Structure, magnetism and transport properties of Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ bulk and thin film materials

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ABSTRACT

The structural and magnetotransport properties of the solid solution \( \text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) were explored using chemical, epitaxial and physical pressure. The experimental procedure involved solid state synthesis and film growth using pulsed laser deposition (PLD). Extensive magnetotransport and structural characterization using x-ray diffraction and Rietveld refinements were carried out to understand the correlations between the structure and properties. Additionally, high pressure neutron powder diffraction (HPNPD) experiments were completed in order to investigate magnetic order as a function of physical pressure.

The magnetoresistance (MR) of several \( \text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) compositions in bulk and thin films were explored. In the bulk, three different regions were defined to help explain their MR properties. Region I was composed of the ferrimagnetic \( x = 1, 0.5 \) compositions which exhibited a sharp low field MR reminiscent of intergranular tunneling magnetoresistance (TMR). Region II contained the \( x = 0.25 \) two-phase composition which exhibited the largest MR of \(-67\%\) MR at 25 K. Finally, region III contained the antiferromagnetic \( x < 0.25 \) compositions which exhibited MR as high as \(-55\%\) for the full Sr analogue. The MR properties of this region are influenced by the increasing size of the AFM domains and formation of magnetic clusters under applied magnetic fields. Additionally, exchange bias (EB) was observed in the MR loops of the Sr-containing compositions but not the ferrimagnetic Ca-end member. This is a good indication that the EB
observed is highly dependent upon the ratio of the antiferromagnetic regions to the ferri-
magnetic regions. In order to minimize grain boundary effects that can dominate the be-
havior of bulk materials, thin films of the \( x = 0, 0.25 \) and 1 compositions were grown and
the magnetotransport data collected. The comparative data of the bulk and film materials
illustrates that their MR and conductivity trends are similar. However, the \( x = 0.25 \) com-
position in the films exhibits the largest negative MR of the samples studied, \(-93\%\) at
low temperatures.

The sensitivity of \( \text{CaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) and \( \text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) films to lattice mismatch
induced grain boundaries effects and different growth atmospheres (respectively) was
determined. \( \text{CaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) films were grown on LSAT and \( \text{SrTiO}_3 \) which have different
lattice mismatches. From this study, the most bulk-like films were grown on LSAT, which has a smaller lattice mismatch than the \( \text{SrTiO}_3 \). \( \text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) films grown in dif-
f erent levels of \( \text{pO}_2 \) exhibited an increase in lattice parameters, but there were limited ef-
fects upon the conductivity, stoichiometry and magnetoresistive properties. This suggests
that the properties of these materials may be relatively insensitive to moderate levels of
oxygen vacancies.

Finally, the magnetic order of orbitally-ordered \( \text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) was monitored us-
ing HPNPD. These experiments were completed at pressures ranging from 0 GPa to
8 GPa and at temperatures above and below the magnetic ordering temperature of 200 K.
Anisotropic compression of the axial bonds containing Jahn-Teller distorted \( \text{Mn}^{3+} \) ions
dominated at pressures below 2 GPa. Above this pressure, an increase in octahedral til-
ing was observed. However, the increase in octahedral tilting at 8 GPa was not enough to
completely destroy the orbital ordering and drive the magnetic order from antiferromagnetic to ferrimagnetic nor a phase transition to lower symmetry.
This dissertation is dedicated to my parents, James and Mary Meyer.
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Chapter 1

Introduction

Property tuning of materials using different methods provides a slew of new and exciting phenomena. For example, one common method of property tuning is by chemical substitution, or chemical pressure. These same compounds may be grown as epitaxial films and their properties adjusted using epitaxial pressure induced by substrates of different crystal lattice size. In some cases, applying external pressure to induce structural changes or phase transitions can also have a large impact upon the physical properties.

One of the most well-known and perhaps tunable structure-types studied in solid state chemistry is the perovskite structure. This is in part due to the inherent flexibility of the structure to accommodate elements of different sizes and charges. As a result, the transport and magnetic properties of this structure type are extremely diverse, including applications in superconductivity\(^1\), solid oxide fuel cells\(^2\), and data storage devices\(^3\).

In this chapter, the goal will be to provide a general background of the various structural and physical properties of perovskite materials in order to guide the reader in topics discussed in this dissertation. A brief summary of the solid solution \(\text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3\) will be presented as well since these compounds are the focus of the discussed research.
1.1 Perovskite Structure

Perovskites are an incredibly versatile and flexible structure-type able to accommodate many different elements and structural distortions. A depiction of a simple cubic $ABX_3$ perovskite (space group $Pm\bar{3}m$) is illustrated in Figure 1.1. The A-site cation contains 12-fold coordination with surrounding oxygen ions to form a cuboctahedron environment. The B-site cation is typically smaller than the A-site cation and sits within an octahedron coordinated to 6 oxygen ions, X. These octahedra are considered “corner-sharing”.

![Diagram of ABX3 perovskite structure](image)

**Figure 1.1:** Structure of $ABX_3$ perovskites structure (center). Upon substitution of second B-site cation, $B'$, leads to either ordered $A_2BB'X_6$ (left) or disordered $AB_{0.5}B'_{0.5}X_3$ (right) perovskite structure.

The introduction of a second cation, $B'$, is illustrated as well. The left is an example of a 1:1 rock salt ordered double perovskite, $A_2BB'X_6$, where two $B$-cations reside on distinct atomic sites resulting in a doubled unit cell edge. The right image illustrates a disordered $AB_{0.5}B'_{0.5}X_3$ perovskite where the two $B$-site cations are randomly oriented. Whether a
perovskite will be fully ordered, partially ordered, or completely disordered is determined by the size and charge differences of the $B$-site cations as well as synthesis conditions. Woodward et al. determined that when the charge difference between $B$ and $B'$ is greater than two, rock salt ordering is observed. If the charge difference between $B$ and $B'$ is equal to two, anti-site disorder (ASD) results. In many cases when the charge difference is equal to two, ASD may be tuned using different synthesis conditions as in the case of $\text{Sr}_2\text{Al(Ta,Nb)}\text{O}_6$.

### 1.1.1 Tolerance Factor

The structural stability of a perovskite is determined by the Goldshmidt tolerance factor, $\tau$, given by equation 1.1:

$$\tau = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$$  \hspace{1cm} [Equation 1.1]

where $R_A$, $R_B$, and $R_X$ are the ionic radii for $A$, $B$, and $X$. Ideal cubic perovskites have tolerance factors of unity, or $\tau = 1$, though the perovskite structure may be stabilized for values of $1.05 > \tau > 0.78$. Deviation from unity occurs when the $A$-site cation is either too large or too small for the network of corner shared octahedra, resulting in $\tau > 1$ or $\tau < 1$ (respectively). These deviations often cause tilting of the $BX_6$ octahedra and hence a reduction in symmetry. Due to the relationship of the tolerance factor and ionic radii, this value provides insight into the likelihood of distortion from the cubic symmetry in many perovskites.
1.1.2 Octahedral Tilting

Since examples of the ideal cubic perovskite with $\tau = 1$ are rare, the variety of physical properties observed often result from various distortion mechanisms. One of the most common distortions within perovskites is octahedral tilting. Octahedral tilting is described by rotations of the octahedra about specific crystallographic axes which result in a reduction of the A-site coordination. This is common when $\tau < 1$. In order to classify the octahedral tilting scheme associated with a certain crystal symmetry, a notation system was developed by Glazer. This classification system was further advanced by the works of Woodward and Howard and Stokes.

Glazer notation describes the tilt with respect to the rotation about the three primary Cartesian axes—$x$, $y$, and $z$. These are labeled as $a$, $b$, and $c$ degrees about the crystallographic axes when the angles of rotation are unequal. When the notations are given positive superscripts, an in-phase tilt is indicated, or one in which the octahedral layers rotate in the same direction. Alternatively, a negative superscript is used when the octahedra rotate in the opposite direction, or an out-of-phase tilt. The designation of a zero superscript is used to indicate no rotation. Representations of in-phase and out-of-phase tilting along the $c$-axis compared to an ideal perovskite structure with no tilting are illustrated in Figure 1.2.
1.1.3 Jahn-Teller Distortions and Orbital Order

Another common distortion in perovskites is that within the $BO_6$ octahedra. An example of this type of distortion is driven by the Jahn-Teller (JT) effect. This effect is commonly observed in compounds containing JT active ions including high spin Mn$^{3+}$, Cr$^{2+}$ ($d^4$, $t_{2g}^3e_g^1$), low spin Ni$^{3+}$ ($d^7$, $t_{2g}^6e_g^1$), and Cu$^{2+}$ ($d^9$, $t_{2g}^6e_g^3$) where the $e_g$ orbitals, $d_{z^2}$ and $d_{x^2-y^2}$, contain an odd number of electrons. Figure 1.3 illustrates the possible JT distortions for a high-spin $d^4$ ion in an octahedral coordination. If the $d_{z^2}$ orbital is occupied, degeneracy is removed by lengthening the metal-oxygen bonds along the $z$-direction and contracting those in the $xy$-plane. This destabilizes (raises in energy) the $d_{x^2-y^2}$ orbital and stabilizes (lowers in energy) all orbitals containing the $z$-component ($d_{z^2}$, $d_{xz}$, $d_{yz}$). Alternately, when the electron resides in the $d_{x^2-y^2}$ orbital, elongation of bonds in the $xy$-plane and contraction of bonds in the $z$-direction causes a loss of degeneracy.

Figure 1.2: Glazer tilt scheme (a) ideal cubic perovskite with no in- or out-of-phase tilting, $a^0a^0a^0$ (b) in-phase tilting about the $c$-axis, $a^0a^0c^+$ and (c) out-of-phase tilting about the $c$-axis, $a^0a^0c^-$. 
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1.1.3.1 LaMnO$_3$, a distorted perovskite with orbital order

Perovskite materials derived from LaMnO$_3$ continually yield exciting properties. For example, the substituted analogues Ca$_x$La$_{1-x}$MnO$_3$ are metallic ferromagnets exhibiting colossal magnetoresistance$^{12}$ while the unsubstituted composition is an antiferromagnetic insulator. This leads to an interesting discussion of the structure of the parent compound. LaMnO$_3$ contains a Mn$^{3+}$ ion which induces a JT distortion due to the singly occupied $e_g$ orbital and leads to formation of two elongated bonds.$^{13}$ It is noteworthy that the JT distortions of the MnO$_6$ octahedra are not independent from one another, but rather they are cooperative. The two long bonds containing the JT distortion are pointed down the $ab$-plane and are oriented 90° from one another in the unit cell. The JT distortion in
LaMnO$_3$ exists in conjunction with another structural phenomenon called orbital order. The pattern of elongated bonds signals ordering of the occupied $e_g$ orbitals. The structure of LaMnO$_3$ and the resultant orbital ordering are illustrated in Figure 1.4.

Figure 1.4: Pictorial representation of the structure of LaMnO$_3$ down several axes. The pattern of orbital order of the $d_{z^2}$ orbitals is included on the far right.

1.2 Types of Magnetic Behavior

Since magnetism is an important topic within this dissertation, a short discussion of the terminology must be presented. Generally speaking, magnetism may be broken up into five areas: diamagnetism, paramagnetism, antiferromagnetism (AFM), ferromagnetism (FM), and ferrimagnetism (FiM). Diamagnetic compounds have electrons which are all paired and hence they have no moment. These include simple diatomics such as O$_2$ or more complex oxides like SrTiO$_3$\textsuperscript{14}. With the exception of paramagnets whose spins
have a random and dynamic orientation, the other classes of magnetic materials magnetically order. A FM is defined as a material whose magnetic spins are oriented parallel with each other which produces a net magnetic moment. A FiM exhibits a very similar experimental signature as a ferromagnet and a net moment, but has antiparallel magnetic spins of different magnitude. Like the ferrimagnet, an AFM has magnetic spins pointed in opposite directions, but they are of the same magnitude and hence have no net magnetic moment. In primitive cubic (or pseudocubic) lattice, the magnetic moments of the AFM may be oriented in three different manners: C-type (alternating columns), A-type (alternating planes), and G-type (alternating within the planes and column). Figure 1.5 illustrates the different configurations of magnetic spins within a lattice for each of the listed areas.
Figure 1.5: Different types of magnetic ordering are illustrated: paramagnetism, ferromagnetism, ferrimagnetism, and antiferromagnetism. Antiferromagnetism is broken down into three different types commonly observed, A-type, C-type, and G-type.

The experimental magnetic signature of a material may be described by studying the hysteresis curves of magnetic moment versus field and magnetic susceptibility versus temperature. From these two measurements, information regarding the saturation magnetization ($M_{\text{sat}}$), coercivity ($H_c$), and the temperature in which magnetic order subscribes to paramagnetism may be obtained. Examples of the experimental measurements for each of these are shown in Figure 1.6. The magnetic ordering temperatures for a ferromagnetic
and ferrimagnet are called the Curie temperature, $T_C$, and for an AFM, the Néel temperature, $T_N$.

![Graphs showing magnetic behavior](image)

**Figure 1.6:** Experimental depiction of magnetic moment (M) versus magnetic field (H) (top) and magnetic moment versus temperature (T) (bottom) measurements for (a) ferromagnetism and ferrimagnetism (b) antiferromagnetism and (c) paramagnetism. The magnetic order temperatures are highlighted in (a) and (b).

### 1.2.1 Frustrated Magnets

Since the magnetic interactions in a material are often complicated, not every magnetic behavior may be described by the traditional terminology. Compounds which suffer from both structural and magnetic inhomogeneity and disorder are often defined by a class of magnetism referred to as “frustrated”. In many cases, systems defined as frustrated are referred to as spin-glasses.\(^{15}\) While this branch of magnetism is very complex, a
“simple” picture of geometric magnetic frustration may be grasped through the representation of a 2D kagomé lattice. For example, compounds with the α-NaFeO$_2$ structure type are highly susceptible to frustration as the structure is composed of layered equilateral triangles. An illustration of this structural arrangement in the compound NaCrO$_2$ is provided in in Figure 1.7. Here, a triangular configuration of three Cr atoms is highlighted with a dotted triangle. The geometry is frustrated as two out of the three spins are oriented opposite one another, but the third spin (labeled with a question mark) has no preference for one orientation or the other. This type of spin disorder leads to frustration. In comparison, traditional FM and AFM materials are able to order based upon the orientation and exchange coupling of neighboring spins.

It may now be obvious that the concept of frustration may further be applicable to other systems which include tetrahedral structures such as pyrochlores$^{16}$ or double perovskites$^{17}$ where only one of the $B$-site cations are magnetic. The potential for many different types of magnetism in a material implies that an accurate picture of the structure is essential in order to fully grasp its magnetic properties.
NaCrO$_2$ structure illustrating geometric frustration due to 2D triangular kagomé lattice. The question mark represents the third spin whose orientation is not coupled with neighboring spins.

