most magnetic specimens, rendering magnetic studies impossible. Some microscopes,
however, are designed with a Lorentz TEM mode in which the objective lens field can
be reduced to zero (or near zero) field and changed \textit{in situ} to allow for very interesting
studies of magnetism on a local level, rather than averaged over entire areas as is the case with many other techniques.

The Lorentz TEM imaging mode is typically made possible by the addition of a secondary lens below the specimen called the Lorentz lens, which, in the case of image aberration corrected microscopes, is incorporated into the corrector. As a consequence of turning off the objective lens and using a Lorentz lens further from the specimen, spatial resolution suffers when compared to HR-TEM in the same instrument. For example, in the image aberration corrected FEI Titan³ G2 60-300 S/TEM used in this work, the spatial resolution decreases from 0.7 Å in HR-TEM to approximately 20 Å in Lorentz TEM. An additional limiting factor for the spatial resolution of this imaging mode is the contrast mechanism.

When a plane wave of electrons is focused on a magnetic specimen, no magnetic contrast is apparent in the image. As shown in Figure 8.1, in-plane magnetic contrast is only observed in Lorentz TEM when the image is defocused, resulting in regions in the image with electron deficiency or surplus, and thus dark or bright contrast, respectively. (Note: because the fast electrons travel normal to the plane of the specimen, Lorentz TEM is not sensitive to the out-of-plane component of magnetism within the specimen.) This is called Fresnel mode Lorentz TEM after the fringes of the same name that are produced as the incident and scattered electron waves interfere with one another. Especially in thin specimens where the magnitude of the Lorentz force felt by the fast electrons can be very small, it can be the case where very large defocus values must be used to see magnetic contrast. Defocus values of
10s to 100s of μm are not uncommon; however, defocus is a first order aberration so the larger the defocus value, the poorer the spatial resolution.

While it is sometimes sufficient just to image the in-plane component of the magnetic structure in the specimen, Lorentz TEM data can be quantified through a reconstruction using the transport of intensity equation (TIE), Equation 8.1. \[9\] TIE reconstruction makes use of a through-focal image series to approximate the derivative of intensity with respect to \( z \), \( \frac{\partial I(0)}{\partial z} \), on the right hand side of the equality in Equation 8.1. Experimentally, an in-focus image is taken along with two out-of-focus images taken at equal magnitude of defocus (\( \Delta f \)) over- and under-focus.

\[
\nabla \cdot (I(0) \nabla \phi) = -\frac{2\pi}{\lambda} \frac{\partial I(0)}{\partial z} \approx -\frac{2\pi}{\lambda} \frac{I(+\Delta f) - I(-\Delta f)}{2\Delta f} \tag{8.1}
\]

In Equation 8.1, \( \nabla \) operates in the plane of the specimen (normal to the path of the electron beam), \( I(0) \) is the in-focus image, \( \phi \) is the total phase shift, \( \lambda \) is the electron wavelength, and \( I(+\Delta f) \) and \( I(-\Delta f) \) represent the over- and under-focus images, respectively. The TIE reconstruction is relatively simple mathematically, and is made more robust with a larger number of images in the focal series to approximate \( \frac{\partial I(0)}{\partial z} \).

The most critical part of the reconstruction process lies in preprocessing the focal series to ensure perfect registration amongst the images. As noted in Figure 8.1, the relatively large defocus values used in Lorentz TEM compared to HR-TEM results in a change in magnification across the focal series, as well as an image rotation in most cases. If the image series is not well registered, reconstruction will not be possible or will provide errant results. For this reason, the smallest
Figure 8.1: Simplified schematic of the contrast mechanism in Lorentz TEM of a specimen with in-plane magnetism. The (a) in-focus condition provides no magnetic contrast as the rays are all focused equally to the image plane. When the image is over- or under-focused (b and c, respectively) the in-plane magnetism of the specimen results in dark and bright contrast, respectively, as the rays are no longer focused to the same place in the image plane. It can also be seen that defocus is accompanied by a change in magnification. [10]
defocus values that give contrast should be used to minimize these effects and reduce spatial-resolution-limiting aberrations.

8.3 Differential phase contrast STEM

While Lorentz TEM offers relatively high spatial resolution and is sensitive to many magnetic structures, its inability to straightforwardly image certain magnetic structures and the fact that TIE reconstructions must be done off-line, rather than live on the microscope, leaves room for improvement by complementary imaging techniques such as DPC-STEM. This mode is operated in essentially the same manner as any other STEM mode with the addition of a segmented detector in the diffraction plane. As the STEM probe rasters across a specimen, any in-plane magnetic (electric)
field will impart a Lorentz (Coulomb) force on the probe, resulting in a shift in the center of mass of the intensity within the transmitted beam. [7, 11–15] The use of a segmented detector over the standard bright field or ADF detector, both of which are radially symmetric, allows for detection of such minor shifts in the center-of-mass of the intensity within the transmitted beam that would otherwise not be detectable. This is shown in a highly schematic way in Figure 8.3 for both cases where the shift in the intensity of the transmitted beam is represented instead by a translation. Note the lack of objective lens in the left hand side of Figure 8.3 indicating zero magnetic field normal to the plane of the specimen; whereas, built-in electric fields can be imaged under normal imaging conditions (high magnetic field). [16] In DPC-STEM it is not necessary to defocus the probe or to take a series of images as it is in Lorentz TEM. This makes imaging more straightforward, and removes the need to register images because all of the data is collected simultaneously.

In most systems with a segmented detector, it is either a quadrant ADF or BF detector, or occasionally a round detector with 8 segments (quadrant ADF + quadrant BF, no annulus). The only limits on the number of segments in a detector are financial and practical, as DPC can be sensitive to shifts in the transmitted beam with as few as 2 segments. A quadrant detector is the practical geometry of choice because it easily facilitates the calculation of difference images by subtracting the signal from opposite segments of the detector. The difference images can than be used to estimate the shift in the transmitted beam at the detector plane, which is related to the in-plane component of the magnetic or electric field.
Difference images can be thought of as vector images with orthogonal deflection vectors. For instance, if the four quadrants of a detector are labeled A, B, C, and D, difference image $I_{A-C}$ can be assigned the crystallographic vector [100] and image $I_{B-D}$ can be assigned [010]. (Note: the assignment of deflection vectors should be done by correlating the specimen reference frame with the orientation of the detector quadrants.) The gradient of the in-plane field is then just the sum of the two vector images and can be used to map the phase and amplitude of the field, as seen at atomic resolution in Figure 8.4 with SrTiO$_3$. [18] The difference images in the left column were used to calculated the phase and amplitude information in middle column, as well as the charge density map in the lower right, which is just the divergence of
the electric field. The primary benefit of DPC-STEM is its ability to simultaneously acquire complementary signals, such as the ADF-STEM image in the upper right hand corner of Figure 8.4, which intuitively shows the atomic structure with Z-contrast. A secondary benefit is that the images in Figure 8.4 are all either acquired or calculated live on the microscope, requiring no post-processing as is necessary in Lorentz TEM.

8.3.1 Segmented detectors

There are currently also highly segmented STEM detectors that allow the user to simultaneously form images under a number of different conditions (i.e. BF, DPC, ADF, etc.) with atomic resolution. [17] In Figure 8.6, such a detector is shown with 16 segments that is called the segmented annular all field (SAAF) detector along with the atomic resolution image formed by signal on each segment for [001]-oriented SrTiO₃. It can be seen that the HAADF images formed by detectors 13–16 are self consistent and show Z-contrast, as would be expected. However, all of the bright field images (detectors 1–4) look different. This is because the low angle segments are sensitive to shifts in the center-of-mass of the transmitted beam even at the atomic level. As the STEM probe is rastered across the atomic columns it is affected by the atomic electric fields within the specimen, shown in Figure 8.5. Just before the probe reaches the atomic column it is attracted toward the column, pulling signal from the left quadrant of the detector to the right quadrant, with the reverse being true after scanning past the column. When the probe is directly on the atomic column, the signal is equal on both the right and left quadrants (assuming the specimen is non-polar). The ability to directly image the gradient of the atomic electrostatic
Figure 8.4: Atomic resolution DPC-STEM of [001]-oriented SrTiO$_3$. The left column shows the $x$- and $y$- components of the shift of the center of mass (COM) of the transmitted beam, which are then used to calculate the projected electric field vector map and corresponding amplitude (strength) shown in the middle column. The right column shows the simultaneously acquired ADF-STEM image (using a different detector) and calculated charge density map. In the ADF image, Sr columns are bright, Ti/O column less intense, pure O columns are not visible. [18]
potential demonstrates just how powerful DPC-STEM is as an imaging mode, and has also led to more complex mathematical formalisms for processing of the difference images, yielding modes that are capable of imaging both light and heavy atoms at the same time with linear contrast, which may be more useful in some materials systems than Z-contrast imaging. [14, 15] This is also clearly shown in the projected electric field and charge density maps of Figure 8.4, which show all three column types of SrTiO$_3$ (Sr, Ti/O, and O).