### 1.3 Exchange Interactions

The impression thus far should be that perovskites are more than just a simple network of octahedra. They are complex structures such that the degrees of freedom including elemental substitution and structural distortions are quite numerous. These degrees of freedom have a large influence in both the magnetic and transport properties. Therefore, it is necessary to present possible exchange interactions which may occur to better understand the physical properties of the materials in this dissertation. While many exchange interactions are possible, the focus will be limited to superexchange and double exchange.
1.3.1 Superexchange

The magnetic character of transition metal oxides is highly dependent upon the mechanism of superexchange.\textsuperscript{18,19} This mechanism describes the indirect magnetic exchange interactions which exist between localized electrons of two transition metals separated by a nonmagnetic oxygen ion. The initial works by Kanamori, Goodenough and Anderson provided the groundwork for predicting the sign and magnitude of magnetism induced by these superexchange interactions.\textsuperscript{19-21} This was achieved by using snapshots of the electronic structure of the magnetic ions involved. Their combined work became known as the Goodenough-Kanamori-Anderson (GKA) rules. For example, in the case of Fe$^{3+}$–O–Cr$^{3+}$, a d$^5$–d$^3$ system, the oxygen 2$p$ orbital overlaps with an empty $e_g$ orbital of the Cr$^{3+}$ cations. Since the spin orientation of the $t_{2g}$ and $e_g$ orbitals must have the same spin as dictated by Hund’s rule coupling, the overall coupling between the two cations is then FM. An illustration of this is shown in Figure 1.8.
Figure 1.8: Ferromagnetic superexchange between a $d^5-d^3$ system. The electron distribution (top) of the metal ions and the orbital interaction between the $e_g$ orbitals and the oxygen $2p$ orbitals (bottom) are illustrated.

There are several variables which determine the strength of these superexchange interactions. One factor to consider are the orientations of the orbitals involved and the types of bonds present in the superexchange. The AFM monoxides MnO, FeO, CoO, and NiO are good examples of how the strength of the superexchange may vary between compounds and affect their magnetic properties.Interestingly, the Néel temperature increases according to MnO<FeO<CoO<NiO which suggests an increase in the strength of the AFM superexchange as the size of the metal ion decreases. Since all of the compounds exhibit 180° superexchange, this trend is best explained by the decrease in the metal-oxygen bond length due to decreased ionic radii. More simply, good orbital overlap is essential for efficient superexchange. In the same way, superexchange involving π-
bonds would be much weaker than those with σ-bonds due to weaker orbital overlap. A pictorial representation of π- and σ-bond based superexchange is illustrated in Figure 1.9.

**Figure 1.9:** Superexchange interactions involving (a) sigma and (b) pi-bonding. The sigma bonds have better orbital overlap than the pi-bonds leading to stronger superexchange.

1.3.1.1 **Superexchange in LaMnO₃**

The interesting orbital order pattern of the compound LaMn³⁺O₃ was previously discussed in Section 1.2. This compound illustrates A-type AFM which is facilitated through superexchange. In order to provide an explanation for how magnetism and superexchange may be correlated, the superexchange interactions of LaMnO₃ are illustrated in Figure 1.10. Here, three different superexchange processes are illustrated, two FM and one AFM. Figure 1.10(a) shows that 180° superexchange interaction between two Mn³⁺
$d_z^2$ orbitals oriented along the $z$-axis occurs when both ions contain one electron of antiparallel arrangement.\textsuperscript{22} The “virtual” hopping of the oxygen $2p_z$ electrons determines the AFM configuration. It is important to distinguish that the term “virtual” hopping is not a physical transfer of the electron as these are localized. Rather, this term describes the transfer of the spin information through the covalent interactions with the diamagnetic oxygen ion. \textbf{Figure 1.10}(b) shows an example of 180° FM superexchange. Here, the first Mn\textsuperscript{3+} ion contains a singly occupied $d_z^2$ orbital but the second contains none. As a result, virtual hopping of the oxygen $2p_z$ electrons to the unoccupied $d_z^2$ site aligns the electrons in a parallel, FM configuration. The third example demonstrates FM superexchange between two Mn\textsuperscript{3+} $d_z^2$ orbitals corner-sharing one oxygen ion. In contrast to \textbf{Figure 1.10}(b), virtual hopping of one electron from the occupied oxygen $2p_z$ and $2p_y$ orbitals induces a 90° FM superexchange between the Mn\textsuperscript{3+} ions. It was previously mentioned that the A-type AFM of LaMnO\textsubscript{3} is dictated by the $d_z^2$ orbitals oriented perpendicular to one another.\textsuperscript{13} In spite of having more FM interactions, the AFM superexchange is considerably stronger.
Figure 1.10: The superexchange pathways of orbitally ordered LaMnO$_3$ are illustrated. The $d_{z^2}$ orbital of each Mn$^{3+}$ ion is occupied by one electron and the $d_{x^2-y^2}$ remains empty (gray). The three oxygen-2p orbitals are fully occupied. Depending on the orbital occupation will determine if the interaction is (a) AFM or (b) and (c) FM. The $t_{2g}$ orbitals are indicated by the grouping of three arrows. Image modified from reference [22]
1.3.2 Double exchange

Many transition metal oxides are susceptible to superexchange interactions. However, a large driving force for FM in the perovskite family is the double exchange (DE) mechanism. Clarence Zener first proposed this mechanism to describe the FM alignment of magnetic moments in the Mn\(^{3+}\) and Mn\(^{4+}\) coupled pair.\(^{24}\) The classical model provided by Zener is depicted in Figure 1.11(a). Here, an indirect coupling between the Mn ions and oxygen 2\(p\) orbital is illustrated. This interaction directs a two electron transfer process from the JT distorted Mn\(^{3+}\) \(e_g\) orbital to the central oxygen 2\(p\) orbital followed by an electron transfer from the oxygen 2\(p\) orbital to the Mn\(^{4+}\) \(e_g\) orbital.

In many cases, however, the indirect coupling of the Mn ions with oxygen is neglected entirely in the DE mechanism. Several theoretical studies have demonstrated a stabilized FM state using only the magnetic Mn ions.\(^{25,26}\) This has been attributed to large Hund’s coupling between Mn ions which minimize their kinetic energy. This action enables direct hopping of the Mn \(e_g\) electrons to other Mn ions. In many ways, the term “double exchange” is not an accurate description of the process, but remains the term most used in scientific literature. A DE model derived from the current understanding of the electron transfer has been used to describe ferrimagnetism in the double perovskite, Sr\(_2\)FeMoO\(_6\).\(^{27}\) An illustration of the modified DE model is shown in Figure 1.11(b).

Regardless of the DE definition, the model maintains several consistencies between the two definitions. In contrast to superexchange, DE requires a pathway between mixed-valent ions. Additionally, the Mn\(^{3+}\) electron is said to be itinerant in that it becomes delocalized throughout the structure. In accordance with Hund’s rules, the itinerant electron does not change its spin direction when moving to the empty Mn\(^{4+}\) \(e_g\) orbit-
The polarized and itinerant character of the transferred electrons lend themselves to many exciting properties observed including colossal magnetoresistance and metallic conductivity.

Figure 1.11: Double exchange mechanism between Mn$^{3+}$ and Mn$^{4+}$ ions. (a) Classical, indirect model proposed by Zener\textsuperscript{24} showing two-electron transfer starting from the occupied Mn$^{3+}$ $e_g$ orbital to the O-$2p$ orbital followed by electron transfer from the O-$2p$ orbital to the empty Mn$^{4+}$ $e_g$ orbital and (b) Direct double exchange model illustrating spin-polarized electron hopping process from Mn$^{3+}$ to Mn$^{4+}$. Double exchange leads to a mixed valent system where Mn$^{3+} \leftrightarrow$ Mn$^{4+}$. Here, the Mn$^{3+}$ ion exhibits a JT distortion.
1.4 Magnetoresistance

A large focus of this dissertation will be placed upon the magnetoresistance (MR) of several different perovskite compounds. Magnetoresistance is undoubtedly one of the most important physical properties observed in correlated electron systems. Not only does MR provide insight into the spin-dependent transport in solids, but also has a dramatic influence upon the efficiency of many data storage devices. The property of MR was realized as early as 1856 by William Thomson (Lord Kelvin) whose experiments revealed an increase in the resistance of certain metals with the application of a magnetic field. However, this “ordinary” MR was only on the order of a few percent. Since then, the discovery of giant (GMR), tunneling (TMR), and the even larger colossal (CMR) magnetoresistance have propelled studies of electronic and magnetic materials.

CMR is often considered an intrinsic property of bulk materials and does not rely on coupling between multilayers as is the case of GMR and TMR. CMR is most often associated with manganite perovskites in which charge ordering and phase separation facilitates the change of resistance with the application of a magnetic field. One of the best examples is with La$_{0.33}$(Ca,Sr)$_{0.67}$MnO$_3$ where the CMR reaches values near 125,000%. The effect is maximized near the magnetic ordering temperature and the metal to insulator transition of the compound. Therefore, searches for materials exhibiting high-$T_C$ ferromagnetism and CMR are perpetually underway.

Baibich et al. discovered GMR in metallic (001)Fe/(001)Cr superlattices where the application of a 2 tesla magnetic field reduced the electrical resistance by nearly two orders of magnitude. Since then, GMR devices have been further developed for technical applications. In a GMR heterostructure, two ferromagnetic metallic layers (FMM),
or electrodes, are ferromagnetically (or antiferromagnetically) coupled through a non-magnetic, metallic (NMM) layer. When the spins of the two FMM are coupled antiparallel ($H_{\text{ext}}=0$), a high-resistance state occurs due to a large amount of spin dependent scattering.\(^{30}\) This process is illustrated in Figure 1.12. Here, the scattering arises when the conduction electrons (shown in red) of the bottom FMM electrode are oriented opposite of the spins direction of the electrodes. When the orientation of the magnetic spins are oriented parallel with the application of a magnetic field ($H_{\text{ext}}\neq0$), a low resistance state occurs and their scattering is minimized. In other words, the conduction electrons oriented in the same direction of the FMM electrodes are not scattered. The reduction in spin dependent scattering at the interfaces of these structures is the crux of GMR efficiency. The GMR effect is very applicable due to the ability to “switch” the magnetic layers from one configuration to the other. This phenomena is called a spin-valve device and illustrates the extrinsic nature of GMR which relies on coupling between two or more components.
Figure 1.12: Heterostructures illustrating the (a) spin dependent scattering processes observed in GMR spin-valves at applied and zero-applied magnetic fields. The red arrows represent the spin-orientation of the up- and down-spin conduction electrons and the narrow red arrows show the scattering processes which occur when their spins are oriented in the same direction as the top and bottom electrodes.

Another branch of MR common to perovskite materials is tunneling magnetoresistance (TMR) which was discovered in 1975 by Jullière.\textsuperscript{31} One of the best visual examples of TMR is magnetic tunnel junctions (MTJs), Figure 1.12(b). MTJs have some similarities to GMR multilayers, but require an insulator instead of NMM separating the two FMM layers. The presence of an insulator prevents strong magnetic coupling between the two electrodes but facilitates spin dependent tunneling of conduction electrons through this layer from the bottom to the top electrode. The weaker coupling between the two
FMM layers causes a much larger change in MR and at much lower fields than in GMR.\(^{30}\)

TMR may also manifest itself in terms of polycrystalline materials containing a certain degree of inhomogeneity. For example, the double perovskite \(\text{Sr}_2\text{FeMoO}_6\) exhibits large TMR effects often attributed to intergranular tunneling of electrons between insulating \(\text{SrMoO}_4\) and \(\text{Sr}_2\text{FeMoO}_6\) grains in bulk samples.\(^{32}\) Additionally, TMR has also been demonstrated in \(\text{Fe}_3\text{O}_4\), \(\text{CrO}_2\) and \(\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3\) materials where the grain size was controlled. One of the largest indicators of TMR in materials is when the two peaks of the magnetoresistance curve, \(H_{\text{C(MR)}}\) occurs at the coercive field, \(H_C\), of the saturation magnetization versus field curve.

It is important to mention that magnetoresistance is an extremely applicable property, but isolating factors which contribute to its magnitude and behavior may be quite challenging. This is particularly the case for structurally disordered materials which may suffer from both magnetic and electronic disorder. Furthermore, bulk materials may be engineered to contain FM of different coercivities, core-shell particles of varying magnetic character, and even magnetic particle embedded matrices. These are all systems which can impact the magnetoresistance.

1.5 \textit{Ca}_x\textit{Sr}_{1-x}\textit{Mn}_{0.5}\textit{Ru}_{0.5}\textit{O}_3, an interesting family of compounds

The disordered perovskites \(\text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3\) are quite interesting for a multitude of reasons. One reason they are intriguing is due to the different properties observed in each of the parent compounds. These properties are listed in Table 1.1. There are not only changes in the magnetic properties, but the electronic properties of each compound.
Perhaps the most notable feature about the solid solution composed of these parent compounds is the unique array of physical and structural properties in spite of the complete absence of long range chemical order of the Mn and Ru ions, as depicted in the right of Figure 1.1. In spite of this disorder, ferrimagnetic, metallic behavior is observed in the Ca end member while antiferromagnetic insulating behavior is present in the Sr end member. The unique electronic and magnetic properties of these compounds warrant a discussion of their crystal structure.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Magnetism</th>
<th>$T_C/T_N$ (K)</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrMnO$_3$ [36]</td>
<td>Antiferromagnetic</td>
<td>235</td>
<td>Insulating</td>
</tr>
<tr>
<td>SrRuO$_3$ [36]</td>
<td>Ferromagnetic</td>
<td>165</td>
<td>Metallic</td>
</tr>
<tr>
<td>CaMnO$_3$ [37]</td>
<td>Antiferromagnetic</td>
<td>120</td>
<td>Insulating</td>
</tr>
<tr>
<td>CaRuO$_3$ [37]</td>
<td>Paramagnetic</td>
<td>–</td>
<td>Metallic</td>
</tr>
<tr>
<td>Strained CaRuO$_3$ [38,39]</td>
<td>Ferromagnetic</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 1.1: Structural and magnetic ordering information for the ternary compounds related to the Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ solid solution. Reference [39] is theoretical.

The magnetism may best be described by the structural distortions which vary across the solid solution. SrMn$_{0.5}$Ru$_{0.5}$O$_3$ exhibits a cooperative Jahn-Teller (JT) distortion corresponding to the occupied Mn$^{3+}$ $d_{z^2}$-orbitals along the elongated c-axis.$^{40-42}$ This distortion is correlated with unique orbital ordering and superexchange pathways which lead to a C-type antiferromagnetic ($T_N = 215$ K), insulating state and a tetragonal unit cell ($I4/mcm, a^0a^0c^-$).$^{40,41}$ A pictorial representation of C-type AFM is provided in Figure 1.5. Like LaMnO$_3$ where the ordered $d_x^2$ orbitals are closely linked with the A-type AFM, C-type AFM in SrMn$_{0.5}$Ru$_{0.5}$O$_3$ is influenced by 1D FM chains of Mn$^{3+}$–O–Ru$^{5+}$ oriented
in the direction of the occupied $d_{z^2}$ orbitals. The formation of FM chains is driven via superexchange described in section 1.3.1.

For full calcium substitution ($x = 1$), ferrimagnetic, metallic behavior replaces the AFM insulating character. Neutron diffraction studies reveal that this is most likely due to the increased tilting of the RuO$_6$ and MnO$_6$ octahedra, disrupting the orbital ordering. The increased tilting is further supported by the loss of tetragonal symmetry with the onset of an orthorhombic distortion ($Pnma$, $a^{-}b^{+}a^{-}$). One other exciting feature of the full Ca-analogue is the predicted 100% spin-polarization in spite of complete chemical disorder. A comparison of the two end members is shown in Figure 1.13.

<table>
<thead>
<tr>
<th>SrMn$<em>{0.5}$Ru$</em>{0.5}$O$_3$</th>
<th>CaMn$<em>{0.5}$Ru$</em>{0.5}$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal, I4/mcm</td>
<td>Orthorhombic, Pnma</td>
</tr>
<tr>
<td>AFM (C-type)</td>
<td>Ferrimagnetic</td>
</tr>
<tr>
<td>Orbital ordering</td>
<td>No orbital ordering</td>
</tr>
<tr>
<td>insulating</td>
<td>“metallic”</td>
</tr>
</tbody>
</table>

Figure 1.13: Comparison of the structural and physical properties of the two end-members in Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. A representation of the crystal structures with octahedral tilting with the tilt system is illustrated below.
1.5.1 Magnetoresistance in Mn and Ru based perovskites

There have been few studies discussing the magnetoresistance of the end members of this solid solution and even fewer of the intermediate compositions. The ternary perovskite SrRuO$_3$ has been studied primarily for its unique itinerant ferromagnetism$^{44}$, but the MR has only been briefly studied. Small substitutions of 10% – 20% manganese for ruthenium were shown to increase the magnetoresistive character of SrRuO$_3$ by several percent.$^{45}$ Zhang et al. reported a large maximum MR of $-41\%$ at 10 K and 7 Tesla for the $x = 0.55$ composition in SrMn$_x$Ru$_{1-x}$O$_3$.$^{46}$ Both studies suggest that the introduction of manganese enhances the MR by significant amounts, primarily due to effects of disorder and antiferromagnetic interactions. It should be noted that the study of MR by Zhang et al. consisted of samples of SrMn$_x$Ru$_{1-x}$O$_3$ which exhibited significant magnetic inhomogeneity, much different than the reports by Woodward et al.$^{40,41}$ It is likely that this inhomogeneity played a significant role in the magnetoresistance. The CaMn$_x$Ru$_{1-x}$O$_3$ system has also been investigated. Raveau et al. observed the CMR effect with up to 10% Ru substitution.$^{47}$ Substitutions near 40% revealed an MR which increased with decreasing temperatures and exhibited a dependence upon magnetic field, contrary to the CMR effect.$^{48}$ The dual substituted composition Ca$_{0.3}$Sr$_{0.7}$Mn$_{1-x}$Ru$_x$O$_3$ was also explored and the MR properties reported.$^{49}$ At 10 K and 5 T, a negative MR of $-30\%$ was observed for the $x = 0.5$ composition and was the highest MR values across the whole substitution range of Mn and Ru. This composition also exhibited the largest magnetic moment and equal concentration of Mn$^{3+}$, Mn$^{4+}$, Ru$^{4+}$ and Ru$^{5+}$ ions. Interestingly, Ricciardo et al. reported this composition as a two-phase mixture of tetragonal and orthorhombic phases while the previous group reported only a single tetragonal phase.$^{42}$ This is likely due to differences
in synthetic conditions, but since this composition lies at the structural and magnetic phase boundary, a two-phase mixture could present interesting MR behavior.

There are clearly no systematic studies of the MR of Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ in the literature. Furthermore, the inconsistencies in the homogeneity between the compositions reported make it challenging to understand the mechanism of the MR in these compounds. If a better grasp of these properties in this system is determined, it may be possible to design and develop new magnetoresistive compounds from other disordered materials.

1.6 Research Summary

The structural complexity and sensitivity of the Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ system to chemical pressure presents an interesting opportunity to further explore structure-property correlations under both epitaxial and physical pressure as well. Film growth of any of the Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compositions is a relatively unexplored area, but could reveal further insight into its structure-property relationships. While much attention is paid to A-site doped manganites which exhibit CMR, little focus has been given to the magnetoresistive properties of Ru-doped perovskites.

The research in this dissertation presents a comprehensive investigation of the crystal and magnetic structure and transport properties of the solid solution Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. These properties were studied via several different methods including both bulk and thin film materials. Bulk materials were prepared via traditional solid state synthesis and thin films were made using pulsed laser deposition (PLD). Using two different synthetic techniques provides a way to differentiate between factors affecting physical
properties such as grain boundaries and sample inhomogeneity. It also grants a practical look into the application of these compounds in thin film devices.

Since several characterization techniques were used, a separate description of the instrument parameters and other experimental information are provided in Chapter 2. Any information specific to the research discussed in subsequent chapters are provided within the experimental sections. These descriptions are provided for PLD (basics and growth parameters), x-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), superconducting quantum interference device (SQUID) magnetometry, transmission electron microscopy (TEM), and neutron diffraction.

Chapter 3 is focused on the magnetotransport properties of bulk \( \text{Ca}_{x} \text{Sr}_{1-x} \text{Mn}_{0.5} \text{Ru}_{0.5} \text{O}_3 \). A comprehensive illustration of the MR as a function of Ca-substitution is presented with an emphasis on the effects of disorder and orbital order. The shift in magnetic and electrical character and degree of orbital order across the solid solution presents a unique opportunity to study the MR systematically. The inhomogeneity due to disorder in these compounds could lead to potential exchange bias phenomena.

A comparative study of bulk and thin film magnetoresistance of the compositions \( x = 0, 0.25, 1 \), where the \( x = 0.25 \) is two-phase, is presented in Chapter 4. This enables minimization (ideally) of grain boundary effects upon the magnetotransport properties. Additionally, thin films of these compositions have been studied very little. Exploration of their properties provides insight into their potential as spintronic device components.

Chapter 5 discusses the PLD growth and characterization of \( \text{CaMn}_{0.5} \text{Ru}_{0.5} \text{O}_3 \) epitaxial films. The goal of this work was to (1) successfully report the growth of the material (2) characterize the transport properties (electrical conductivity, magnetic properties,
MR) and (3) determine the effect of lattice mismatch. The properties of the films were tuned using epitaxial lattice mismatch by growing on SrTiO$_3$ and LSAT substrates.

Chapter 6 covers the PLD growth and characterization of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ epitaxial films. As in Chapter 5, the goal is to grow the material and provide characterization of the structural and magnetotransport properties. Additionally, the effect of oxygen vacancies upon the transport and structural properties was investigated. This was achieved by tuning the growth atmosphere and pressure.

The final chapter presents the results from high-pressure neutron powder diffraction experiments of SrMn$_{0.5}$Ru$_{0.5}$O$_3$. This compound contains orbital order along the c-axis and a Jahn-Teller active Mn$^{3+}$ ion. Therefore, the application of high-pressure presents an opportunity to simulate chemical pressure and potentially create new structural and magnetic phases.

1.7 References


5. V. M. Goldschmidt, Naturwissenschaften, 14 (1926), pp. 477–485


Chapter 2

Experimental Methods

2.1 Introduction

When investigating bulk and thin film materials, a wide variety of synthesis and characterization techniques are utilized. The purpose of this chapter is to introduce the technique of solid state synthesis and provide an introduction to pulsed laser deposition, one of the primary techniques utilized in this work. The properties of the films under investigation were tuned via many methods including varying the growth atmosphere, temperature and substrate composition. Additionally, a wide variety of analytical characterization techniques were employed for this project. In order to prevent redundant descriptions in subsequent chapters, these techniques are described in the following sections.

2.2 Bulk Powder Synthesis

Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ ($x = 0, 0.125, 0.25, 0.50, 1$) bulk powders were synthesized according to tradition solid state synthesis. Stoichiometric amounts of CaCO$_3$, SrCO$_3$, RuO$_2$ and Mn$_2$O$_3$ were ground in an agate mortar and pestle until the powder was uniform. The powder was placed in an alumina crucible and heated in a high-temperature box furnace at 1385 °C for 8 hours at a heating and cooling rate of 10 °C/min. Pure-phase powder was obtained and then ground for 3 hours to reduce the crystallite size.
2.3 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is one of the most versatile, quick and cost-effective techniques to grow films of many different compositions.\(^1\) However, nearly thirty years of technological advances in lasers and vacuum systems occurred before PLD became a technique capable of efficient device fabrication. It was not until the first high-power ruby laser was introduced in the 1960’s by Theodore Maiman that provided evidence of interactions between a laser and a material’s surface.\(^1,2\) Shortly after this development, deposition of dielectric and semiconducting thin films were achieved by A. F. Turner and H. M. Smith.\(^3\) Several decades later, PLD became a truly viable technique of fabrication with the deposition of the high-T\(_C\) superconductor, YBa\(_2\)Cu\(_3\)O\(_7\).\(^4\) This growth was the first demonstration of stoichiometric transfer of a complex oxide from a target material to a film.

While PLD has many advantages over other deposition methods, several disadvantages are apparent. One of the greatest limitations of traditional PLD is maintaining uniform deposition. Since the plume which contains the target material has a specific orientation and conical shape, large substrates must be avoided in order to reduce thickness gradients. Understanding the dynamics of the plume, specifically methods to tune its size and shape via growth conditions, is one means to maintain the film uniformity. Another common issue is the potential for large droplet formation (also known as the splashing effect) during the growth and nucleation of the film.\(^5,6\) Droplet formation during growth leads to a poor surface structure not ideal for heterostructures or for obtaining homogeneous films. The formation of these particulates are caused by factors such as the laser fluence (or laser energy per unit area, J/cm\(^2\)) or loss of oxygen at the target surface.\(^7,8\) In or-
der to prevent this from occurring, careful optimization of growth conditions such as the laser fluence and target conditions are necessary.

In the following subsections, the mechanism of PLD will be discussed in more detail. A focus will be placed upon (1) interaction between the laser and the target surface (2) plume dynamics and (3) the growth and nucleation of the film.

2.3.1 PLD Process

The experimental set up utilized for the growths described in this dissertation are illustrated in the top portion of Figure 2.1. A Lambda Physik© 248 nm KrF excimer laser and 12-inch Neocera © vacuum chamber equipped with a 6-target carousel and conducting substrate heater was utilized. The distance between the target and substrate heater may be adjusted manually. A schematic of the internal framework of the PLD chamber is included in the bottom portion of Figure 2.1.

In the PLD process, very short laser pulses are fired through a series of lenses, apertures and mirrors into a vacuum chamber containing a target of a specific composition. With each laser pulse, a high-energy plasma plume is formed which contains the ablated material from the target surface. The plume expands and propagates forward in the chamber towards an awaiting substrate which collects the ablated material. Finally, growth and nucleation occurs, forming a film of the target composition.
Figure 2.1: Top: Experimental set-up including the excimer laser and Neocera © PLD chamber. Bottom: Schematic of pulsed laser deposition process illustrating (1) interaction of laser with the target surface (2) expansion and propagation of the plume (3) growth and nucleation of the material.

2.3.1.1 Interaction between the laser and target surface

The interaction of the laser with the target is of the utmost importance for successful stoichiometric transfer. One of the most important aspects of this step is ensuring congruent melting of the target surface with every pulse. Therefore, pulsed laser ablation of the target materials must occur via non-thermal vaporization. In order to achieve this, the laser must be fired at a fast enough rate and laser energy high enough in order to equalize the melting points and vapor pressures of the target constituents. If the target is heated slowly or the ablation threshold (energy required to ablate material) has not been
met, components with different vapor pressure or melting points would evaporate non-uniformly, leading to non-stoichiometric films, i.e. thermal vaporization.  

A depiction of the interaction between the target and laser is illustrated in Figure 2.2. The laser pulse of the appropriate energy is absorbed by the target inducing a phase transformation at the surface to a molten state. The target surface can heat up to nearly 5000 K depending upon the laser energy and spot size which ensures uniform melting. This molten region then evaporates to form a very high energy plasma plume containing ionized and neutral species and clusters of the target constituents. It must also be noted that the penetration depth of the laser must be shallow enough to prevent subsurface boiling which causes large aggregate formation.

Figure 2.2: Laser-target interaction where (a) shows the congruent molten region that forms upon initial laser contact (b) evaporation of the constituents (c) evaporation and plume formation.

2.3.1.2 Plume Behavior

The plume is considered to be one of the most important aspects of PLD film growth. Upon laser ablation, the ejected particles from the target surface create an “abla-
tion cloud”, otherwise known as the plume. As previously mentioned, the plume is composed of excited, ground-state neutrals, electrons, and ions that contribute to its overall physical nature. Understanding the behavior of those components is possibly the most complex thing about PLD growth. However, the simple picture of the expansion and propagation of the plume may be described using chemical intuition.

Successful PLD growth is dependent upon optimal growth parameters of pressure, temperature and substrate to target distance. Each of these parameters have the ability to effect the plume propagation by altering its’ kinetic energy. There is experimental evidence illustrating that decreasing the substrate to target distance will increase the velocity of the ablated species with respect to the substrate position. Additionally, the diffusivity of the plume species with respect to increasing pressure and temperature also impacts the kinetic energy. The plume at lower pressures would be considerably more diffuse than those grown at higher pressures. A more “compact” plume has the potential to reduce the diffusion of individual plume species and hence affect their respective stoichiometry. A pictorial representation of the shape and intensity of plume tuned by pressure and temperature is shown in Figure 2.3. While plume dynamics are notably very complicated, the simplified representations presented provide a logical way to gauge parameters affecting the propagation of the plume.
2.3.1.3 Growth and nucleation

Following plume formation and propagation is growth and nucleation of the material upon the substrate surface. The nucleation process is initiated when the deposited species, or adatoms, diffuse across the substrate surface until they find an energetically favorable position. This favorable position is correlated with sites that increase the adatom coordination and hence stabilize the species. The bonding energies of adatoms upon a bare substrate and already deposited species are therefore important parameters to consider in order to fully understand film nucleation.

There are three main mechanisms for growth and nucleation of films, Figure 2.4. The first mechanism to be discussed is 3-dimensional island or Volmer-Weber nucleation. The simple description of this model is one where adatoms are more readily bonded to each other than to the surface layer resulting in cluster formation and island growth.