8.4 In situ capabilities

For most magnetic studies, it is very useful to have control over the applied magnetic field and temperature such that the phase space can be explored in more depth. The average temperature at the plane of the specimen in a TEM or STEM is relatively
Figure 8.6: (left) Diagram of the segmented annular all field detector and (right) images from each of the individual segments of [001]-oriented SrTiO$_3$. [17]
close to room temperature in the absence of any special hardware. There exist several different forms of in situ temperature control specimen holders, from heating holders capable of reaching temperatures in excess of 1500 K, to cryogenic holders capable of temperatures less than 100 K with liquid nitrogen and 6 K with liquid helium. From a materials characterization standpoint, this opens up the possibility of exploring a very broad range of material properties in situ with very high spatial resolution and complementary spectroscopic techniques such as EDX and/or EELS. Practically, the additional control of temperature adds complexity to the experiment, usually at the cost of reduced spatial resolution and/or specimen stability. For example, whether using a heating or cooling holder, thermal drift can reach rates that make imaging the same region of the specimen nearly impossible. Also, when using a cooling holder, instabilities can arise from the process of pumping coolant through the holder (in the case of liquid helium), as well as the liquid boiling off, especially in the case of liquid nitrogen, where the dewar is usually open to atmosphere.

All of the magnetic imaging (Lorentz TEM and DPC-STEM) presented in Chapter 9 was performed using a Gatan double tilt liquid nitrogen cooling holder capable of reaching a minimum temperature of about 90 K. The holder consists of a standard TEM sample rod with a liquid nitrogen dewar on the end that sits outside of the microscope connected to the specimen via a heat sync rod that runs the length of the holder. The specimen temperature was varied using the Gatan SmartSet cold stage controller, which monitors the temperature via a thermocouple and runs current to an electrical heater at the specimen. This allows intermediate temperatures to be stabilized for tens of minutes, with the minimum temperature remaining stable for a
reported 3.5–4 hours (i.e. when the heater is not engaged). The double tilt capability was critical for specimen orientation either on a specific crystallographic direction or slightly tilted away to reduce diffraction contrast in the image.

Most of the magnetic imaging followed a strict zero-field-cooling procedure in which the specimen was inserted into the microscope above its magnetic ordering temperature (room temperature was sufficient for all specimens studied) and then the specimen temperature was reduced only after shutting off the objective lens to ensure zero field conditions. Once the specimen was stabilized at the temperature of interest, a magnetic field could be applied by re-exciting the objective lens to the desired value. At this point, the maximum magnitude of the objective field strength is not yet well characterized on the microscope used; however, it is assumed to be in the range of 2–2.5 T. All field values are read as a percentage of the maximum objective lens excitation.

**Lorentz STEM**

The Titan³ G2 60-300 S/TEM microscope used has a dedicated Lorentz TEM mode, which makes *in situ* field control a rather intuitive process. For STEM, however, Lorentz mode is only enabled through a manual bypass mode and has required significant manual control to align as it is a non-standard operating mode. To get field-free conditions at the plane of the specimen, the objective lens is shut off, much like in Lorentz TEM, except that STEM mode is more strongly affected by the change in optics than TEM.

The first major optical change that occurs when in Lorentz STEM mode is a major reduction in the probe convergence semi-angle, $\alpha$. As an example, for a given
probe-forming aperture (C2 = 50 μm) the convergence angle reduces from 10 mrad to 140 μrad. In essence, this gives a much more parallel probe (less convergent) resulting in poorer spatial resolution. To combat this, the microscope was operated with the strongest C1 lens setting possible to physically reduce the diameter of the probe on the specimen. While this has the effect of reducing probe current, the monochromator allows for an additional means by which to change (in this case increase) probe current. Additionally, as mentioned above, because Lorentz STEM is a non-standard operating mode, all of the subsequent lens settings were manually aligned using free lens control, including control of the objective lens excitation. The most critical basic alignments for Lorentz STEM are to ensure that the probe is completely converged on the specimen (C2 lens strength) and that the diffraction pattern is centered with respect to the detector(s) being used to form the image. With

![Figure 8.7: Electron ray diagram for STEM around the specimen plane. As rays converge out of the condenser system (not shown), they are rastered by the scan coils and refocused by the condenser mini-lens and objective lens (CM and OL, respectively). Descan coils below the specimen serve to bring the scattered beam back on axis by counterbalancing the scan coils. Adapted from [19]](image)
an eye towards Lorentz DPC-STEM, it is also very important to make sure that the transmitted beam does not move as the probe is rastered. This is called descan and involves a pair of scan coils below the specimen that operate in a reciprocal fashion to the scan coils that raster the beam across the specimen, shown in Figure 8.7. If descan is not well aligned, DPC-STEM imaging will not be possible in a meaningful way. While the alignment and development of the Lorentz STEM imaging mode is still ongoing in cooperation with the manufacturer, a spatial resolution of at least 3.5 nm has already been achieved under field-free conditions, as shown in Figure 8.8.
The techniques discussed above, including Hall measurements, Lorentz TEM, and Lorentz DPC-STEM, in conjunction with traditional high resolution STEM and EDX have all be used to characterize magnetic skyrmion material systems, as will be discussed in Chapter 9. Much of the work is ongoing, thus a description of the results to date and a plan for future work will also be presented.

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CHAPTER 9
STRUCTURAL AND MAGNETIC CHARACTERIZATION OF SKYRMION MATERIALS

The materials used in current generation electronic devices for logic and data storage are quickly reaching the limits of their functionality, driving a significant push for next-generation materials and device designs. One class of materials that has been of great interest lately has been chiral magnetic materials such as those that host the magnetic skyrmion phase because they have been predicted to allow for ultra-high density data storage and extraordinarily low critical currents when compared to current technologies ($10^5 - 10^6 \times$ less), which will ultimately lead to lower power consumption. This chapter will describe the current state of research on skyrmions, including the results of a large collaborative effort at the Ohio State University, as well as a plan for ongoing and future work in the field.

9.1 Background

Magnetic skyrmions are topological spin textures that can form in certain materials and systems through a competition between two different interactions: the Dzyaloshinskii-Moriya (DM) interaction and the exchange interaction ($J$). [1–4] The former arises in materials or systems that have strong spin-orbit coupling and lack
bulk inversion symmetry (i.e. non-centrosymmetric crystals) and/or have broken mirror symmetry (i.e. heterostructures). The DM interaction is proportional to the cross product $D \cdot (S_i \times S_j)$ between adjacent spins, $S_i$ and $S_j$, such that spin canting is favored. In contrast, the exchange interaction favors parallel spins as it is proportional to $-JS_i \cdot S_j$. Depending on the strength of each interaction, spontaneous spin textures like spirals or skyrmions can be stabilized over a range of magnetic fields and temperatures. Additionally, the DM interaction can arise from either type of symmetry breaking (bulk, Dresselhaus DM; surface/interfacial, Rashba DM), which will also affect the type of skyrmion observed. When Dresselhaus DM is dominant, Bloch type skyrmions form as vortex-like structures shown in Figure 9.1(a); whereas, when Rashba DM dominates, Néel type skyrmions form with the so-called hedgehog-like structure, as seen in Figure 9.1(c). By tuning the ratio of Dresselhaus to Rashba DM interactions, skyrmions of mixed Bloch and Néel character have been predicted, [5, 6] as shown in Figure 9.1(b), though they have not yet observed experimentally. The Dresselhaus and Rashba contributions can be tuned through the presence of interfaces, strain engineering, magnetic anisotropy. [6]

Skyrmions have been experimentally observed using a majority of the techniques first mentioned in Section 8.1. [7–12] While electron microscopy was the primary and most conclusive technique used in this work, topological Hall data was also used as evidence for the presence of skyrmions. Skyrmions are defined mathematically by the presence of an integer winding number, $n$, which describes the number of times the magnetic spins rotate across a magnetic feature. A winding number of unity is considered a skyrmion, with other variants including anti-skyrmions ($n = -1$).
Figure 9.1: Schematic representation of the magnetic spin textures in (left) Bloch and (right) Néel skyrmions, as well as a the predicted mixed Bloch/Néel type skyrmion (middle), which has yet to be observed experimentally. Below each image is a profile across the core of the skyrmion showing that the spins make a full rotation in each, and thus have a winding number of exactly 1.

having been observed experimentally in some alloys, [13] and higher-order skyrmions ($n = -2$) predicted. [14] Below each schematic in Figure 9.1 is a profile of the spins across the core of the skyrmion, showing that in each case the spins precess through a full $2\pi$ rotation ($n=1$). Topological Hall measurements are sensitive to the presence of a winding number. Though not necessarily conclusive proof of the presence of skyrmions, it is generally used as a good indicator and a helpful starting point for in situ microscopy.

**Topological Hall measurements**

Hall effect measurements have been used to study a number of phenomena, especially charge carrier density and velocities in semiconductors. The measurements are generally taken in a physical property measurement system (PPMS), and can
be taken in variable magnetic fields and temperatures (usually down to liquid He temperatures). Figure 9.2 shows a magnetization hysteresis loop and Hall resistivity data for a thin film specimen of FeGe grown on (111)Si via off-axis magnetron sputtering. [15] The specimen is made into a bar geometry with a width of 0.5 mm and a constant current of density of 2000 A/cm² is applied. As the applied magnetic field is changed, charge carriers in the specimen are deflected due to the Lorentz force resulting in a transverse voltage, called the ordinary Hall effect. [16] As a function of magnetic field, $H$, the longitudinal and Hall resistivities, $\rho_{xx}$ and $\rho_{xy}$, respectively can be measured in the PPMS.

The total Hall resistivity, $\rho_{xy}$, is generally considered to consist of three components, namely the ordinary and anomalous Hall effects, [16, 17] which can be subtracted off leaving just the topological Hall signal, [18, 19] as shown in Figure 9.2 and Equation 9.1:

$$\rho_{xy} = R_0 H + R_S M + \rho_{TH},$$  \hspace{1cm} (9.1)

where $R_0$ is the ordinary Hall coefficient, $R_S$ is the anomalous Hall coefficient, $H$ and $M$ are the magnetic field and out-of-plane magnetization, and $\rho_{TH}$ is the topological Hall resistivity. The ordinary Hall effect is subtracted off by fitting the linear region of the high-field resistivity (red line in Figure 9.2(b)), resulting in anomalous and topological resistivities ($\rho_{AH}$ and $\rho_{TH}$) in Figure 9.2(c). The anomalous Hall resistivity is more involved to remove and thus will not be described here; however, we described the process in more detail in Appendix D. While these measurements were taken by collaborators, they are foundational starting points for the microscopy experiments described in the rest of this chapter.
Figure 9.2: (a) Out-of-plane magnetic hysteresis loop of a 36 nm FeGe film taken at 5 K shows a small coercivity of 500 Oe after subtraction of the diamagnetic background from Si. (b) The total Hall resistivity, $\rho_{xy}$ (green curve) and high field linear fit (red) for the same film. The arrows indicate sweeping directions of the magnetic field. The ordinary Hall effect can be extracted from the slope of linear fit at high field. (c) The Hall resistivity after subtracting the ordinary Hall effect. (d) The topological Hall resistivity after further subtraction of the anomalous Hall effect described in Appendix D. [7]
9.1.1 Early skyrmion imaging

A majority of the early work imaging spin textures like skyrmions and helices was done on bulk specimens using Lorentz TEM [8, 20, 21] because the technique has been well established, offers high spatial resolution, can be performed in situ, and requires fairly minimal additional hardware upgrades to conventional TEMs, which are widely used. The most commonly studied family of materials are the B20 crystals (space group: P2_13), which are non-centrosymmetric and chiral, giving rise to Dresselhaus DM interaction and thus Bloch type skyrmions under certain experimental conditions. The materials that have been studied the most include transition metal silicides/germanides like MnSi, FeGe, and (Fe,Co)Si, as well as some other closely related alloys along the lines of Fe_{1-x}Co_{x}Si, some of which are compiled in Table 9.1. [22] Figure 9.3 shows early Lorentz TEM imaging of spin textures including the skyrmion lattice in Fe_{0.5}Co_{0.5}Si as a function of applied magnetic field and temperature. [23] Similar work has been done on other bulk B20 crystals to map the stability of the helical and skyrmion phases as a function of magnetic field, temperature, and specimen thickness. An example of the effect of specimen thickness on the stability of skyrmion lattice is shown in Figure 9.4 where the field-temperature phase diagrams are generated based on skyrmion density from Lorentz TEM images. [8] It is immediately evident that skyrmion lattice is far more stable in thinner crystals, which can be attributed to the thickness reducing below the helical pitch length, \( L_D \) or \( \lambda \), which is the distance between oppositely signed helices. When the specimen thickness is less the \( L_D \), helices become less energetically stable because of geometric confinement in favor of skyrmions. In FeGe, the helical pitch length is \( L_d \approx 70 \text{ nm} \).
The phase diagrams also show the boundaries separating the different phases including helical (H), skyrmion lattice (SkX), and ferromagnet (FM).

The early imaging of skyrmion materials helped to better understand the nature of skyrmion lattice formation and stability under variable field and temperature conditions for different thickness. Real space imaging in the TEM highlighted the strengths of the technique, allowing crystal lattice defect nomenclature to be applied to magnetic structure with the observation of dislocations in both the helical and skyrmion phases, as shown by the white arrows in Figure 9.3(a) and 9.3(c). While these studies were certainly foundational, they largely ignored Néel type skyrmions and focused on bulk rather than thin film systems, which are more applicable for applications in real world devices; whereas, the results discussed later in this chapter will pertain almost exclusively to studying both Bloch and Néel skyrmion systems in thin films.

9.1.2 Advanced imaging

Lorentz TEM has been the primary mode for imaging magnetic materials in general, especially skyrmions; however, the way in which the contrast is formed makes it unsuitable for imaging Néel type skyrmions. Figure 9.5 shows a schematic of the in-plane moments for both Bloch and Néel skyrmions (black arrows) and their associated Lorentz deflections (red arrows). From the figure it can be seen that in a Bloch skyrmion, the Lorentz deflections lead to a focusing (or defocusing) of the fast electrons depending on the chirality of the skyrmion; whereas, in a Néel skyrmion the hedgehog structure results in no focusing of intensity in the image, and thus Lorentz
<table>
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<th>Material</th>
<th>$T_N$ (K)</th>
<th>$\lambda$ (nm)</th>
</tr>
</thead>
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<tr>
<td>MnSi</td>
<td>30</td>
<td>18</td>
</tr>
<tr>
<td>Epitaxial thin film</td>
<td>45</td>
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<tr>
<td>$\text{Mn}_{1-x}\text{Fe}_x\text{Si}$</td>
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<td></td>
<td>$x = 0.08$</td>
<td>10.6</td>
</tr>
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<td></td>
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<td>6.8</td>
</tr>
<tr>
<td>$\text{Fe}_{1-x}\text{Co}_x\text{Si}$</td>
<td>$x = 0.10$</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$x = 0.5$</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>$x = 0.6$</td>
<td>24</td>
</tr>
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<td></td>
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<td>7</td>
</tr>
<tr>
<td>MnGe</td>
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<td>170</td>
</tr>
<tr>
<td></td>
<td>$T = 100$ K</td>
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<td></td>
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<td>-</td>
</tr>
<tr>
<td>$\text{Mn}_{1-x}\text{Fe}_x\text{Ge}$</td>
<td>$x = 0.35$</td>
<td>150</td>
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<tr>
<td></td>
<td>$x = 0.5$</td>
<td>185</td>
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<tr>
<td></td>
<td>$x = 0.7$</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>$x = 0.84$</td>
<td>220</td>
</tr>
<tr>
<td>FeGe</td>
<td>Bulk</td>
<td>278</td>
</tr>
</tbody>
</table>

Table 9.1: List of some B20 compounds that have been investigated and their reported magnetic transition temperature ($T_N$) and helical pitch length ($\lambda$). *Adapted from [22]*
Figure 9.3: Lorentz TEM of spin textures in [001]-oriented Fe$_{0.5}$Co$_{0.5}$Si as a function of (left) field and (right) temperature. The top row shows the helical state, while the third row shows the hexagonal skyrmion lattice. The second row demonstrates a transition where both states co-exist, and the bottom row shows the ferromagnetic phase. The middle column is FFTs of the left column to highlight the symmetry of the magnetic structure. [23]
Figure 9.4: Field ($B$) and temperature ($T$) phase diagrams of bulk FeGe based on Lorentz TEM observations of skyrmion density. *Adapted from [8]*

TEM is not sensitive to Néel skyrmions that are oriented normal to the path of the electron. It has been shown that by applying large specimen tilts ($\pm 30^\circ$), magnetic contrast can be produced in Lorentz TEM from Néel skyrmions; however, this is experimentally impractical. [24, 25]

Instead, Lorentz DPC-STEM, as described in Section 8.3, can be used assuming access to a microscope with a segmented detector and Lorentz lens. Because Lorentz DPC-STEM uses a focused nm-sized probe, it is sensitive only to the local magnetic field at the region of the specimen with which the probe is interacting. This makes DPC-STEM sensitive to both Bloch and Néel type skyrmions, and in theory any mixed variant between the two. Figure 9.6 shows DPC-STEM data of bulk FeGe
taken at an applied field $H = 796$ Oe and temperature $T = 250$ K. [12] The sample and detector geometries are shown in Figure 9.6(a), while difference images are shown in 9.6(b) and 9.6(c). As was previously explained, the difference images are used to calculate the amplitude and phase components of the total in-plane magnetic field (Figures 9.6(e), (f), and (d), respectively). A combination of conventional Lorentz TEM and Lorentz DPC-STEM data will be discussed below for a range of systems from bulk and thin film FeGe that exhibit Bloch skyrmions, to perovskite bilayer systems that exhibit Néel type magnetism, and B20 superlattices that may be the key to fully tunable, highly stable skyrmion materials that can be used in devices.