The probability for island formation increases if the first several pulses of growth deposit...
enough material to cover the bare substrate allowing adatoms to attach to existing islands.\textsuperscript{12}

The second mode of growth, most ideal and perhaps most difficult to obtain is 2-dimensional layer-by-layer growth or Frank-van der Merwe growth. This mode occurs when the binding energy of incoming adatoms is less than or equal to the binding energy of the film adatoms and substrate surface.\textsuperscript{16} The ability for this growth mode to occur is highly dependent upon PLD system parameters in addition to the kinetics of the deposition.\textsuperscript{12} For example, slow growth rates tend to increase the tendency for layer-by-layer growth and nucleation.

The third mechanism is Stranksi-Krastinov, or a blend of both layer-by-layer and island growth. This mode manifests itself after several layer-by-layer monolayers have been deposited followed by cluster formation. The effects of strain-relaxation in lattice-mismatched films are often driving forces for this mechanism as a result of defect formation.\textsuperscript{16}

\textbf{Figure 2.4:} Schematic illustration of (a) Volmer-Weber 3-D island growth and nucleation (b) Frank-van der Merwe 2-D layer by layer growth and nucleation (c) Stranski-Krastinov mixed 2-D to 3-D growth and nucleation.
2.3.2 Epitaxy

PLD has the capability of producing polycrystalline, amorphous and single crystalline films based upon the crystal structure and orientation of the selected substrate. The process of growing a film on top of a substrate is coined epitaxy which is derived from the Greek language. Here, ‘epi’ means ‘above’ and ‘taxis’ means ‘in ordered manner’. This may be more aptly described as growing a crystalline film on top of a single-crystal substrate of a specific orientation.\footnote{17}

Epitaxy may be further broken down into homoepitaxy and heteroepitaxy. Homoepitaxy is when the material grown is of the same composition as the substrate and heteroepitaxy is one when material grown is different than the substrate composition. Heteroepitaxy is illustrated in Figure 2.5. In order to have successful heteroepitaxy, the lattice between the film and substrate must be within a certain threshold or non-uniform, defect-prone films result. This threshold is material dependent and may be quantified using lattice mismatch, \(f\). This value is calculated using the following equation:

\[
f = \frac{a_f-a_s}{a_s} \tag{Equation 1.1}
\]

where \(a_f\) and \(a_s\) are the in-plane lattice parameters of the film and substrate, respectively. When the size of the film lattice is different than the substrate, interfacial strain is produced. When the in-plane lattice parameters of the film are smaller, compressive strain result, labeled with a positive sign. When the in-plane lattice parameters are expanded from the substrate, this is tensile strain, labeled with a negative sign. Since lattice mis-
match strain tends to be more prevalent close to the substrate-film interface, relaxation of the film lattice to the bulk value may occur after a critical thickness is reached.

Figure 2.5: Illustration of heteroepitaxial film growth.

2.3.3 Target Synthesis

The powder was prepared as reported earlier in this chapter. The target was formed by pressing a 1-inch × 5 mm disc using a Carver © hydraulic press and then sintering at 1400 °C for 2 hours at a heating and cooling rate of 10 °C/min. The target was placed onto a target holder using set screws and silver paste prior to installing in the PLD chamber.
2.4 Characterization Techniques

2.4.1 X-ray Diffraction

In order to determine the lattice parameters, crystallinity and phase purity of our materials, x-ray diffraction (XRD) must be done. This technique provides a convenient and non-destructive way to probe the crystal structure. The bulk lattice parameters and out-of-plane lattice parameters of the films were characterized using a Bruker D8 Advance (40 kV, 50 mA, sealed Cu X-ray tube, $\lambda = 1.5406$ Å, equipped with an incident beam Ge (111) monochromator and a LynxEye™ position sensitive detector).

More specific thin film structural details were determined using a Bruker D8 Discover (40 mA, 40 kV, sealed Cu X-ray tube, $\lambda = 1.5406$ Å, equipped with a Ge (220) 4-bounce monochromator, and a variable slit Pathfinder detector). The first measurements done were rocking curves which provide a measure of the degree of texture, or preferred orientation, of the planes within the film. Ideally, the rocking curve full-width-at-half-max (FWHM) will be less than 0.1°, similar to that of the substrate. Larger values suggest a low level of texture. This measurement is done by positioning the detector to the 2-theta of the desired Bragg reflection and “rocking” the sample about omega (omega is equivalent to theta when theta and 2-theta are decoupled as in traditional XRD scans).

The second measurement carried out is determination of the in-plane lattice parameter which reveals to what extent tensile or compressive strain has occurred in the film. It may also be a good indication of whether strain-relaxation has occurred. For the (100)-oriented substrates, the substrate is re-oriented such that the (110)-plane is in line with the XRD beam. This is done by moving the chi (X) angle to 45° and doing a ga–2-theta scan of the h10 peaks.
Determination of the SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ lattice parameters, phase purity and rocking curve FWHM were completed using the Rietveld method via the software package TOPAS.$^{19,20}$

### 2.4.2 Magnetic Measurements

The magnetic properties of CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films were identified using a Quantum Design © superconducting quantum interference device (SQUID) with a reciprocating sample option (RSO) attachment. Unlike traditional DC measurements, the RSO is highly sensitive to magnetic moments as low as $5 \times 10^{-9}$ electromagnetic units (emu).$^{21}$ It can also collect data at temperatures as low as 2.4 K and up to 400 K.

The samples were prepared using a non-magnetic straw with the sample placed at the midway point and held in place using a string pulled taut around its edges in order to minimize the background. The string is secured to the straw using nonmagnetic kapton tape and is then placed on the RSO sample rod. An example of the sample mounting procedure is illustrated in Figure 2.6.

In order to obtain the low-temperature $M_{\text{sat}}$ and coercivity ($H_C$) of the sample, a hysteresis loop was measured. This was achieved by cooling the sample to 5 K with no applied magnetic field and measuring longitudinal moment (in emu) with an applied magnetic field varying from +30,000 Oe to −30,000 Oe. In addition, zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibility measurements were obtained in which the longitudinal moment was measured as a function of temperature. For the ZFC measurement, the sample was heated to 300 K (above the magnetic ordering temperature) and cooled with no applied field. Once down to 5 K, a field of 100 Oe was applied and
the longitudinal moment was measured up to 400 K. The sample was cooled under constant field of 100 Oe and the longitudinal moment was measured once again to 400 K to complete the field-cooled measurement. All magnetic data were converted to \( \mu_B/\text{f.u.} \) for hysteresis measurements and emu/mol for susceptibility measurements.

Figure 2.6: Straw sample mounting for SQUID with RSO attachment.

2.4.3 Transport Measurements

Four-point probe DC resistivity measurements were completed using a Quantum Design © physical property measurement system (PPMS). Contacts were made using copper leads and pressed indium for the films and silver paste for bulk materials.

Magnetoresistance data was collected using the PPMS as well. For CaMn0.5Ru0.5O3 films, zero-field cool measurements was heated greater than 250 K (above the magnetic ordering temperature) between measurements and then cooled with zero applied field. Field-cool measurements to check the spin-valve effect was achieved by heating the sample to above 250 K, applying the desired field, and then cooling to the measurement temperature.

2.4.4 Rutherford Backscattering Spectroscopy

Since pulsed laser deposition is dependent upon stoichiometric transfer of the target material to the substrate, determining the composition is essential to understanding
the film properties. One of the best methods in which to do this is Rutherford backscattering spectroscopy (RBS). This elastic scattering tool is ideal because it is non-destructive and may provide other information including roughness and film thickness.

In this process, energetic alpha (He\textsuperscript{4+}) particles composing the incident beam collide with stationary target atoms, transferring energy in the process\textsuperscript{22}. These particles are then backscattered at a scattering angle, $\beta$, into the detector with a lower energy. The degree in which the particles are back scattered after the elastic collision depends upon the mass of the target atoms; therefore providing the identities of the target atoms. This process is illustrated in Figure 2.7:

![Figure 2.7: Schematic of a typical RBS experimental setup.](image)

Due to restrictions in the detector resolution, heavy Z elements are difficult to measure. In addition, RBS is not sensitive enough for low Z elements such as oxygen and may not be quantitatively measured.
RBS data were collected at Rutgers University using a standard ORTEC Si surface barrier detector with a scattering angle of $163^\circ$ and a detector energy resolution around 17 keV. The RBS data were analyzed using the program SIMNRA.\textsuperscript{23}

2.4.5 Transmission Electron Microscopy

Characterization of the structure of $\text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$ films and atomic resolution images were obtained utilizing the FEI Titan\textsuperscript{TM} 80-300 housed at The Ohio State University. Aberration corrected STEM (scanning transmission electron microscopy) images were gathered using the HAADF (high-angle annular dark-field) mode. TEM samples were prepared using a dual-beam FEI Helios NanoLab\textsuperscript{TM} 600 DualBeam\textsuperscript{TM} focused ion-beam (FIB). Crystallographic directions of the sample were determined using EBSD (electron backscatter diffraction) technique and a FIB foil was sectioned along the $<110>$ direction in order to probe potential atomic ordering as well as observe the interface.

2.4.6 High Pressure Neutron Diffraction

Neutron powder diffraction (NPD) is a powerful technique with many advantages over x-ray diffraction. The information provided by XRD is limited since scattering occurs off of an atom’s electrons. This suggests that there is not only an angular dependence to the scattering, but also upon the atomic number, $Z$.\textsuperscript{24} Therefore, the atomic positions of lighter elements such as hydrogen or oxygen cannot be accurately determined via X-rays. The ability for neutrons to scatter off of the atom’s nucleus eliminates not only the angular dependence but also the $Z$-dependence since scattering power is a nuclear property and varies from one atom to the next. In addition, neutrons have a magnetic moment which enables magnetic scattering to occur and the ability to solve the magnetic structure.
The sample discussed in Chapter 7 was prepared by pressing approximately 225 mg of sample using a standard hydraulic press into a toroid. Pressure was applied to the sample using a Paris-Edinborough (PE) press. Data was collected at the Spallation Neutron Source Oak Ridge National Laboratory, USA using the Spallation Neutron and High-Pressure (SNAP) diffractometer. For this experiment, a total of six detector banks were used. A bandwidth chopper was used to define a wavelength range between 0.5–4 Å for detector banks 1–4 and 0.99–8 Å for detector banks 5–6. Individual time–of–flight (TOF) spectra were measured using a highly pixelated Anger camera centered on a scattering angle of 42.16° (Banks 1–4) and 84.53° (Banks 5–6). The data was converted to neutron counts versus d-spacing and summed to give a measured intensity averaged across the entire detector bank.

2.5 References


Chapter 3

Magnetoresistance in chemically disordered Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$

3.1 Introduction

The property of magnetoresistance (MR), or the ability of a compound to change its electrical resistivity in the presence of a magnetic field, is highly sought after for various data storage applications. The MR effect manifests itself in many different ways including colossal magnetoresistance (CMR) in the doped manganites$^1$ or as giant magnetoresistance$^1$ (GMR) in multilayer films, or tunneling magnetoresistance$^3$ (TMR) in bulk and films. Perhaps one of the most intriguing phenomena linked to MR is the observation of exchange bias (EB). The effect which traditionally manifests itself with shifts in magnetization versus field hysteresis loops,$^4$ has also been observed with MR versus field loops. The most common example of this behavior is the EB-induced spin-valve effect associated with GMR-based multilayer films. In these multilayers, the spin-valve behavior is reliant upon EB at the interface between an antiferromagnet (AFM)/ferromagnet (FM), FM/spin-glass, or soft FM/hard FM layers.$^5$ However, EB also occurs when the microstructure of a material is structurally and magnetically inhomogeneous such as in embedded matrices, core-shell particles, and other polycrystalline systems.$^6$ As a result, its appearance relies heavily upon the inter- and intra- granular microstructure of the ma-
eral. For example, a spin-valve type MR has been observed in FM double perovskites (Sr,Ca,Ba)$_2$FeMoO$_6$ and Sr$_2$FeReO$_6$. The manifestation of EB and spin-valve type MR in these materials has been attributed to a complex grain structure composed of soft ferromagnetic grains coated with a magnetically distorted skin layer.

The matter of exchange-bias effects observed in the MR in polycrystalline materials is notably complex since accurately defining the interfaces involved in EB can be quite challenging without extensive microstructural and magnetic domain characterization. This challenge lies with the fact that one must deconvolute between inhomogeneous intragrain (magnetic clusters, atomic structure, etc.) and intergrain (grain boundaries, magnetic impurities, particle size, etc) characteristics. Chemically disordered compounds have the capability to exhibit intragranular effects upon EB in MR properties since inhomogeneity may exist within the grain itself. For example, studies have established that the EB effect may be tuned by introducing chemical order to a disordered compound through tailored synthetic conditions which creates heterogeneous magnetic order. This allows for one to study EB in a homogeneous chemical composition in the presence of magnetic inhomogeneity—a key feature of EB. More often than not, disorder leads to highly frustrated magnetism which exhibits no magnetic order such as in spin-glasses. However, systems which exhibit unconventional magnetic order amidst chemical disorder have the potential to produce not only interesting MR effects but also provide a better understanding of EB in polycrystalline, disordered materials.

A model system for this type of study is the solid solution Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. These compounds exhibit no long-range chemical ordering of the Ca, Sr, Mn, or Ru ions. In spite of this disorder, ferrimagnetism is observed in the Ca end member while
antiferromagnetism is produced in the Sr end member. The magnetic properties of Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ rely heavily upon the presence of orbital order in the Sr-rich compositions described in Chapter 1. Intragranular effects will play a role in the magnitude of MR because the degree of orbital order may be tuned by changes in the Sr/Ca ratio, and the presence of orbital order is closely linked to the antiferromagnetic ordering. The potential for EB in these compounds has not been explored, but is warranted due to the heterogeneity of the system.

This chapter will focus on efforts to understand how destruction of orbital order and the transition from antiferromagnetic insulator to ferrimagnetic metal impacts the MR properties in disordered perovskites. This was achieved by performing a series of magnetotransport measurements on five compositions in Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. Field-cooled and zero-field cooled measurements were also performed to test for the presence of EB across the solid solution.

### 3.2 Experimental

#### 3.2.1 Bulk Synthesis

Bulk samples of Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ (x = 0, 0.5, 0.25, 0.125, 0) prepared via traditional solid state synthesis using stoichiometric amounts of SrCO$_3$ and CaCO$_3$. Each sample was heated to 1385 °C for 8 hrs in air. Pellets for conductivity and magnetotransport measurements were pressed and sintered at 1400 °C for 2 hrs in air. It is noteworthy that the pellet density were fairly similar, with values of 64%, 54%, 49%, 52%, and 52% for the x = 1, 0.5, 0.25, 0.125 and 0 compositions, respectively.
3.2.2 Magnetic Measurements

Saturation magnetization ($M_{sat}$) and magnetic susceptibility measurements were obtained using a Quantum Design® Superconducting Quantum Interference Device (SQUID). Field-cooled (FC) and zero-field cooled (ZFC) measurements were completed using an applied field of 500 Oe.