Figure 9.5: Schematic representation of the Lorentz force (red arrows) felt by fast electrons as they travel through a Bloch or Néel skyrmion based on the direction of the in-plane component of the magnetic moment (black arrows). The Lorentz deflections in a Bloch skyrmion with anti-clockwise (clockwise) chirality can be seen to focus the electrons away from (toward) the core, resulting in a dark (bright) core in Lorentz TEM. Néel skyrmions do not provide contrast in Lorentz TEM when oriented normal to the electron beam.
Figure 9.6: DPC-STEM dataset for bulk FeGe with an applied field of $H = 796$ Oe at $T = 250$ K. (a) is a schematic of the detector geometry used to generate difference images in (b) and (c) with the detector orientation noted by the double headed arrows. (d) is the total in-plane magnetic field and (e) and (f) are the amplitude and phase components of (d). The color wheel indicates the direction associated with a given color (i.e. red indicates a magnetic moment oriented vertically in the image). [12]
9.2 B20 systems

The B20 crystals have been so intensely investigated because of the wide range of magnetic ordering temperatures \(T_N\) and helical pitch lengths \(\lambda\) found across the family (Table 9.1). From MnGe with a pitch length \(\lambda = 3\) nm to FeGe with ordering temperature \(T_N = 278\) K, and alloys with intermediate values, it represents a rich space for studying skyrmions. The general trend is that of increasing pitch length with ordering temperature, which represents a challenge for creating high density devices that can operate at or above room temperature. The work reported here is mainly focused on FeGe because of its high ordering temperature near room temperature, and ways in which this can be increased. Additional emphasis has been placed on promoting skyrmion stability at zero applied field, another critical factor for feasible use in devices. We start first with high resolution characterization of the thin films grown using HAADF-STEM and EDX and then report magnetic properties from \textit{in situ} microscopy and Hall measurements.

9.2.1 Structural and compositional analysis

High spatial resolution HAADF-STEM imaging of the B20 specimens was performed using a probe spherical aberration corrected FEI Titan\(^3\) 80-300 S/TEM to confirm the quality of the thin films before magnetic investigation. Specimens were grown by two methods: off-axis magnetron sputtering \([7]\) and molecular beam epitaxy (MBE). \([6]\) Both methods proved successful in growing high quality films of FeGe on Si(111), with a representative image of the interface and lattice shown in Figure 9.7. \([7]\) The B20 structure preferentially forms an orientation relationship with
the diamond cubic structure of Si (space group: Fd\(\bar{3}\)m) such that [111]\(_{\text{Si}}\) || [111]\(_{\text{FeGe}}\) and [11\(\bar{2}\)]\(_{\text{Si}}\) || [110]\(_{\text{FeGe}}\). This is confirmed by X-ray diffraction (XRD) for the sputtered films, and XRD and \emph{in situ} reflection high-energy electron diffraction (RHEED) for the films grown by molecular beam epitaxy, in in Figure D.3 and E.1, respectively.

In addition to FeGe, for the first time thin film B20 superlattices were grown on Si(111) via molecular beam epitaxy, including [MnGe/FeGe]\(_8\), [CrGe/FeGe]\(_{10}\), and [CrGe/MnGe/FeGe]\(_8\). [6] The films were confirmed to be high-quality by \emph{in situ} RHEED and XRD (see [6]), as well as high resolution HAADF-STEM and EDX. A representative HAADF-STEM image of part of the [CrGe/FeGe]\(_{10}\) superlattice is
Figure 9.8: HAADF-STEM image of a [CrGe/FeGe]_{10} superlattice oriented along the [110] direction. Scale bar is 5 nm.

shown in Figure 9.8 where the bottom layer is FeGe and the contrast modulates with the composition of the superlattice layers as the image is a Z-contrast image.

The [CrGe/MnGe/FeGe]_{8} superlattice was also very high-quality and showed clear epitaxy and very distinct compositional segregation between the layers. The presence of the small FeSi seed layer can be seen by the extended Si tail (cyan) into the first layer (FeGe) in Figure 9.9. Additionally, a small amount of Mn can also be seen at the interface, which is expected to be residual in the growth chamber due to the high vapor pressure of Mn. The ability to grow extremely high quality B20 superlattices is a significant step towards realizing fully tunable skyrmion systems. By starting with non-centrosymmetric materials like the B20 compounds, the strength of the Dresselhaus DM interaction can be tuned, while the presence of interfaces
incorporates Rashba DM interaction. It is important to note that the Rashba DM interaction arises from broken mirror symmetry. In a single material thin film, there is just one interface, and thus Rashba DM interaction. In a two component superlattice, however, with repeats [ABAB...] the Rashba DM interaction cancels out as the AB and BA interfaces contribute the same magnitude of Rashba DM interaction with opposite sign. A three component system does not necessarily have such an issue as the AB, BC, and CA interfaces are unlikely to have Rashba DM terms that fully cancel. By varying the ratio of the Dresselhaus and Rashba DM interactions, it is predicted that mixed Bloch/Néel skyrmions can tuned to better engineer their size and stability.

9.2.2 Magnetic measurements

The effect of film thickness on skyrmion stability was first investigated using topological Hall signal ($\rho_{TH}$) as described above for sputtered film thicknesses of 100, 65, and 36 nm as a function of field ($H$) and temperature ($T$), as shown in Figure 9.10. [7] These thicknesses were chosen to highlight the effect of relative thickness compared to helical pitch length as the ratio of the two are approximately 1.4, 0.93, and 0.37, respectively. It can be seen from the results that topological Hall signal persists at zero field for all temperatures, but especially lower temperatures. The magnitude of the topological Hall signal found in these films (indicated by the red and blue color scheme) increases with decreasing film thickness, indicating that skyrmion formation is more energetically favorable in thinner films, resulting in higher densities of skyrmions (and thus more topological Hall signal). In the bottom row of
CHAPTER 9  SECTION 9.2

Figure 9.9: (left) HAADF-STEM image of part of the [CrGe/MnGe/FeGe]_8 superlattice oriented along the [110] direction. (right) EDX line scan along the [111] growth direction of a larger portion of the superlattice showing distinct layers approximately 2 nm thick. Scale bar is 5 nm.
Figure 9.10 is a more highly magnified portion of the data for the 36 nm film showing the robust nature of the skyrmion formation as predicted by $\rho_{TH}$. In the case of films grown by molecular beam epitaxy, similar behavior is seen in the topological Hall resistivity, as seen in Figure 9.10(j).

The topological Hall studies were performed on the films with the magnetic field aligned along the out-of-plane direction [111], which is a more challenging direction from which to make a specimen for the TEM. Instead, a 1.5 $\mu$m film of FeGe was grown on Si(111) via MBE such that a cross-sectional specimen with [110] orientation could be prepared using the standard FIB procedures outlined in Section 3.2.1, which was the specimen orientation used to study the quality of the films and their interfaces in the previous section.

In Figure 9.11, under-focused Lorentz TEM images from a full field sweep are shown for the cross-section of a FeGe thin film. The specimen was zero field cooled (ZFC) to 265 K and then the field was ramped in 30 mT steps and allowed to settle before each image was taken. It can be seen in the initial image (top left) that the helical phase is stable at zero field. As the field increases to 30 mT, skyrmions (white circles) begin to preferentially form at the upper left corner of the specimen and co-exist with the helical phase. By 60 mT a full skyrmion lattice is present and then begins to field polarize by 90 mT. At 120 mT, the specimen appears to be fully field polarized; however, it was taken to 150 mT to ensure that there was no remnant texture. As the field reverses, the skyrmion lattice reemerges in a reciprocal fashion to how it disappeared until 30 mT where significantly more skyrmions are stable in the mixed skyrmion/helical phase.
Figure 9.10: (a-h) Contour plots of topological Hall resistivity $\rho_{TH}$ for sputtered films of thicknesses (a,b) 100 nm, (c,d) 65 nm, and (e-h) 36 nm indicating that skyrmion formation persists at 0 field for temperatures $T = 5 - 275$ K. (i) One slice of the contour plots for $T = 5$ K showing the increase in $\rho_{TH}$ with decreasing thickness. [7] (j) $\rho_{TH}$ shows similar behavior for a 35 nm film grown by molecular beam epitaxy. Adapted from [26]
Figure 9.11: Montage of Lorentz TEM images from an entire field sweep starting from a zero field cooled (ZFC) condition. Field sweep follows the images in a snake-like fashion from top left to bottom right. Scale bar is 500 nm, defocus is $\Delta f = -200 \ \mu m$, $T = 265 \ K$. 
On the negative portion of the field sweep, the magnetic contrast inverts (skyrmions become dark circles) and can be seen to persist to far higher fields. This is especially evident at -120 mT where the skyrmion lattice is still mostly intact; however, after fully saturating the field at -150 mT, the skyrmion and helical phases appear to be stable in the same regions of the phase space as the initial field ramp (ZFC to 150 mT).

It should be noted that the magnitude of the applied magnetic fields in the Lorentz TEM images are less than those predicted by the topological Hall measurements. This may be attributed to the fact that \( \rho_{TH} \) can not definitively be attributed solely to skyrmions. There may exist additional contributions to the topological signal, for example, from terminations of helices. While topological Hall measurements should not be sensitive to a perfect helical phase, the presence of terminations in the helical phase, as seen in the ZFC of Figure 9.11, may contribute to the signal as they must have some winding contribution. When compared to Lorentz TEM data from bulk FeGe, the magnitude of the applied field as a function of temperature and specimen thickness (in the electron transmission direction) are very similar. This can be seen in Figure 9.12 where the focal series and TIE reconstructed images from single crystal FeGe are presented.