3.2.3 Magnetotransport Measurements

Four-point probe DC resistivity measurements were measured from 5 K to 400 K using a Quantum Design © physical property measurement system (PPMS). Magnetoresistance data were collected under ZFC and field-cooled FC conditions of positive and negative fields of 14 tesla. Before each measurement, the samples were heated above the magnetic ordering temperature and then cooled.

3.3 Results

3.3.1 Structural

A plot of the X-ray diffraction patterns of each of the five samples is illustrated in Figure 3.1. A summary of the structural data for each bulk sample is included for reference in Table 3.1. The reduction in symmetry from tetragonal to orthorhombic with addition of Ca is described by increased tilting of the MnO$_6$ and RuO$_6$ octahedra and loss of orbital ordering. The $x = 0.25$ composition exhibited the most unique structural features. The initial sample (as-made) contained a mixture of tetragonal (20.5%) and orthorhombic (80.5%) phases where the phase percentages were refined used Rietveld refinement. An XRD spectrum of the same sample (stored in a sealed vial) collected after 13 months revealed an orthorhombic ($Pnma$) crystal structure with no visible tetragonal splitting pre-
sent. This demonstrates the metastable behavior of the tetragonal crystal structure in the \( x = 0.25 \) composition. A comparison of two regions where tetragonal splitting should be observed are shown in Figure 3.2.

![Figure 3.1](image)

**Figure 3.1:** \( \theta-2\theta \) XRD pattern of bulk \( \text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) of composition \( x = 0, 0.125, 0.25, 0.5, 0. \)

The two-phase character of the as-made sample is in good agreement with reports by Ricciardo et al.\textsuperscript{14} In contrast, Mizusaki et al. reported a similar composition as orthorhombic only which agrees well with the sample composition after 13 months.\textsuperscript{15} The variation in structural features are most likely attributed to differences in synthesis conditions as well as time passed between diffraction measurements. A more detailed discussion of the structure of the rest of these compositions is reported elsewhere.\textsuperscript{12-14}
Table 3.1: Structural and magnetic ordering information for the Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compound. Magnetic ordering information was obtained from reference [14].*This structure is pseudocubic. *These values were obtained from this study.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystal System</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>T$_C$/T$_N$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>Orthorhombic</td>
<td>5.4305(3)</td>
<td>7.5870(2)</td>
<td>5.3403(1)</td>
<td>T$_C$ =230</td>
</tr>
<tr>
<td>Ca$<em>{0.50}$Sr$</em>{0.50}$</td>
<td>*Orthorhombic</td>
<td>5.4467(3)</td>
<td>7.6984(3)</td>
<td>5.4494(3)</td>
<td>T$_C$ =290</td>
</tr>
<tr>
<td>#Ca$<em>{0.25}$Sr$</em>{0.75}$</td>
<td>*Orthorhombic (80.5%)</td>
<td>5.465(2)</td>
<td>7.7383(6)</td>
<td>5.465(2)</td>
<td>T$_C$ =250</td>
</tr>
<tr>
<td>Ca$<em>{0.125}$Sr$</em>{0.875}$</td>
<td>Tetragonal (19.5%)</td>
<td>5.4204(4)</td>
<td>7.8516(8)</td>
<td>5.465(2)</td>
<td>T$_C$ =220</td>
</tr>
<tr>
<td>Sr</td>
<td>Tetragonal</td>
<td>5.4587(3)</td>
<td>7.9193(4)</td>
<td>5.465(2)</td>
<td>T$_N$ =190</td>
</tr>
</tbody>
</table>

Figure 3.2: Comparative $\theta$–$2\theta$ XRD patterns of Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ collected as made and 13 months after the synthesis. Tetragonal peaks are labeled with a “T” and orthorhombic peaks with an “O”. The overall loss of intensity between the two peaks is due to degradation of the Cu tube in the XRD source.

3.3.2 Electrical Properties

The log$_{10}$ conductivity for each composition is illustrated in Figure 3.3. In contrast to earlier reports, the conductivity steadily decreases going from Ca ($x = 1$) to Sr ($x = 0$). The difference in magnitude between reports is most likely due to variations in
the synthesis conditions. It is important to reiterate that the same synthetic conditions were used for each sample discussed in this chapter and their pellet densities are similar since variations may affect the transport properties. Each sample exhibits similar temperature dependence as previous reports in spite of the different magnitude in conductivity.\textsuperscript{14} We note that at approximately 50 K a slight kink is present in the conductivity of the $x = 0.25$ composition. At the time of measurement, this sample was two-phase.

![Figure 3.3](image)

**Figure 3.3**: Log$_{10}$ conductivity of bulk Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ materials as a function of temperature and composition.

### 3.3.3 Magnetic Properties

The magnetic properties of three compositions, SrMn$_{0.5}$Ru$_{0.5}$O$_3$, Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and CaMn$_{0.5}$Ru$_{0.5}$O$_3$, have been measured in order to provide insight into the magnetotransport properties discussed in the following section. The magnetic properties of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ have been previously reported as an AFM with $T_N$ of
However, a contrasting report of single crystalline \( \text{SrMn}_x\text{Ru}_{1-x}\text{O}_3 \) illustrated the competition of ferromagnetism and antiferromagnetism for the entire composition range, including \( x = 0.55 \). This magnetic inhomogeneity is present in spite of a pure-phase diffraction pattern. Examples of the FC and ZFC susceptibility magnetization for these two references are shown in Figure 3.4. It is clear from these data that the magnetic properties of this system are non-uniform, even from one reference to the next. In Figure 3.4a, a \( T_N \) is present near 200 K, but the bifurcation suggests some frustrated magnetism. Similarly, Figure 3.4b illustrates several transitions including a \( T_N \), ferromagnetic transition near 125 K, and a freezing temperature, \( T_f \), corresponding to cluster formation. The most likely cause for this diverse magnetic behavior is the intrinsic chemical disorder of the system which may lead to frustrated magnetism as well as cluster formation.

![Figure 3.4: FC ad ZFC susceptibility magnetization data for SrMn\(_x\)Ru\(_{1-x}\)O\(_3\) samples collected from (a) Reference [12] and (b) Reference [15]. Reference 12 data was collected at 500 Oe.](image)
The magnetic properties for SrMn$_{0.5}$Ru$_{0.5}$O$_3$ collected in this study are shown in Figure 3.5(a). The ZFC susceptibility magnetization shows a temperature dependence reminiscent of an AFM. However, the large bifurcation that occurs between the FC and ZFC data upon field cooling in 500 Oe implies some degree of frustration. There is also a potential ferrimagnetic contribution near 180 K, though a precise transition temperature is difficult to ascertain. From the saturation magnetization (\(M_{\text{sat}}\)) of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ the hysteresis suggests the presence of a weak ferromagnetic response upon applying a field. This sample compared to the samples in Figure 3.4 reveal the intrinsic magnetic inhomogeneity of SrMn$_{0.5}$Ru$_{0.5}$O$_3$, most likely due to the propensity to form magnetic clusters.

Figure 3.5(b) illustrates the susceptibility magnetization of the two-phase composition, Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. A ferrimagnetic transition is present with \(T_C = 250\) K which agrees well with the composition Ca$_{0.3}$Sr$_{0.7}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ reported previously.\(^{16}\) However, a bifurcation of the FC and ZFC data suggests frustrated behavior as well. The most notable feature of this figure is the sudden decrease in susceptibility near 50 K. A kink in the ZFC data is observed at this same temperature. It is interesting that this feature in the susceptibility coincides with a subtle kink in the conductivity for the same composition shown in Figure 3.3. The measurement was repeated with a second sample of the same composition which revealed identical results. This unusual behavior was not observed in the previous reports.\(^{14,16}\) The variation in the magnetic data is likely due to the metastable nature of this composition since it lies near the AFM-FM boundary. The \(M_{\text{sat}}\) for this composition was determined as well, Figure 3.5(b). An \(M_{\text{sat}}\) of 1.1 \(\mu_B\)/f.u. was determined and illustrates the overall ferrimagnetic nature of this composition.
The magnetic properties of CaMn$_{0.5}$Ru$_{0.5}$O$_3$ were also verified, Figure 3.5(c). A ferrimagnetic transition at $T_C \sim 200$ K and an antiferromagnetic transition at $T_N \sim 95$ K were confirmed. These values agree well with previous studies.$^{14}$ An $M_{\text{sat}}$ of 1.4 $\mu_B$/f.u. was determined at 5 K which is larger than the value of 0.8 $\mu_B$/f.u. determined by Ricciardo et al.$^{14}$ This difference is not surprising since their data was collected at a higher temperature of 80 K which can lead to smaller $M_{\text{sat}}$ values.
Figure 3.5: FC ad ZFC magnetic susceptibility data collected at 500 Oe (left) and saturation magnetization (right) collected at 5 K for (a) SrMn$_{0.5}$Ru$_{0.5}$O$_3$ (b) Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and (c) CaMn$_{0.5}$Ru$_{0.5}$O$_3$. 

M$_{sat}$ = 1.4 μB/f.u.
3.3.4 Magnetotransport Properties

The MR for each composition in Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ is plotted at different temperatures and 14 tesla, Figure 3.6. The temperature dependence of the MR are summarized in Figure 3.7. From these data, three regions of the MR can be identified. The first region (region I) describes the ferrimagnetic compositions $x = 1$ and 0.5 where the values for the MR at 5 K and 14 tesla reach maximums of $-10\%$ and $-33\%$, respectively. This region also exhibits a sharp low-field MR which is more dramatic for the $x = 1$ and 0.5 compositions. The second region (region II) is the structurally inhomogeneous $x = 0.25$ composition which has an MR as high as $-67\%$ at 25 K that decreases down to $-55\%$ at 5 K. It is important to note that this sample was two-phase for the magnetotransport measurements. The third region (region III) is composed of the antiferromagnetic $x = 0.125$ and $x = 0$ compositions which exhibit values of MR as high as $-54\%$ and $-58\%$ (respectively) at 5 K. If the compositions studied behaved like the doped-manganites, an increase in the MR near the transition temperature would be expected. From Figure 3.7, it is evident that this is not the case since each composition exhibits an overall decrease in the MR as the temperature is increased.
Figure 3.6: Magnetoresistance for \( \text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) collected at 14 tesla at 5 K, 25 K, 50 K, 100 K, 150 K, 200 K, 250 K, and 300 K.
The question remains as to what is causing the varied MR as the Ca/Sr ratio decreases? The MR loops provide insight into potential mechanisms for the three regions. One of the notable features in Figure 3.6 is the distinct “butterfly” hysteresis in the MR loops as a function of field, particularly at low temperatures. The enhancement in the butterfly hysteresis and MR becomes greater with increasing Sr-content in $\text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$. This may be quantified by identifying the maximum resistivity (peak maximum at 0% MR) as the coercivity of the MR, $H_{\text{C(MR)}}$. The following values for $H_{\text{C(MR)}}$ were found: 1000 Oe, 800 Oe, 1800 Oe, 6400 Oe, and 7600 Oe for the $x = 1$, 0.5, 0.25, 0.125, 0 compositions in $\text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ (respectively) and is represented in Figure 3.8(a) and Figure 3.8(b). The $H_{\text{C(MR)}}$ increases as temperature decreases which is a strong indicator of magnetic domain size becoming larger. In this case, the antiferromagnetic order is increasing as more Sr is introduced. Since the pellet densities in each of the

![Figure 3.7](image-url)
measured samples in our study are similar to one another (~50%), the change in $H_{\text{C(MR)}}$ and enhanced MR cannot be attributed to extrinsic variations such as grain size. Therefore, the increased MR with increasing Sr is likely related to the changing magnetic domain structure within (i.e. magnetic cluster formation with applied magnetic field) and/or between (i.e. grain boundaries acting as nonmagnetic insulators) each grain. For SrMn$_{0.5}$Ru$_{0.5}$O$_3$, neutron diffraction confirms C-type antiferromagnetism under zero-applied field. However, the magnetic data in Figure 3.5 suggests formation of FM clusters with the application of a magnetic field. The observation of magnetic clusters in the AFM region III (0 < x < 0.25) might lend itself to a more intragranular-type MR.

![Diagram](image)

**Figure 3.8:** (a) Example of the $H_{\text{C(MR)}}$ hysteresis and designating the coercive field of the MR and (b) five compositions in Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ with their $H_{\text{C(MR)}}$ listed. The $H_{\text{C(MR)}}$ generally increases with increasing Sr-content.
In many ways, the butterfly hysteresis in the MR loops—especially for the region I compositions—are reminiscent of tunneling magnetoresistance (TMR) observed in other transition metal oxide bulk and film materials including Fe$_2$O$_4$, La$_x$Ca$_{1-x}$MnO$_3$, Sr$_2$FeReO$_6$, and Sr$_2$Fe(W$_{1-x}$Mo$_x$)O$_6$. The TMR may manifest itself in the form of intergranular tunneling which occurs between grains or via an intragranular tunneling which occurs within the grain and may be related to factors such as formation of clusters of different magnetic and electrical character. The latter would be applicable to SrMn$_{0.5}$Ru$_{0.5}$O$_3$ assuming TMR was the dominant mechanism.

In order to better verify the potential mechanism for MR, low field MR must be addressed as this is often a feature of materials exhibiting tunneling of spin-polarized electrons, or TMR. One thing to keep in mind is that TMR is traditionally observed in ferro(i)magnetic materials rather than antiferromagnetic insulating materials as the mechanism requires tunneling of conduction electrons between ferro(i)magnetic metallic regions through nonmagnetic, insulating regions. The MR for the compositions in region I, CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.50}$Sr$_{0.50}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, show a distinctly sharper low field MR than the other compositions. For example, the MR obtained at 5 K and a field of 1 tesla for CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.50}$Sr$_{0.50}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, −3% and −15% (respectively), are roughly 30% and 44% of the total change in %MR at 14 tesla. In comparison, the MR obtained under similar conditions is much less for the Sr end-member, only 18% of the total change in %MR at 14 tesla. Similar comparisons were made for the other compositions and tabulated in Table 3.2 and also do not show significant changes in MR at lower fields. It is important to note that the low-field MR in CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.50}$Sr$_{0.50}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ appears at temperatures below 100 K which implies some degree
of temperature dependence. Above 100 K, the MR behavior is similar to the other compositions which exhibit a decrease in MR as temperature increases. The fast rise in MR at lower fields in the CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.50}$Sr$_{0.50}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ compositions is likely due to their ferrimagnetic domains aligning more easily with an applied magnetic field. This would imply that the ferrimagnetism is “softer” at 1 tesla than at larger fields. As Sr-content increases through the $x = 0.25$ composition, the propensity for orbital order increases and the system becomes more magnetically hard, eliminating the steeper MR response at low fields.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ca</th>
<th>Ca$<em>{0.5}$Sr$</em>{0.5}$</th>
<th>Ca$<em>{0.25}$Sr$</em>{0.75}$</th>
<th>Ca$<em>{0.125}$Sr$</em>{0.875}$</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$%$MR at 1 tesla</td>
<td>-3</td>
<td>-15</td>
<td>-6</td>
<td>-7</td>
<td>-10</td>
</tr>
<tr>
<td>$%$MR at 14 tesla</td>
<td>-10</td>
<td>-33</td>
<td>-55</td>
<td>-58</td>
<td>-54</td>
</tr>
<tr>
<td>% MR at 1 tesla</td>
<td>31%</td>
<td>45%</td>
<td>11%</td>
<td>11%</td>
<td>19%</td>
</tr>
<tr>
<td>contribution to total MR</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**Table 3.2:** Comparison of the MR at 1 tesla and 14 tesla for each composition. The percent contribution of the MR from fields below 1 tesla to the total MR at 14 tesla is provided.

In many cases, the MR in materials may be described by two regions: (1) a low magnetic field region dominated by spin-polarized tunneling between grains and (2) a temperature independent, high magnetic field region.\textsuperscript{23} From the data illustrated in Figure 3.6 and Table 3.2 there is evidence that a model based on intergranular tunneling of spin-polarized conduction electrons dominates at lower fields in ferrimagnetic CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.50}$Sr$_{0.50}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ below 100 K. A similar low-field MR response influenced by intergranular effects (as opposed to intragranular) has also been observed in ferromagnetic Sr$_2$FeMoO$_6$.\textsuperscript{24,25}
Further support for intergranular TMR in these two compositions can be obtained by comparing the $H_{C(MR)}$ and the coercivity of the $M_{sat}$, $H_C$, versus magnetic field. Intergranular TMR has been shown to dominate when the $H_{C(MR)}$ is equivalent to $H_C$. These two values were compared for ferrimagnetic CaMn$_{0.5}$Ru$_{0.5}$O$_3$ in Figure 3.9. This figure shows an $H_C$ that is only slightly larger than the $H_{C(MR)}$, producing a small $H_C/H_{C(MR)}$ ratio of 1.33. While good agreement between the maximum in resistivity and coercivity of the magnetization may be ascribed to an intergrain spin-polarized tunneling, we acknowledge that a similar response at $H_C$ can occur due to a reduction in scattering at the grain boundaries upon application of a magnetic field.

**Figure 3.9:** Comparison of the saturation magnetization versus field and magnetoresistance versus field curves collected from ±1.5 tesla of ferrimagnetic CaMn$_{0.5}$Ru$_{0.5}$O$_3$ bulk material. Red lines designate the larger coercive field of the $M_{sat}$.
It is clear that this type of low-field response is not present in the Sr-rich compositions. Once sufficient amount of Sr is added (compositions where $x<0.25$), the magnetic and electronic grain structures become mostly antiferromagnetic and insulating which results in a loss of low-field MR and efficient spin-dependent tunneling through the grains. For compositions greater than $x = 0.25$, where orbital order associated with the cooperative JT distortion is not present, intergranular effects dominate. In contrast, the MR for Sr-rich compositions seems to be dominated by intragranular effects likely influenced by orbital order.

We note that the mechanism for the two-phase composition is more complex and less obvious since the magnetic and electronic properties as well as inhomogeneous crystal structure appear to be linked with the magnetotransport properties. The non-linear trend in MR at temperatures below 50 K for the $x = 0.25$ composition occurs near a temperature where both the magnetic susceptibility and conductivity elicit unusual behavior. Since this composition is structurally inhomogeneous, it is logical to assume the orthorhombic component is FM while the tetragonal phase exhibits different magnetic character, most likely AFM in nature. This is based on the fact that the FM portions ($x>0.25$) of the solid solution are orthorhombic and the AFM compounds ($x<0.25$) are tetragonal. The simple mechanism for the greater MR in this two-phase region is likely due to factors related to competing structural and magnetic phases under applied magnetic field.

### 3.3.5 Potential for Exchange Bias

The presence of disorder and short range ordered magnetic clusters in $\text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ materials lend themselves to natural interfaces with different mag-
netic and electrical properties. As a result, the phenomenon of EB, which has been observed in ferromagnetic double perovskites exhibiting TMR\textsuperscript{7-9}, has potential to manifest itself under the correct experimental field-cooled (FC) conditions. The MR of CaMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3}, Ca\textsubscript{0.25}Sr\textsubscript{0.75}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} and SrMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} bulk samples were field-cooled down to 5 K at ±14 tesla and compared to the ZFC data. The data are illustrated in Figure 3.10(a)–(c).

The presence of EB in these compounds would be demonstrated by a shift of the $H_{C(MR)}$ to the right with negative FC and left with positive FC. It is clear that CaMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} does not exhibit very drastic changes upon field-cooling. In contrast, the two phase region, Ca\textsubscript{0.25}Sr\textsubscript{0.75}Mn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3}, and SrMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} show the distinct signature of EB. The effect is greatest for SrMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3} which contains the largest amount of antiferromagnetic, orbitally ordered regions. Since each composition maintains no long-range order of the $B$-site and were made under the same synthetic procedure, the observed effects of enhanced MR, large $H_{C(MR)}$ and EB must be related to the microstructure and variation of the magnetic structures within the samples themselves. That being said, different inter- and intragranular structures likely exist between the three compositions which is supported by the different regions describing the MR.
Figure 3.10: Evidence for exchange bias at 5 K under ZFC conditions (black line) and FC conditions of +14 tesla (red dashes), −14 tesla (grey dashes) for (a) CaMn$_{0.5}$Ru$_{0.5}$O$_3$ (b) Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and (c) SrMn$_{0.5}$Ru$_{0.5}$O$_3$. 
3.4 Discussion

The MR properties of Ca$_{x}$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ may be broken up into three different regions, I, II, and III. Region I includes CaMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ which are both nearly fully ferrimagnetic, containing roughly 5% G-type AFM and 5% C-type AFM (respectively) at temperatures below 95 K. These two compositions exhibit no orbital ordering due to increased octahedral tilting and have the most uniform magnetic properties in the solid solution. They also exhibit fairly sharp low-field magnetoresistance reminiscent of intergranular TMR and the smallest $H_{C(MR)}$ values. Region II contains the two-phase composition, Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_3$, where the magnetism appears to be predominately ferrimagnetic, though unusual magnetic and electrical behavior below 50 K set it apart from the other compositions. Region III includes the orbitally ordered antiferromagnetic compositions, SrMn$_{0.5}$Ru$_{0.5}$O$_3$ and Ca$_{0.125}$Sr$_{0.875}$Mn$_{0.5}$Ru$_{0.5}$O$_3$. These both exhibit antiferromagnetism, though magnetic frustration and cluster formation appear under applied magnetic fields at temperatures less than 180 K in the pure Sr compound.

The potential for intragranular and intergranular-based MR and exchange bias in Ca$_{x}$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ may lie somewhere within the intrinsic chemical disorder of the Mn and Ru ions. The lack of long-range B-site order in this family of compounds is verified by pair-distribution functional (PDF) analysis$^{28}$, and NPD and XRD experiments$^{12-14}$. The presence of this disorder has the potential to form regions or clusters rich in Sr, Ca, Mn, or Ru ions with an applied magnetic field. These regions may disrupt the magnetic and electronic interactions in each composition. If the Mn or Ru rich regions are large enough to form clusters, the properties could be similar to the ternary perovskites derived from
the solid solution such as CaMnO$_3$, CaRuO$_3$, SrMnO$_3$ and SrRuO$_3$. Each of these compounds have very different types of magnetic order and conductivity which are listed in Table 3.3. Any composition across the Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ solid solution could have a combination of antiferromagnetic and ferromagnetic (or paramagnetic) rich “regions” based upon the local coordination environment. This lends itself to interesting exchange coupling at the interfaces of these regions, creating the possibility of exchange bias.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Magnetism</th>
<th>$T_C/T_N$ (K)</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrMnO$_3$ [25]</td>
<td>Antiferromagnetic</td>
<td>235</td>
<td>Insulating</td>
</tr>
<tr>
<td>SrRuO$_3$ [25]</td>
<td>Ferromagnetic</td>
<td>165</td>
<td>Metallic</td>
</tr>
<tr>
<td>CaMnO$_3$ [30]</td>
<td>Antiferromagnetic</td>
<td>120</td>
<td>Insulating</td>
</tr>
<tr>
<td>CaRuO$_3$ [30]</td>
<td>Paramagnetic</td>
<td>–</td>
<td>Metallic</td>
</tr>
<tr>
<td>Strained CaRuO$_3$ [31,32]</td>
<td>Ferromagnetic</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 3.3: Structural and magnetic ordering information for the ternary compounds related to the Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ solid solution. Reference [27] is theoretical.

The relationship of disorder, increased MR effects and EB in Region III can be visualized by using a qualitative model similar to Sr$_2$Fe(W$_{1-x}$Mo$_x$)O$_6$. An example of this is illustrated in Figure 3.11. In this picture, small regions exhibiting short range C-type AFM order are separated by orbitally disordered regions or magnetic clusters. While no long range order is present, short range order in SrMn$_{0.5}$Ru$_{0.5}$O$_3$ has been suggested previously by several authors as a means to explain the orbital order and C-type AFM. Additionally, the presence of short range order of Mn and Ru ions has been demonstrated in the related disordered perovskite, LaSrMnRuO$_6$. Therefore, a model containing small clusters of ordered and disordered regions of varying magnetism and
electronic conductivity is plausible, particularly for the Sr-rich compounds. In fact, the magnetic inhomogeneity of the Sr analogue was verified in Figure 3.5(a).

![Figure 3.11: Cartoon of Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ region III samples where pink areas represent small ordered regions separated by clusters either Mn-rich and Ru-rich or orbitally disordered sections in gray.](image)

For the region III compositions, the ordered areas (pink) in Figure 3.11 represent the dominant antiferromagnetism which relies upon 1-D ferromagnetic chains of Mn$^{3+}$–O–Ru$^{5+}$ randomly oriented antiparallel to one another via short range interactions. Since the disordered regions (gray) create boundaries which may disrupt various short-range interactions, the response to a magnetic field is quite large. Additionally, the boundaries are likely composed of FM and AFM components which lead to the proportionate number of interfaces necessary for the EB effect to occur. Since region II contains both orthorhombic and tetragonal phases, it is likely that areas of AFM and orbital order
are surrounded by ferrimagnetic areas. This helps to explain why region II and III compositions manifest the EB effect while the representative sample of region I did not.

The differences between region I and region III arise from the fact that the mechanism for MR in region I relies upon intergranular tunneling as opposed to intragranular effects caused by orbital order in region III. This implies that Figure 3.11 is not valid for compositions such as CaMn_{0.5}Ru_{0.5}O_3 as they do not have these large regions of orbital order and hence antiferromagnetic order. That being said, the lack of observed EB coupled with the small phase fraction of antiferromagnetism to ferromagnetism in region I agrees very well with studies of exchange-biased multilayers where increasing ferromagnetic layer thickness led to a reduction in EB.\(^5\) Previous reports of exchange bias in Ru-doped CaMnO_3\(^{34}\) and Sm_{0.5}Ca_{0.5}MnO_3\(^{35}\) systems also demonstrated that the EB effect is roughly inversely proportional to the size of the ferromagnetic component.

### 3.5 Conclusions

The solid solution Ca\(_x\)Sr\(_{1-x}\)Mn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) produces a unique electrical resistivity response in the presence of large magnetic fields. The MR was shown to increase at 5 K from \(-10\%\) to \(-55\%\) at 14 T with increasing Sr-content. Additionally, an enhancement in the coercivity of the MR was observed with increasing Sr-content. This behavior coincides with a general increase in the size of the C-type AFM domain structure. The transition from a disordered perovskite containing no orbital order (Ca-analogue) to one with short range orbital order (Sr-analogue) created different microstructures and magnetic clusters responsible for the observed EB effect. The different microstructures imply different compositional regions which can be broken down into \(x > 0.25\) (region I), \(x = 0.25\)
(region II), and \( x < 0.25 \) (region III). Region I showed no EB effects and a low-field MR reminiscent of intergranular TMR similar to the half-metallic \( \text{Sr}_2\text{FeMoO}_6 \). Regions II and III exhibited EB in the MR which was linked to the ratio of AFM to FM regions. In Region III, the formation of magnetic clusters in the presence of a magnetic field in addition to orbital order supports an intragranular mechanism dominating the MR.

This work demonstrated that the trends in MR across \( \text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \) are related to the microstructure and the ratio of antiferromagnetism to ferrimagnetism. It is very common that disordered materials do not possess much technological applications due to frustrated magnetism. However, disordered compounds which exhibit magnetic order may provide a new niche in devices due to their tunable spin-valve like behavior.

### 3.6 References


Chapter 4

Magnetoresistance in disordered $\text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ films

4.1 Introduction

The previous chapter demonstrated the effects of the disruption of orbital order in $\text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ bulk material upon the magnetoresistance (MR). Additionally, an exchange bias (EB) effect in the MR was confirmed under different field-cooled conditions in the Sr-rich compositions, $x = 0$ and 0.25. The intriguing MR and EB effects present an opportunity to explore these properties in thin films. Epitaxial films are not only more technologically applicable, but they have the potential to reduce grain boundary effects which impact bulk sample properties. Therefore, films of this solid solution may answer the question of whether the EB effect and MR properties in the bulk material are linked to the microstructure created by orbital order. Additionally, the influence of chemical pressure in epitaxial films would also allow for determination of the intrinsic properties across the solid solution.

The goal of this chapter will be to present the structure and characterization of films of composition, $x = 0$, 0.25, 1, which were grown by pulsed laser deposition. An emphasis will be placed upon the conductivity and magnetoresistive properties as they compare to bulk and thin films.
4.2 Experimental

Epitaxial films of the $x = 0, 0.25, 1$ compositions were grown using pulsed laser deposition from sintered targets. The targets were prepared via traditional solid state synthesis using stoichiometric amounts of SrCO$_3$ and CaCO$_3$. Each sample was heated to 1385 °C for 8 hrs in air. A 1 inch target was pressed for each sample and then sintered at 1400 °C for 2 hrs in air. We note that the $x = 0.25$ composition was two-phase. The targets were pre-cleaned with 1000 pulses prior to growth. A substrate temperature of 800 °C and argon pressure of 75 mTorr were used for SrMn$_{0.5}$Ru$_{0.5}$O$_3$ and 600 °C for the Ca-substituted analogues. The laser fluence and substrate to target distance were optimized to ~2 J/cm$^2$ and 38 mm (respectively).