The bulk FeGe in Figure 9.12 was also used in the development of Lorentz DPC-STEM because it offered a large uniform area of skyrmion lattice that was already well-characterized in terms of field/temperature dependence. Figure 9.13 shows the individual quadrant images (a-c), as well as the difference images under the same conditions as in Figure 9.12. A benefit of DPC-STEM is that the difference
Figure 9.12: Lorentz TEM image of bulk FeGe. Focal series of images where defocus $\Delta f =$ (top) 200 $\mu$m, (middle) 0 $\mu$m, (bottom) -200 $\mu$m. \textit{(right)} TIE reconstructed image showing the direction of the in-plane magnetic moment, where direction is specified by the color wheel. $T = 265$ K, $B_\perp = 50$ mT.
images, which are the partial gradient images of the in-plane magnetic field, are largely free of diffraction contrast when compared to the individual quadrant images. This is because the difference images are renormalized by the annular bright field image (total sum of the quadrant detectors), which effectively removes most diffraction contrast. This is similar to the process used in [12], with the exception that their detector was not annular, but an 8-segment circular detector seen in Figure 9.6(a).
9.3 Perovskite systems

While the B20 skyrmion systems leverage the Dresselhaus DM interaction that arises from broken inversion symmetry of the crystal structure, another approach has also been taken by tuning Rashba DM at interfaces in centrosymmetric crystals, specifically perovskite thin films. This work is ongoing as part of the effort to stabilize magnetic skyrmions at room temperature with diameters less than 10 nm, which will ultimately be most practical for use in real devices. Perovskites have been widely studied for their interesting magnetic and electronic properties, and their growth has been characterized and optimized in a number of systems resulting in very high quality films with precise control over film thickness/growth rate. [27, 28]

Rashba DM interaction at interfaces requires the presence of strong spin-orbit coupling, which scales approximately as $Z^4$, where $Z$ is atomic number. [29] Recently, it was shown that a very thin bilayer of SrIrO$_3$/SrRuO$_3$ grown on SrTiO$_3$ can produce strong topological Hall resistivity $\rho_{TH}$. [30] SrRuO$_3$ is a ferromagnet, with all of the spins aligned in the same direction; whereas, SrIrO$_3$ is paramagnetic with strong spin-orbit coupling from the Ir. In [30] it was shown that the strength of the Rashba DM interaction was strongly dependent on the number of unit cells of each layer. Schematically, this is represented in Figure 9.14 showing that with a 2 unit cell layer of SrIrO$_3$, if the number of unit cells of ferromagnetic SrRuO$_3$ exceeds 6 it would over power the Rashba DM resulting in an overall ferromagnetic response. For 6 or fewer unit cells of SrRuO$_3$, the strong spin-orbit coupling contribution from the
SrIrO$_3$ provides Rashba DM at the interface, promoting the stabilization of Néel type skyrmions.

### 9.3.1 Structural analysis

All three materials share the same crystal structure (*space group*: Pm3m), *A*-site cation (Sr), *B*-site valence ($B^{4+}$), and the lattice mismatch is relatively small (<0.5%), encouraging high quality growth. The lattice parameters of SrIrO$_3$, SrRuO$_3$, and SrTiO$_3$ are $a = 0.3942$ nm, 0.3942 nm, and 0.3950 nm, respectively, and the orientation relation is cube on cube. Films were grown via off-axis magnetron sputtering on SrTiO$_3$(001) and TEM specimens were made using the FIB. In order to protect the very thin SrIrO$_3$ layer, the specimen used for cross-sectional STEM imaging was capped with an additional layer of SrRuO$_3$. Figure 9.15 shows the high quality growth and precise control over layer thickness. The bright SrIrO$_3$ layer is exactly 2 unit cells thick and fully coherent with the SrRuO$_3$ layer, which is 10 unit cells thick.
9.3.2 Magnetic measurements

Hall measurements have been performed on the (2 unit cell)SrIrO$_3$/(10 unit cell)SrRuO$_3$ specimen and show topological signatures up to 110 K, the peaks seen in Figure 9.16; whereas, specimens with 25 unit cells of SrRuO$_3$ show no such signal, in agreement with [30]. The magnetic characterization of the perovskite system is currently limited to topological Hall data; however, plan-view [001] specimens of the uncapped SrIrO$_3$/SrRuO$_3$ bilayer are currently in progress. Skyrmions are predicted to be Néel type, due to the Rashba DM, with a diameter on the order of 10 nm or less. This makes Lorentz DPC-STEM the ideal imaging technique to observe skyrmions in this system for the first time.
CHAPTER 9

9.4 Ongoing and future work

As work continues in the search for stable skyrmion systems at room temperature, zero field, and with diameters less than 10 nm, there is some ongoing work that will be described here.

**B20 systems**

As mentioned above, B20 heterostructures have been demonstrated that show promise for highly tunable DM interactions. While $\lambda$ in most of the B20s is on the order of 10s of nanometers (see Table 9.1), there are a couple of examples near or less than 10 nm, namely MnGe and Mn$_{1-x}$Fe$_x$Ge ($x = 0.35$) that still have moderately high ordering temperatures. Film growth of MnGe has already been achieved, though
it is not as optimized as that of FeGe. Interestingly, MnGe does not form a hexagonal skyrmion lattice like FeGe, but rather a square lattice. [31]

Additionally, the effect of Rashba DM on B20 layers is currently being investigated by depositing heavy metals on FeGe thin films. Lorentz TEM is to be performed in cross-section to see if the effect of strong spin-orbit coupling at the metal-B20 interface can promote skyrmion formation at higher temperatures and/or lower fields.

**Perovskite systems**

With the perovskite skyrmion system, the main challenge lies in sample preparation for the TEM since the film itself is only 12 unit cells thick (<5 nm) and imaging must be performed along the growth direction. A combination of mechanical polishing and FIB-based techniques are being tested to see which provides the best results. A secondary challenge is skyrmion size and the unknown magnitude of the scattering for image formation in Lorentz DPC-STEM from such a thin film. One potential route that may be explored to counteract this is by growing multiple repeats of the bilayer system; however, a spacer layer would be necessary to ensure that the interfacial Rashba is not canceled out by symmetric interfaces.

**Chiral bobbers**

Theory has predicted the presence of the so-called chiral bobber phase in non-centrosymmetric materials, which is shown in Figure 9.17 along with a schematic of the skyrmion phase. [26] Chiral bobbers are confined to the surface while the bulk is the conical phase. This combination is predicted to be the true stable state for thicknesses greater than about 1.5 times the helical pitch length, $L_D$. Magnetic susceptibility data in Figure 9.18 appears to confirm the presence of a transition from
a thickness-dependent phenomenon to a constant one around 40 nm for FeGe, which is approximately $L_D/2$, in agreement with the schematic in Figure 9.17. For such thin specimens, it is predicted that the chiral bobber would then span the entire thickness, creating a full skyrmion tube.

Experimental observation of such features will be challenging, though using an in-plane magnetizing TEM holder rather than the objective lens (out-of-plane) to
Figure 9.18: Magnitude of the derivative of magnetic susceptibility $\chi$ with respect to applied field $H$. For thicknesses above 40 nm, the trend appears to be related to a surface phenomenon; whereas, below 40 nm, it is constant. [26]

apply magnetic field could possibly allow for imaging of such features in cross-section, rather than top-down where they would likely show similar contrast to skyrmions.

9.5 Conclusions

Magnetic skyrmions represent an exciting new class of topological spin texture that show promise for next-generation spintronics because of their potential for robust, ultra-high-density, low power devices. The ability to quantitatively image their magnetic structure in real space with high spatial resolution and in situ as a function of applied magnetic field and temperature enables a diverse set of experiments to be performed to establish structure-property relationships that will be critical when real devices are to be fabricated. In this chapter two electron microscopy methods were used to image skyrmions and other spin textures in both bulk and thin films,
as well as classical high resolution STEM and EDX to characterize the quality of the films. The development and application of Lorentz DPC-STEM marks a turning point in imaging of magnetic materials, where the imaging technique is no longer limited to certain types of magnetic features and requires no intensive off-line post processing. This technique also has the added benefit of being operated in such a way that complementary imaging and spectroscopy modes like EELS, EDX, and HAADF-STEM can all be acquired simultaneously, further advancing the fundamental goal of understanding structure-property-processing relationships.

BIBLIOGRAPHY


CHAPTER 10
SUMMARY AND FINAL CONCLUSION

The goal of the research presented in this dissertation was to gain better understanding into the relationship between atomic-scale phenomena and electronic and magnetic properties. The unifying theme was the use of state-of-the-art electron microscopy and spectroscopy along with a quantum mechanical electron scattering model and first principles calculations. Such a combination of experiment and theory allows for unprecedented insight into both the physical and electronic structure of materials and their properties. In addition, modeling the complex nature of electron-solid interactions provides a clearer explanation for experimental electron microscopy experiments, while also enabling virtual experiments that would otherwise be impossible to design and/or observe in an actual microscope.