In order to determine the lattice parameters, crystallinity and phase purity of our materials, x-ray diffraction (XRD) was done. The bulk lattice parameters and out-of-plane lattice parameters of the films were characterized using a Bruker D8 Advance (40 kV, 50 mA, sealed Cu X-ray tube, $\lambda = 1.5406$ Å, equipped with an incident beam Ge (111) monochromator and a LynxEye$^\text{TM}$ position sensitive detector). More specific thin film structural details were determined using a Bruker D8 Discover (40 mA, 40 kV, sealed Cu X-ray tube, $\lambda = 1.5406$ Å, equipped with a Ge (220) 4-bounce monochromator, and a variable slit Pathfinder detector). These measurements included rocking curves and off-axis scans for in-plane lattice determination.

Four-point probe DC resistivity measurements were completed using a Quantum Design © physical property measurement system (PPMS) up to 400 K. Magnetoresistance data was collected using the PPMS as well. Zero-field cool and field-cool meas-
measurements were completed via similar methodology as the susceptibility measurements in applied fields of $\pm 1.5 \text{ tesla}$ ($\text{CaMn}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$) and $\pm 10 \text{ tesla}$ for the Sr-containing films.

4.3 Results and Discussion

4.3.1 Structure

A full $\theta$-2$\theta$ XRD pattern of $\text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$, $\text{Ca}_{0.25}\text{Sr}_{0.75}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$, and $\text{CaMn}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$ films grown on LSAT under optimal conditions are illustrated in Figure 4.1. From the patterns, the films appear to be phase pure with the exception of clay contamination from the sample mounting of the holder (designated with an asterix). The high-structural quality of the Sr-containing films is illustrated by the presence of Laue oscillations obtained from high-resolution XRD, Figure 4.2. The lack of Laue oscillations within the full-Ca film is likely due to a larger lattice mismatch which could cause various defects.
Figure 4.1: Full $\theta$–$2\theta$ XRD pattern for (a) CaMn$_{0.5}$Ru$_{0.5}$O$_3$–$\delta$ (b) Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_3$–$\delta$, and (c) CaMn$_{0.5}$Ru$_{0.5}$O$_3$–$\delta$ (CMRO) films grown on LSAT. The asterix (*) represents the LSAT substrate peaks. (#) represents clay contamination from the sample holder.
The structural data for the three films are summarized in Table 4.1. The lattice parameters and volume increase with increasing strontium content, leading to an overall larger volume. The trends are in good agreement with bulk samples. The in- and out-of-plane lattice parameters for the $x = 0$ film are larger than their bulk counterpart by nearly 1.5% and 0.3% (respectively). We believe the expansion is due to the introduction of oxygen vacancies which produces lower valent, and therefore larger, Mn and/or Ru ions. Evidence for oxygen vacancies will be discussed in more detail in Chapter 6 but they are believed to be formed due to reduction caused by the higher growth temperatures and relatively low oxygen partial pressure in the growth atmosphere. In contrast, the film containing both Sr and Ca, $x = 0.25$, has in- and out-of-plane lattice parameters of 3.8609(3) Å and 3.8328(2) Å (respectively). The bulk lattice parameters for this composition are quite close to the LSAT substrate and it is evident that the negligible lattice mismatch causes minimal lattice expansion. The full Ca film, $x = 1$, exhibits a smaller out-of-plane lattice parameter of 3.759 Å, compared to the average value of 3.77 Å for the bulk. This film was fairly thin which made determining the in-plane lattice challenging since
performing off-axis XRD tends to reduce the intensity of the peaks. The large lattice mismatch +1.4% between the in-plane lattice of the film and the substrate would suggest some degree of tensile strain along the in-plane. Further discussion of lattice mismatch effects upon the full Ca films will be continued in Chapter 5.

The rocking curve FWHM have been measured and are also summarized in Table 4.1. This value is a gauge for the degree of texture of c-axis oriented (00l) planes in the films. The FWHM for the film decreases with decreasing lattice mismatch. This suggests that Ca-substitution is not the driving force for high-quality rocking curves but rather the extent of lattice mismatch. The small FWHM obtained for the $x = 0.25$ film validates an excellent orientation of the 00l planes corresponding to the smallest lattice mismatch of +0.03% (tensile).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ca</th>
<th>Ca$<em>{0.25}$Sr$</em>{0.75}$</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Mismatch</td>
<td>+1.4%</td>
<td>+0.03%</td>
<td>+0.23%</td>
</tr>
<tr>
<td>Film Out-of-plane Lattice Parameter (Å)</td>
<td>3.759</td>
<td>3.8328(2)</td>
<td>3.96981(1)</td>
</tr>
<tr>
<td>Film In-plane Lattice Parameter (Å)</td>
<td>N/A</td>
<td>3.8609(3)</td>
<td>3.91657(4)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>54.68</td>
<td>57.09</td>
<td>60.87</td>
</tr>
<tr>
<td>Rocking Curve (°)</td>
<td>0.05</td>
<td>0.007</td>
<td>0.02</td>
</tr>
<tr>
<td>Bulk Lattice Parameters (Å)</td>
<td>$a_p = 3.839$</td>
<td>$a_p = 3.864$</td>
<td>$a_p = 3.859$</td>
</tr>
<tr>
<td></td>
<td>$b_p = 3.794$</td>
<td>$b_p = 3.870$</td>
<td>$b_p = 3.859$</td>
</tr>
<tr>
<td></td>
<td>$c_p = 3.776$</td>
<td>$c_p = 3.864$</td>
<td>$c_p = 3.959$</td>
</tr>
</tbody>
</table>

*Table 4.1:* Structural summary for Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_{3-δ}$ films grown on LSAT (lattice parameter = 3.868 Å). The bulk lattice parameters for the two-phase sample were selected based upon the majority orthorhombic component in the sample.
4.3.2 Electrical Properties

The electrical conductivity for the three films of composition $x = 0$, 0.25 and 1 grown on LSAT are compared in Figure 4.3. The Sr-containing compositions, $x = 0.25$ and $x = 0$, have temperature dependencies similar to their semiconducting bulk counterparts, though larger in magnitude. The enhanced conductivity may be attributed to a reduction in grain boundary scattering as discussed below. CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ is metallic with similar conductivity as reported in the bulk. There is a correlation between the change in conductivity on going from bulk to film and the degree of lattice mismatch. The percent lattice mismatch increases as follows: Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ (+0.03%), SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ (+0.23%) and CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ (+1.4%). It is likely that the increased conductivity seen for Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$, and to a lesser extent SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$, is due to the smaller lattice mismatch which leads to higher quality films and hence less grain boundary formation. CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films on a perfectly lattice matched substrate might exhibit conductivity larger than their bulk counterpart. However, large tensile strain of +1.4% for CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ lends itself to a higher grain boundary concentration and reduced conductivity.
Figure 4.3: $\log_{10}$ conductivity of $\text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ films of composition $x = 0, 0.25$ and $1$. Bulk data are added for comparison.

4.3.3 Magnetoresistance

Since the MR is highly dependent upon the structure and magnetic phases of the bulk, investigating this property in the films is of interest. Overall, the lattice mismatch should be considered a contributing factor to variations in MR between the bulk and film.
material since this would be a directly influence the microstructure of the material. The temperature dependence of the MR up to 14 tesla for the films compared to the bulk are illustrated in Figure 4.4. The CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ film exhibits a temperature dependence similar to its bulk counterpart. However, the MR increases to $-27\%$ at 5 K as compared to the $-10\%$ for the bulk at the same field. The Ca analogue has the potential to form more grain boundaries due to a large lattice mismatch leading to enhanced intergranular MR effects. The MR for the SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ film is $-45\%$ as compared to $-58\%$ for the bulk at 5 K and 14 tesla. The lower MR value may be a result of less grain boundaries which may have contributed slightly to the overall MR in the bulk. The $x = 0.25$ composition exhibits very similar values in MR as its bulk counterpart down to $\sim 50$ K. Below this temperature, the film reaches a large value of $-93\%$, much higher than the $-54\%$ for the bulk. The lattice mismatch for the $x = 0.25$ sample was the smallest leading to relatively similar MR values. However, one thing to keep in mind is that the film may not be composed of two structural phases as in the bulk, but may have preferentially grown one phase versus the other. Therefore the large increase in MR at temperatures below 50 K may be due to structural discrepancies between the bulk and film material.

The low temperature data for the three films are shown in Figure 4.5. The butterfly hysteresis is present in all three films which is similar to the bulk. This could be an indication that the mechanism for MR observed in bulk samples reported in Chapter 3 may be similar to the mechanism for the films. The most notable feature in this picture is the low-field MR of the $x = 0.25$ composition which is quite large. At this point, the large MR for Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ may not be described by the same mechanism observed for the full Ca and Sr films. The interesting behavior in the magnetic and magnetotran-
sport properties of the bulk material suggests something which may be linked to the inherent inhomogeneity of the composition. Further studies are necessary to fully understand its presence, but the large value is an intriguing feature of these films.

Figure 4.4: Temperature dependent magnetoresistance of Ca$_x$Sr$_{1-x}$Mn$_0.5$Ru$_0.5$O$_{3-\delta}$ epitaxial films of composition $x = 0$, 0.25 and 1. Bulk data are added for comparison.
Figure 4.5: Magnetoresistance loops for Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ epitaxial films with composition $x = 0, 0.25$ and $1$ collected at $5$ K and fields up to $14$ tesla.

4.3.4 Exchange bias in Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films

The presence of EB in the bulk materials provides an interesting study for the epitaxial films. The previous chapter showed that the MR and the EB effect were sensitive to the effects of chemical disorder of the Mn and Ru ions and the amount of antiferromagnetic and ferro(i)magnetic regions. In the case of the Ca-analogue which exhibits ferromagnetism in spite of chemical disorder$^1$, the EB effect was not observed. This was due to a different mechanism of MR (intergranular-vs-intragranular) and larger ratio of ferromagnetism to antiferromagnetism which suppressed EB. Figure 4.6(a)–(c) illustrates the MR loops obtained for the CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$, Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ and SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films grown on LSAT at low temperature under different field-cool
conditions. Here, the ZFC loops show hysteretic behavior similar to the bulk materials. In the case of the Sr-containing compounds, EB is observed and behaves similarly to the bulk. Perhaps the most unique feature of this data is the EB observed in the CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ film under field-cooling of $\pm 1.5$ tesla. Due to the large lattice mismatch, formation of grain boundaries are likely which can influence the EB effect. In addition, it is also possible that the ratio of magnetic phases is different for the film than it is for the bulk. This will be discussed further in Chapter 5.
Figure 4.6: Evidence for exchange bias in (a) CaMn$_{0.5}$Ru$_{0.5}$O$_3$ (b) Ca$_{0.25}$Sr$_{0.75}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ and (c) SrMn$_{0.5}$Ru$_{0.5}$O$_3$ films grown on LSAT. (a) was collected at ±1.5 tesla and 5 K and (b) and (c) were collected at 10 K and ±10 tesla. The black line is the ZFC, gray dashes are negative FC, and red dashes are positive FC. Note that the scale of the x-axis in (a) is not the same as in (b) and (c).
4.4 Conclusions

The structural, electrical and magnetic properties of the $\text{Ca}_x\text{Sr}_{1-x}\text{Mn}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$ films grown on LSAT were discussed for $x = 0$, 0.25 and 1 compositions. The structural integrity of the strontium containing films were considerably better than the calcium end member. This was verified using high-resolution XRD which showed Laue oscillations, indicative of a uniform film. In addition, a rocking curve FWHM of 0.007° was obtained for the $x = 0.25$ two-phase composition, narrower than the 0.02° for the strontium end member and rocking curve of the calcium analogue. This is likely due to the small lattice mismatch for the $x = 0.25$ composition. The electrical properties of the $x = 0.25$ and 0 composition were both semiconducting, while the $x = 1$ composition was metallic, in good agreement with bulk samples. The two phase composition had the highest conductivity which may be attributed to the smallest lattice mismatch of $+0.03\%$ and the lowest concentration of grain boundaries.

The MR associated with this solid solution in bulk and thin film presents some very interesting results. Not only are exceptionally large magnetoresistance values as high as $-67\%$ (bulk) and $-93\%$ (film) observed with for the $x = 0.25$ composition, but a unique exchange bias behavior is present. Surprisingly, the exchange bias is observed in $\text{CaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ films but not within $\text{CaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ bulk. This illustrates that the larger lattice mismatch of $+1.4\%$ forms grain boundaries that enhance the MR and exchange bias effect.
4.5 References


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Chapter 5

Structural, magnetic and transport properties of CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films

5.1 Introduction

The potential for 100% spin polarization in the ferromagnetic double perovskite Sr$_2$FeMoO$_6$ has led to much interest in magnetic recording devices. These remarkable properties were reported in 1998 and since then hundreds of papers have been published discussing its structure and properties. Reports discussing the implementation of this material into devices such as magnetic tunnel junctions are surprisingly limited. This is primarily due to the extreme sensitivity of the magnetic and magnetotransport properties of Sr$_2$FeMoO$_6$ to chemical disorder of the Fe and Mo cations. Efforts to grow “perfect” Sr$_2$FeMoO$_6$ are numerous, but have yet to satisfy commercial standards.

The design of new materials with similar properties as Sr$_2$FeMoO$_6$, particularly the 100% spin polarization, may lie with compounds whose magnetic order is not dependent upon chemical order. A model compound to explore is the disordered perovskite, CaMn$_{0.5}$Ru$_{0.5}$O$_3$. This compound exhibits no long range order of the Mn and Ru ions and is described as orthorhombic (space group = Pnma) following the tilt system $a^-b^+a^-$. Neutron diffraction and DC and AC magnetic susceptibility measurements determined
that CaMn$_{0.5}$Ru$_{0.5}$O$_3$ exhibits ferromagnetism ($T_C \sim 210$ K) as well as small amounts of G-type antiferromagnetism ($T_N \sim 95$ K). The most interesting detail about this compound are the recent theoretical studies performed by Mishra et al. which predict 100% spin-polarization in spite of complete chemical disorder. This result contrasts largely with Sr$_2$FeMoO$_6$ where the spin-polarization is disrupted with disorder of the Fe and Mo cations.