In Chapters 3 and 4, fundamental background for the experimental and theoretical methods used was presented first with an eye towards the research performed over the course of this dissertation, but also in the greater context of the field of materials characterization. It was shown that the electron microscope is a powerful and versatile tool capable of imaging across many different length scales, while also providing complementary information about chemical, compositional, magnetic,
electronic, and structural properties. The use of a quantum mechanical model for simulating electron scattering physics rather than a semi-classical one was justified by its ability to separate elastic and inelastic scattering events, which play a pivotal role in understanding experimental data, including atomic resolution images and spectroscopy.

A fundamental use of electron microscopy, especially at the atomic scale, is to directly image and study the structure of materials to develop structure-property relationships. Chapter 5 presents an example of the critical role of such imaging in characterizing the thin film growth mechanism of pyrochlore \( \text{Nd}_2\text{Ir}_2\text{O}_7 \) via off-axis magnetron sputtering. As the films were deposited amorphous and then post-growth annealed, a study of the film quenched mid-anneal was performed revealing the grain growth process, which begins at the film/substrate interface. In doing so, this also exposed the presence of an Ir-rich growth front, which was then explained thermodynamically by calculating a local temperature increase due to the exothermic crystallization process. This rise in temperature was enough to decompose the constituent \( \text{IrO}_2 \) leaving behind metallic Ir, which was directly imaged around the grains at the interface between the grain, amorphous film, and substrate. This level of characterization of the growth mechanism and subsequent understanding of the apparent interfacial structure through EDX could only be achieved using high spatial resolution imaging and spectroscopy in the electron microscope.

In addition to studying the structural properties of materials, electron microscopy allows for probing the electronic structure of materials using EELS. The fast electron in the beam may excite atomic electrons into unoccupied electronic states that can
then be used to more fully understand the electronic and magnetic properties of the material. To explain the experimental EELS data in Chapter 6, first principles calculations were used to determine the spin-polarized density of unoccupied states in a system of six different osmium-based double perovskites in which the $A$-site atom was changed to impose structural distortions, and the $B$-site atom was changed to modify the $d$ valence electron count. The effects of these changes were quite prominent in the experimental data and were correlated back to the calculated densities of states. While the experimental data was performed on bulk powders, it serves as a proof-of-concept that such investigations may be performed on thin films near features of interest such as interfaces and other defects. The ability to study the spatial dependence of electronic structure with respect to defects at resolutions as high as the atomic-scale could help to better explain device performance, as well as motivate the use of functional defects in oxide electronic materials.

The first part of the dissertation ends with an in-depth theoretical study of the effects of atomic ordering on contrast in HAADF-STEM imaging, using double perovskite $\text{Sr}_2\text{CrReO}_6$ as a test case. It is shown that the so-called $Z$-contrast imaging mode is strongly affected by the presence of structural defects such as antiphase domains and antisite disorder. Where the overly simplistic description of $Z$-contrast involves a nearly quadratic dependence of image contrast on average atomic number, the results in Chapter 7 demonstrate that there is a much more complex relationship. Electron scattering simulations show that the contrast mechanism in HAADF-STEM can be exploited to learn 3D ordering information from 2D images as they are encoded with such information as the electron transmits through the specimen. Image
simulations were performed using high performance computing on a supercomputer allowing for a massive number of computations and a greater understanding of the major factors influencing image contrast.

The final body of work involves an ongoing study of magnetic skyrmions in bulk and thin films using \textit{in situ} Lorentz electron microscopy. Two microscopy methods – Lorentz TEM and Lorentz DPC-STEM – are explained in Chapter 8, including applications, limitations, and practical aspects of each technique. These techniques were then employed in Chapter 9 to study topological spin structures, especially skyrmions, in bulk and thin film FeGe, while setting up future work in multilayer B20 heterostructures and perovskite bilayers.

In conclusion, this dissertation has demonstrated the effective use of high spatial resolution electron microscopy and spectroscopy to characterize structural, electronic, and magnetic properties of materials that are of great interest for future spin-based devices. The experimental and theoretical methods used here are applicable well beyond such materials, proving the breadth of electron microscopy as a characterization tool.


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Appendices
APPENDIX A

SUPPLEMENTARY MATERIAL FOR “EPI TAXIAL GROWTH OF IRIDATE PYROCHLOR E Nd$_2$Ir$_2$O$_7$ FILMS”

Note: This appendix is the supplementary information submitted with the paper “Epitaxial growth of iridate pyrochlore Nd$_2$Ir$_2$O$_7$ films” presented in Chapter 5. [1]

The powders were analyzed on beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using high-resolution synchrotron powder x-ray diffraction (XRD) using a wavelength of 0.413191 Å with a step size of 0.001° and a scan speed of 0.01°/s, as shown in Figure A.1 for Nd$_2$Ir$_2$O$_7$. Rietveld refinement analysis was conducted utilizing the GSAS-II software package. [2] The inset to Figure A.1 shows that the diffraction peaks are asymmetrical. The asymmetry had significant $2\theta$ dependence, revealing a continuous range of lattice constants in the sample possibly due to an oxygen off-stoichiometry distribution near the surface of the particles. The asymmetry could not be accounted for with realistic instrumental parameters. We modeled the asymmetric peak shape with a three-phase fit utilizing different lattice parameters: one primary phase with a refined smaller lattice constant and two oxygen-deficient pyrochlore phases with slightly larger fixed lattice constants.
The remaining refinement parameters were constrained to be equivalent in each phase. The results of the fit are shown in Figures A.1(a) and A.1(b). The refined lattice parameters and locations of the atoms in Nd$_2$Ir$_2$O$_7$ powders are reported in Table A.1.

Magnetization ($\chi$) measurements on the powder were taken using a Quantum Design superconducting quantum interface device (SQUID) magnetometer at a magnetic field $H = 100$ Oe and at temperatures ranging from 2 to 300 K with both field and zero field cooling protocols [Figure A.2(a)]. The temperature dependence appears roughly Curie like ($1/T$) in character. However, by taking the difference between the field and zero field cooled measurements [Figure A.1(b)], two features likely associated with magnetic phase transitions emerge: a stronger one at 34 K and a more subtle one at 119 K. The nature of the magnetic ordering transition is a topic of continuing debate. For simpler pyrochlores with only one magnetic species such as in Eu$_2$Ir$_2$O$_7$ and Y$_2$Ir$_2$O$_7$, clear magnetic ordering of the Ir site to an all-in-all-out structure has been reported around 120 K. [3–7] Nd$_2$Ir$_2$O$_7$ is more complicated due to the Nd on the A site also having a magnetic moment. Neutron diffraction is sensitive to the larger Nd moment and reveals Nd ordering around 15 K. [8, 9] However this technique is much less sensitive to the much smaller iridium moment and did not observe any evidence of higher temperature ordering. [10] It is known other (Mo based) pyrochlores with multiple magnetic species may have multiple ordering transitions temperatures. [11] Since the Ir-Ir exchange interactions are stronger than those between Nd-Nd or Nd-Ir due to the greater spatial extent of 5$d$ transition metal electronic orbitals, it is anticipated that the Ir sublattice would undergo magnetic ordering at a higher temperature. Therefore, we speculate that the 120 K
transition may be due to an onset of Ir ordering while the 34 K transition represents the onset of Nd spin freezing. The roughly Curie-like temperature dependence of the magnetization is thus interpreted as arising from paramagnetic contributions of the larger Nd moment which persist below the Ir ordering transition. At lower temperatures the interplay between the two sublattices becomes more significant. Though our 34 K transition temperature agrees with previous research, [12] there is considerable variation in the temperature at which this Nd ordering occurs. [6, 8, 9] We hypothesize that this is due to the effect of the ionic radius of the rare earth ion on magnetic ordering temperature. The magnetic ordering temperature in the pyrochlore iridates depends heavily on the A-site ionic radius. The ionic radius of the Nd is such that the system is close to the transition to a spin liquid phase which does not order at low temperatures. [13] Therefore, small variations in lattice constant due to sample stoichiometry or lattice strain may cause significant change in magnetic ordering temperature.
Figure 1. $\theta/2\theta$ XRD scans (red symbols) of Nd$_2$Ir$_2$O$_7$ powders taken at the Argonne National Laboratory’s Beam Line 11 with x-ray wavelength of 0.413191 Å. The Rietveld refinements (blue curve) give the structural parameters shown in Table I. The green curve is the difference between experimental data (red) and calculated pattern (blue). The insets show the pyrochlore (440) peaks where the asymmetry is due to the inhomogeneous oxygen stoichiometry in the powders.
Table A.1: Rietveld refinement results of the synchrotron XRD data for Nd$_2$Ir$_2$O$_7$ powders, which give the $xyz$ coordinates of each atom in the unit of lattice constant $a$. The data was refined with the 3 phases of Nd$_2$Ir$_2$O$_7$ with different lattice constants (dominate phase in **bold**), but with atomic parameters constrained to be equivalent. The two less prevalent phases had larger fixed lattice parameters while the dominant phase $a$ was refined. The three lattices constants used in each phase are displayed, with the dominate phase listed first. The fitting quality is described by $R_{wp} = 12.83\%$, $R_p = 9.09\%$, and $\chi^2 = 4.338$.

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<tr>
<th>Atom</th>
<th>x</th>
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<th>z</th>
<th>Site</th>
<th>$U_{iso}$ (Å$^2$)</th>
<th>Lattice constant $a$ (Å)</th>
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Figure A.2: (a) Magnetic susceptibility of the Nd$_2$Ir$_2$O$_7$ powders measured at $H = 100$ Oe for both FC and ZFC samples. (b) The difference between ZFC and FC curves in (b) indicated two magnetic phase transitions, the first at 34 K and the second at 119 K.
BIBLIOGRAPHY


APPENDIX B

OSMATE DOUBLE PEROVSKITE STRUCTURES

This appendix includes the full crystallographic information for the six double perovskites studied in Chapter 6. Table 6.1 is reproduced for convenience in Table B.1.

<table>
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Table B.1: Crystallographic information for the Os-based double perovskites studied.
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Table B.2: Ca$_2$CrOsO$_6$ crystallographic data

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Table B.3: Ca$_2$FeOsO$_6$ crystallographic data
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Table B.4: Ca$_2$CoOsO$_6$ crystallographic data

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Table B.6: Sr$_2$FeOsO$_6$ crystallographic data

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Table B.7: Sr$_2$CoOsO$_6$ crystallographic data
APPENDIX C

ADDITIONAL INFORMATION ON CHANNELING SIMULATIONS

The results highlighted in Chapter 7 are the result of a larger investigation into the effects of atomic-scale ordering on probe channeling and the resultant HAADF-STEM image intensity, the details of which will be explained here in greater detail.

C.1 Experimental explanations

The effect of probe channeling can be seen in the experimental image in Figure 7.1 in the presence of an antiphase domain. As explained in Chapter 7 and shown schematically in Figure 7.2, the antiphase domain results in pure Re (Cr) columns becoming Re (Cr) on top of or below Cr (Re) when imaging along the [100] direction of Sr$_2$CrReO$_6$ (SCRO). Depending on the location of the antiphase boundary with respect to the thickness of the TEM specimen, the relative Cr:Re ratio will change. For example, if the boundary is located 80% of the way through the thickness of the foil, the columns that would have been pure Re will then be 80% Re-20% Cr, and vice versa for the columns that would have otherwise been pure Cr.

This can be measured experimentally to get a better idea of where the boundary lies within the thickness. In the experimental image of Figure 7.1, reproduced and annotated in Figure C.1, it can be seen that the (011) planes of pure Re (brightest
columns) and pure Cr (least intense columns) still have different intensities within the antiphase region where the columns are mixed Cr/Re. This shows that the antiphase boundary is not located midway through the specimen, but rather towards one of the surfaces (entrance or exit). From the line scan in Figure C.2 it can be seen that the antiphase domain contains less material ordered like that of the top left hand portion of Figure C.1. This is most apparent in the reversal of column intensity from the Re columns on the left hand side (ordered) to the right hand side (two antiphase domains), indicating that the columns that were pure Re in the single domain portion now contain more Cr than Re, with the opposite being true for columns that contain pure Cr in single domain. If the antiphase domain contained more material ordered like that of the lefthand side of the image, the columns that originally contained pure Re would remain brighter (shown in Figure C.2 as columns with a blue, Re, atom on top of a yellow, Cr, atom).

The ability to understand such three-dimensional information from a single two-dimensional HAADF-STEM image then rose the question “can more complex atomic-scale ordering information be probed in three dimensions via HAADF-STEM images?” To do this experimentally would require exact knowledge of and control over the atomic structure, which is not feasible; however, this is a fundamental part of image simulation.

### C.2 Image simulations

In Chapter 7, one possible, representative structural model of an antiphase domain structure was modeled to give qualitative agreement with the experimental data.
Figure C.1: Experimental HAADF-STEM image of an antiphase domain in SCRO from Figure 7.1, viewed along the [100] direction. Yellow and blue lines trace (110) planes of pure Cr and Re, respectively. The red dashed line indicates the (001) plane integrated in the line scan shown in Figure C.2.
Figure C.2: Integrated line scan from the red box in Figure C.1 showing the well-ordered B-site sublattice on the left with Cr and Re columns (yellow and blue, respectively). The antiphase boundary parallel to the probe crosses the line scan at 0 Å along the x-axis, with the mixed Cr/Re columns on the right hand side.

To test the capability of HAADF-STEM imaging to probe more subtle changes in atomic-scale ordering, models with fixed composition (i.e. Cr/Re ratio) were generated via scripting where the different permutations of Cr/Re ordering were represented. A portion of such a model is shown in Figure C.3 with the O atoms hidden for clarity. As described in Chapter 7, the naïve model of HAADF-STEM imaging would assume that given exactly the same average atomic number of each column ($\bar{Z} = 50\% Z_{Re} + 50\% Z_{Cr} = 49.5$) the HAADF-STEM intensity of all of the columns should be the same. This is, however, very much so not the case due to different probe channelling on any given column.

The results of simulating such antisite disorder in SCRO are shown in Figure C.4 for the complete model from Figure C.3 showing all 252 possible nontrivial permutations for a 10 atom thick 50:50 binary specimen ($n = (10!)/[(10 - 5)!5!]$).
CHAPTER C

SECTION C.2

Figure C.3: A portion of a structural model of SCRO with Cr/Re antisite disorder. The Cr:Re ratio is identical for all columns (50% each), while the ordering is permuted. O atoms are hidden for clarity.

In this structural model, it can clearly be seen in both the false color simulated image in Figure C.4(a), and the line scan and histograms in Figures C.4(b) and (c), respectively, that the B-site sublattice columns have a varied range of intensities. While this nicely demonstrates the effects of probe channeling, it is convoluted by the effects of channeling from and channeling onto nearest neighbor columns and beyond. For this reason, the columns were also simulated in isolation, where they were only coordinated by their bonding O atoms.

By simulating the columns individually, while not necessarily physically realistic, the first order effects of probe channeling can be better understood. The individual column intensities in Figure C.4 show an interesting behavior where the columns with the higher HAADF-STEM intensities have the lighter atoms (i.e. Cr) near the entrance surface. As described in the text of Chapter 7, this is attributed to a “pre-focusing” action by the Cr atoms, such that the probe then channels more strongly down the column and is subsequently more strongly scattered by the heavier
Figure C.4: Simulated HAADF-STEM image of the structural model of SCRO with antisite disorder on the Cr/Re sublattice shown in Figure C.3. All columns on the $B/B'$ sublattice have the same Cr:Re ratio (50% of each); however, their relative intensities vary by up to ±20%, shown in the (b) line scan and (c) histogram of intensities.
Re atoms near the exit surface. This can be thought of, to a first approximation, as a column’s center of mass. Figure C.5 shows the same three columns as Figure 7.4 with their respective centers of mass denoted by a dashed line. The first column (Cr on top of Re) results in the highest HAADF-STEM signal; whereas, the second and third columns are 15.9% and 21.7% less intense due to weaker probe channeling. While the center of mass is not solely responsible for HAADF-STEM intensity and has a weaker influence than total average atomic mass, it does appear to have a significant effect for a given crystallographic direction and set of microscope parameters (i.e. probe convergence semi-angle, accelerating voltage, etc.).
C.3 Future work

The number of factors that affect HAADF-STEM intensity is great. They most certainly vary in the strength of their effect from specimen to specimen; however, the simulations presented here clearly show that the simple, nearly quadratic $Z$-contrast relationship often assumed is heavily over-simplified. On the other hand, it is also evident that probe channeling can be exploited to understand three-dimensional ordering phenomena because it is convoluted into the final HAADF-STEM image intensity. In order to quantitatively understand experimental data, experiments must be carefully performed and well-characterized, preferably with complementary information like compositional data. The use of high performance computing allows for many permutations to be simulated and a best match to be found. Future work on the subject should explore the effects of microscope parameters such as probe convergence semi-angle and acceleration voltage, as well as the effect in other systems and along other crystallographic directions in presence of nearest neighbor columns. By simulating a few common structures and directions, an even clearer understanding of the probe channeling process can be developed.
APPENDIX D

SUPPLEMENTARY MATERIAL FOR “ROBUST ZERO-FIELD SKYRMION FORMATION IN FeGe EPITAXIAL THIN FILMS”

Note: This appendix is the supplementary information submitted with the paper “Robust Zero-Field Skyrmion Formation in FeGe Epitaxial Thin Films,” discussed in Chapter 9. [1]

D.1 Optimization of FeGe Growth Conditions

FeGe epitaxial films were grown on Si(111) substrates using ultrahigh vacuum off-axis magnetron sputtering at various substrate temperatures ($T_s$) to identify the optimal deposition temperatures. Figure D.1 below shows the 2θ-ω X-ray diffraction (XRD) scans of four FeGe films grown at $T_s$ = 420, 315, 290, and 265 °C. The deposition temperature of 290 °C results in only one film peak at $2\theta \approx 33^\circ$, which is the expected position of the FeGe(111) peak of B20 phase, demonstrating the growth of phase-pure B20-FeGe(111) epitaxial film on Si(111). Figure D.2 shows the full range XRD scan between $2\theta = 10^\circ$ and 80° where no impurity peaks are observed. At higher substrate temperatures [Figures D.1(a) and D.1(b)], the Ge(111) peak at $2\theta \approx 27.3^\circ$ appears, indicating the formation of Ge epitaxial phase. At lower substrate temperatures
[Figure D.1(d)], an impurity peak at $2\theta \approx 36^\circ$ appears, which can be attributed to the formation of hexagonal B35-phase FeGe [see [2]]. The optimal temperature window for the epitaxial deposition of pure B20-phase FeGe films is between 280 °C and 300 °C.

D.2 X-ray reflectivity and $\Phi$-scans of the FeGe films

Figure D.3(a) shows the X-ray reflectivity (XRR) spectra for the 36 and 65 nm FeGe films. The clear XRR peaks indicate that the films are uniform, and from these peaks the thicknesses of the films were calibrated. Figure D.3(b) shows the $\Phi$-scans of the FeGe(200) and Si(400) peaks of the 100 nm film taken at a tilt angle of 57.4° from the film normal. The six-fold symmetry of the B20 FeGe(200) and the three-fold symmetry of the diamond-structure Si(400) have a 30° rotation relative to each other as expected from epitaxial growth.

D.3 FeGe Topological Hall Effect Extraction

The anomalous Hall (AH) resistivity ($\rho_{AH}$) can be modeled into a power law form of longitudinal resistivity ($\rho_{xx}$),

$$\rho_{AH} = R_SM = (b\rho_{xx}^2 + c\rho_{xx})M; \quad (D.1)$$

where the quadratic term ($b\rho_{xx}^2$) is due to a scattering independent mechanism and the linear term ($c\rho_{xx}$) is caused by skew scattering, both dependent on $\rho_{xx}$. All of our FeGe films show very small magnetoresistance ($<0.7\%$ at fields up to 7 T) as shown in Figure D.4(a), indicating that $R_S$ is approximately magnetic field independent. A log-log plot of $\rho_{AH}$ vs. $\rho_{xx}$ at $|H| = 4$ T (where the magnetization is saturated) and at various temperatures reveals a linear dependence with a slope of 2.3 [Figure D.4(b)],
suggesting that the anomalous Hall effect is dominated by the scattering independent mechanisms and the $c\rho_{xx}$ term can be neglected (see references [3–5]). At $|H| \geq 2$ T, the FeGe films are in the saturated ferromagnetic state and the topological Hall effect is absent ($\rho_{TH} = 0$) due to the lack of skyrmions. Given that $\frac{\rho_{xy}}{H} = R_O + b\frac{\rho_{xx}^2 M_S}{H^2}$ (see main text, [1]), by plotting $\frac{\rho_{xy}}{H}$ vs $\frac{\rho_{xx}^2 M_S}{H^2}$ at $|H| \geq 2$ T, which exhibits a linear dependence as shown in Figure D.5, $R_O$ and $b$ can be obtained from the $y$-intercept and the slope, respectively.

The procedure to extract topological Hall resistivity is shown in Figure D.6. Figure D.6(a) shows the out-of-plane hysteresis loop at $T = 5$ K for the 36 nm FeGe film, which exhibits the typical behavior for an out-of-plane magnetic field. Figure D.6(b) shows the field dependence of total Hall resistivity. At high fields ($H \geq 2$) the data are linear and its slope represents the ordinary Hall coefficient $R_O$. After subtraction of the ordinary Hall effect, Figure D.6(c) looks similar to but does not follow the magnetization hysteresis loop in Figure D.6(a). Using the extracted parameter $b$ and magnetoresistivity data [Figure D.4(a)], we subtracted the anomalous Hall effect contribution and obtained the topological Hall resistivity as shown in Figure D.6(d).

Figure D.7 shows the topological Hall resistivities at $T = 250$ K for the three FeGe films. The topological Hall effect is very large for all three FeGe films, e.g., $\rho_{TH} = 918 \pm 5$ n$\Omega$-cm for the 36 nm film, which is more than five times larger than the highest values of $\rho_{TH}$ previously reported for B20 skyrmion materials.
Figure D.1: Semi-log 2θ-ω XRD scans for 200 nm FeGe films grown on Si(111) at substrate temperatures of (a) 420 °C, (b) 315 °C, (c) 290 °C, and (d) 265 °C. The XRD results indicate that 290 °C is the optimal deposition temperature which gives a pure B20 phase, (111)-oriented epitaxial FeGe film on Si(111). Higher substrate temperatures lead to the growth of Ge(111) phase while at lower temperatures, an impurity peak at 2θ ≈ 36° appears, which is likely due to the formation of hexagonal B35-phase FeGe. The optimal temperature window for B20-phase FeGe epitaxial growth is rather narrow, between 280 °C and 300 °C.
Figure D.2: Full range semi-log $2\theta$-$\omega$ XRD scan for a 200 nm FeGe film grown on Si(111) at substrate temperature of 290 °C, demonstrating pure B20 phase of the FeGe epitaxial film.
Figure S2: Full range semi-log $2\theta$-ω XRD scan for a 200-nm FeGe film grown on Si(111) at substrate temperature of 290°C, demonstrating pure B20 phase of the FeGe epitaxial film.

Figure S3: (a) XRR scans of the 65 and 36 nm FeGe films. (b) $\Phi$-scans of the Si(400) peaks and FeGe(200) peaks of the 100 nm FeGe reveal a 30° rotation between the Si and FeGe cubic lattices.

Figure D.3: (a) XRR scans of the 65 and 36 nm FeGe films. (b) $\Phi$-scans of the Si(400) peaks and FeGe(200) peaks of the 100 nm FeGe reveal a 30° rotation between the Si and FeGe cubic lattices.
Figure S4: (a) Magnetoresistance of a 36 nm FeGe film at 5 K, which is less than 0.7%. (b) A log-log plot of the anomalous Hall resistivity ($\rho_{AH}$) vs the longitudinal resistivity ($\rho_{xx}$) taken at $|H| = 4$ T and various temperatures. A least-squares fit (red) reveals a slope of 2.3.

Figure S5: Plot of $\rho_{xy} H$ vs $\rho_{xx}^2 M_S H$ yields a linear relationship. The slope and the $y$-intercept of the linear fit are coefficients $b$ and $R_O$, respectively.
Figure D.6: (a) Out-of-plane magnetic hysteresis loop of the 36 nm FeGe film taken at 5 K shows a small coercivity of 500 Oe after subtraction of the diamagnetic background from Si. (b) The total Hall resistivity, $\rho_{xy}$ (green curve) and high field linear fit (red) for a 36 nm FeGe film taken at 5 K. The arrows indicate sweeping directions of the magnetic field. The ordinary Hall effect can be extracted from the slope of linear fit at high field or the method described in Figure D.5. (c) The Hall resistivity after subtracting the ordinary Hall effect. (d) The topological Hall resistivity after further subtraction of the anomalous Hall effect by using the coefficient $b$, $\rho_{xx}$ and magnetization hysteresis obtained from Figure D.5, Figure D.4(a), and Figure D.6(a), respectively.
Figure D.7: The topological Hall resistivity ($\rho_{TH}$) hysteresis loops for the 36 nm (green), 65 nm (blue), and 100 nm (red) FeGe films at 250 K show very large values of $\rho_{TH}$ up to 918 nΩ-cm.
BIBLIOGRAPHY


APPENDIX E

Additional Figures from “Molecular beam epitaxy growth of [CrGe/MnGe/FeGe] superlattices: Toward artificial B20 skyrmion materials with tunable interactions”

Note: This appendix includes figures from the paper “Molecular beam epitaxy growth of [CrGe/MnGe/FeGe] superlattices: Toward artificial B20 skyrmion materials with tunable interactions,” discussed in Chapter 9. [1]

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Figure E.1: (a) Cross-sectional diagram of FeGe showing the (111) lattice constant of 8.104 Å and the quadruple layer (QL) period of 2.701 Å. (b) Diagram of the epitaxial alignment of FeGe(111) on Si(111) with 30° lattice rotation. (c, d) RHEED images of a 7 × 7 reconstructed Si(111) surface shown for in-plane directions of [112] and [110], respectively. Inset of (c) RHEED after deposition of the Fe seed layer, showing a characteristic asymmetric pattern. (e, f) RHEED patterns measured along the [110] and [112] in-plane directions of the ~40 nm FeGe film, respectively. (g) XRD scan of the FeGe film. Single-phase, single crystal FeGe is shown amongst the Si substrate peaks. [1]
Figure E.2: RHEED and XRD characterization of a three-component superlattice [CrGe/MnGe/FeGe]$_8$. (a-c) RHEED patterns are shown for the topmost layers FeGe, MnGe, and CrGe layers, respectively. The patterns are measured along the [110] in-plane direction of the films. Qualitatively, the RHEED images are very similar between each layer. (d) XRD scan of the trilayer superlattice shows a single (111) peak with satellite peaks from the superlattice structure (arrows in the inset). [1]