The literature on CaMn$_{0.5}$Ru$_{0.5}$O$_3$ films has been limited to superlattices composed of CaMnO$_3$ and CaRuO$_3$ and an alloy of CaMn$_{0.5}$Ru$_{0.5}$O$_3$ grown on SrTiO$_3$ and LaAlO$_3$. However, CaMn$_{0.5}$Ru$_{0.5}$O$_3$ undergoes tensile strain on SrTiO$_3$ due to a large lattice mismatch of 2.3% and the more well-matched LaAlO$_3$ substrates contain twin boundaries which may impact film properties. Therefore, the magnetic and electronic properties of films grown on this substrate may not represent the intrinsic properties of less strained CaMn$_{0.5}$Ru$_{0.5}$O$_3$. In this chapter, we present the growth of CaMn$_{0.5}$Ru$_{0.5}$O$_3$ films grown by pulsed laser deposition (PLD) on SrTiO$_3$ and LSAT. Our purpose is to highlight some of the effects that epitaxial strain may have upon the structure, conductivity, magnetism and magnetoresistance and draw correlations to its bulk counterpart.

5.2 Experimental

5.2.1 Target Synthesis

The CaMn$_{0.5}$Ru$_{0.5}$O$_3$ target was synthesized according to the same procedure described in Chapter 2. The only notable difference is the replacement of CaCO$_3$ for SrCO$_3$ as a stoichiometric precursors. The $\theta-2\theta$ XRD scan of the as-prepared CaMn$_{0.5}$Ru$_{0.5}$O$_3$ target is illustrated in Figure 5.1.
5.2.2 PLD Film Growth

CaMn$_{0.5}$Ru$_{0.5}$O$_3$ films were grown on 0.29(LaAlO$_3$):0.35(Sr$_2$TaAlO$_6$) (LSAT) and SrTiO$_3$ (STO) (100)-oriented substrates using pulsed laser deposition (PLD). The two substrates were placed side by side to ensure uniform growth. A substrate temperature of 600 °C and a pressure of 75 mTorr of argon were used. All films were cooled in the same atmosphere used during growth. Since oxygen was absent during growth, oxygen vacancies are likely in which case the formula becomes CaMn$_{0.5}$Ru$_{0.5}$O$_3$–$\delta$. A laser fluence of 2 J/cm$^2$, repetition rate of 5 Hz, and 2000 pulses were used. All films were grown when a base pressure of 10$^{-7}$ Torr was achieved and after the target was pre-ablated with 1000 pulses. The substrate-to-target distance was set to 38 mm.
5.3 Results

5.3.1 Structural Properties

The $\theta-2\theta$ XRD patterns for Ca$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films grown on LSAT and SrTiO$_3$ are illustrated in Figure 5.2. The XRD patterns do not show evidence of secondary phases. The lattice parameters of the bulk Ca$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ are $a_p = 3.839$ Å, $b_p = 3.79$ Å and $c_p = 3.77$ Å. Tensile strain of +1.4% and +2.3% was calculated for LSAT and SrTiO$_3$ (respectively) based upon an average in-plane lattice of 3.815 Å. Since Ca$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ has two in-plane lattice parameters, $a$ and $b$, due to its orthorhombic symmetry, we recognize these values are strictly qualitative.

As can be seen from the XRD patterns, the film peaks are relatively weak in intensity due to a film thickness of only 23 nm. Therefore, accurate determination of the in-plane lattice parameters was difficult since the resolution tends to decrease when doing off-axis scans. The out-of-plane lattice parameter for the films grown on LSAT and SrTiO$_3$ are very similar with values of 3.759(3) Å and 3.757(6) Å (respectively). Since each substrate has larger lattice parameters than CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ tensile strain is expected, which would be expected to cause a contraction of the out-of-plane lattice parameter. This contraction should be somewhat larger for the film grown on SrTiO$_3$, since it has a larger lattice mismatch. However, the experiments show that both films have out-of-plane lattice parameters similar to the unstrained bulk value of 3.77 Å. The most likely explanation for this behavior is that the films relax within the first few nanometers.

The rocking curve full-width-at-half-the-max (FWHM) values are compared in Figure 5.3. In both cases, sharp peaks indicating a relaxed portion of the film protrude out of a much broader peak representing the strained part of the film. Analysis of rocking
curves of CeO$_2$ films containing different degrees of strain-relaxation showed similar behaviour.$^{12}$ Similar to the out-of-plane lattice, the degree of texture between the two films are not very different. Since each film is approximately the same thickness, it is likely that structural similarities arise from the relaxed portion of the material. Since the lattice mismatch is larger for the SrTiO$_3$ film than the LSAT film, it is likely the grain boundary formation would be greater in the former case. The structural properties of the films are summarized in Table 5.1.
Figure 5.2: $\theta$–$2\theta$ XRD spectra of CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ grown on LSAT (top) and SrTiO$_3$ (bottom).
Figure 5.3: Rocking curve for CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ grown on LSAT and SrTiO$_3$ substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>% Lattice Mismatch</th>
<th>Out-of-plane (Å)</th>
<th>FWHM (°)</th>
<th>$M_{\text{sat}}$ (μB/f.u.)</th>
<th>$H_C$ (Oe)</th>
<th>$T_C$ (K)</th>
<th>$T_2$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSAT</td>
<td>+ 1.4</td>
<td>3.759(3)</td>
<td>0.05</td>
<td>1.2</td>
<td>2800</td>
<td>185</td>
<td>95</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>+ 2.3</td>
<td>3.756(6)</td>
<td>0.05</td>
<td>0.5</td>
<td>1900</td>
<td>160</td>
<td>95</td>
</tr>
</tbody>
</table>

Table 5.1: Structural and magnetic data for the CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films on LSAT and SrTiO$_3$.

5.3.2 Electrical Properties

The log$_{10}$ conductivity of the CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films were measured in order to study the impact of the large lattice mismatch upon the electron transport. The data are illustrated in Figure 5.4. The film grown on LSAT exhibits “bad” metallic behavior similar to the bulk material and reaches a room temperature conductivity of 2 S/cm.$^3$ As the lattice mismatch is increased for SrTiO$_3$, the conductivity becomes significantly more semiconducting, decreasing by several orders of magnitude at low temperatures. The likely cause for this behavior is the presence of grain boundaries and defects leading to
inhomogeneity. It is important to note that grain boundaries are still likely present in the LSAT case, but not to the same extent.

![Conductivity vs Temperature Graph]

**Figure 5.4:** $\log_{10}$ conductivity of CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films grown on LSAT and SrTiO$_3$.

### 5.3.3 Magnetic Properties of CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$

The $M_{\text{sat}}$ of the CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films were explored using SQUID magnetometry, Figure 5.5.
The LSAT film has the highest $M_{\text{sat}}$ of 1.2 $\mu_B$/f.u. considerably larger than the film grown on SrTiO$_3$ with a value of 0.5 $\mu_B$/f.u. Comparatively, a second report of CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ film grown on SrTiO$_3$ produced an $M_{\text{sat}}$ of 0.6 $\mu_B$/f.u. $^7$ The similar $M_{\text{sat}}$ values obtained for these films suggest that the diminished values may be an intrinsic character of CaMn$_{0.5}$Ru$_{0.5}$O$_3$ grown on SrTiO$_3$. Since the lattice mismatch is quite large, the magnetization of more strained films such as this one may be limited by defect formation. From the previous chapter, bulk CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ at 5 K produced an $M_{\text{sat}}$ of 1.4 $\mu_B$/f.u. which is close to the value obtained in the film. Theoretical studies predict an $M_{\text{sat}}$ of 1.1 $\mu_B$/f.u. for ferrimagnetic CaMn$_{0.5}$Ru$_{0.5}$O$_3$. $^5$ The good agreement between theory and experiment implies that growth on LSAT is near the ideal ferrimagnetic ground state of CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$.

Figure 5.5: Saturation magnetization of CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films collected at 5 K.
The coercivity (H_C) of each sample decreases with increasing degree of lattice strain, reaching a minimum of 1900 Oe. In contrast, bulk samples have a much smaller H_C of approximately 200 Oe. In general, soft materials are described as having coercivities less than ~12 Oe. This suggests that these films are more magnetically hard than the bulk. The increased H_C may also be linked with some form of anisotropy. This data is summarized in Table 5.1.

FC and ZFC susceptibility measurements of each sample are shown in Figure 5.6. The data is interesting for multiple reasons. The LSAT sample exhibits a distinct ferrimagnetic transition near 185 K in addition to a second transition, T_2 at 95 K. The ferromagnetic transition temperature is in good agreement with bulk samples which have a reported T_C near 200 K. We note that the bulk phase has a T_N of 95 K for the G-type AFM phase. A bifurcation is observed in the ZFC and FC curves near T_2. This divergence is a strong indicator of disorder and is often coupled with the onset of antiferromagnetic and/or ferrimagnetic cluster formation. The temperature in which the divergence occurs is often denoted the freezing temperature, T_f. The intrinsic chemical disorder of bulk CaMn_{0.5}Ru_{0.5}O_{3−δ} and antiferromagnetic and ferrimagnetic phases below 95 K supports this observation within the film.

The SrTiO_3 grown film is distinctly more magnetically inhomogeneous as illustrated by the multiple magnetic phase transitions. A ferrimagnetic transition is visible near 160 K as well as a transition greater than 280 K. The FC-ZFC curves diverge significantly as an effect of disorder and show a similar transition temperature of 95 K similar to the LSAT film. The inhomogeneity in the susceptibility measurement is inconsistent with the CaMn_{0.5}Ru_{0.5}O_{3−δ} film on SrTiO_3 previously reported.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>$M_{\text{sat}}$ ($\mu_B$/f.u.)</th>
<th>$H_C$ (Oe)</th>
<th>$T_C$ (K)</th>
<th>$T_2$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSAT</td>
<td>1.2</td>
<td>2800</td>
<td>185</td>
<td>95</td>
</tr>
<tr>
<td>STO</td>
<td>0.5</td>
<td>1900</td>
<td>160</td>
<td>95</td>
</tr>
</tbody>
</table>

Table 5.2: Summary of magnetic data obtained from SQUID measurements for the three films grown on LSAT and STO.

Figure 5.6: Field-cool (closed circles) and zero-field cooled (open circles) susceptibility measurements of CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films grown on LSAT and SrTiO$_3$ substrates.
5.3.4 Magnetoresistance

The MR of the films were obtained as a function of field and variable temperatures at 10 tesla in Figure 5.7 and Figure 5.8, respectively. Here, percent MR was calculated using \((R_H - R_0)/R_0 \times 100\%\) where \(R_H\) is the resistivity with an applied field and \(R_0\) is the resistivity at zero applied field. A decrease in the resistivity with increasing applied magnetic field is observed. Unlike \(A\)-site substituted manganites which exhibit colossal magnetoresistance\(^{18}\), there is no maximum in the MR near the \(T_C\) of 200 K for \(\text{CaMn}_{0.5}\text{Ru}_{0.5}\text{O}_3-\delta\). However, the MR values obtained are appreciable. Enhanced MR has also been illustrated in magnetic \(\text{Sr}_2\text{FeMoO}_6\) due to a large sensitivity to intergranular effects.\(^{19}\) Mechanistically speaking, grain boundaries tend to weaken the exchange interactions. This leads to easier alignment of the magnetic domains with an applied magnetic field and reduction of scattering.\(^{20}\) The film grown on LSAT reaches a maximum MR of approximately \(-27\%\) at 10 tesla and 5 K. At lower fields of 1 tesla, the MR is reduced to approximately \(-5\%\). The film grown on \(\text{SrTiO}_3\) behaves similar until about 150 K, increases rapidly to a value of \(-46\%\) at 50 K, and then proceeds to a large, positive value of nearly \(+150\%\). Taking into consideration the conductivity and magnetic data previously discussed, it is clear that this sample is magnetically inhomogeneous and likely contains a large amount of grain boundaries contributing to insulating behavior. The data itself shows that this sample exhibits non-linear magnetoresistance below 150 K, most likely due to a non-uniform magnetism and conductivity.
Figure 5.7: Field dependent magnetoresistance data at different temperature. The top dataset is for the film grown on LSAT and the bottom for the film grown on SrTiO$_3$. The percent magnetoresistance for each of the films collected at different temperatures. The lowest attainable temperature for the SrTiO$_3$ film was 20 K.

In addition to intergranular effects, B-site disorder may introduce various intragranular variations in the crystal structure leading to nonuniform properties. Previous reports of large, positive magnetoresistance have been observed in composite semiconductors and nonmagnetic compounds doped with small amounts of silver. The presence of positive MR in these systems was correlated with random disorder in the conductivity, or
electronic disorder. The perovskite La$_{0.7}$Pb$_{0.3}$MnO$_3$ also exhibited positive MR below 50 K in conjunction with colossal MR above this temperature.$^{23}$ This has been described by quantum interference effects, also related to disorder in a material. The chemical disorder and inhomogeneity created by the large lattice mismatch in the film grown on SrTiO$_3$ may be the origin of the intriguing positive MR.

![Figure 5.8](image)

**Figure 5.8**: The percent magnetoresistance for each of the films collected at different temperatures.

### 5.4 Discussion

The structure-property relationships of CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films grown on substrates with different lattice mismatch is complicated by the fact that its crystal structure is a distorted, orthorhombic perovskite containing rotations of the Mn/Ru–O$_6$ octahedra. This fact ties into the recent interest regarding the impact of octahedral rotations of non-cubic films grown on cubic substrates leading to misfit strain. Structural parameters such as lattice parameters and rocking curve FWHMs of the CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films appear quite similar. However, the variation in magnetic, electronic and MR properties between
the two samples implies that the bulk of the film contains different degrees of grain boundaries which could be due to varying misfit strain effects. The octahedra rotations in orthorhombic films were investigated by Rondinelli et al. In this study, the octahedral tilting in a noncubic film was controlled for several layers by using a cubic substrate as a template. Tilting eventually became more severe due to strain relaxation. A primitive sketch of this is shown in Figure 5.9. As an orthorhombic compound, CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ grown on cubic LSAT and SrTiO$_3$ substrates may indeed exhibit both a strained (non-tilted) region, followed by a relaxed (tilted) region. In fact, the rocking curves for both films suggest both a strained and relaxed region which may correspond to such a scenario. This model helps to explain the propensity for greater grain boundary formation in the film grown on SrTiO$_3$ which has greater lattice mismatch.

The explanation of misfit strain effects helps to explain the notable enhancement in the MR going from LSAT to SrTiO$_3$. This trend may best be explained by an increase of grain boundaries and cluster formation with increased lattice mismatch. Enhanced MR has also been illustrated in magnetic Sr$_2$FeMoO$_6$ due to a large sensitivity to intergranular effects. Mechanistically speaking, antiphase boundaries and grain boundaries tend to weaken the exchange interactions. This leads to easier alignment of the magnetic domains with an applied magnetic field and reduction of scattering.
In a sense, the ease in which CaMn$_{0.5}$Ru$_{0.5}$O$_3$ may be grown, in spite of a lattice mismatch of +1.4% for LSAT, makes this material rather appealing from a technological standpoint. Since the magnetic order is not dependent upon the ordering of the Mn and Ru ions, this eliminates one crucial element that spintronic material Sr$_2$FeMoO$_6$ is so dependent upon. The trade-off between the two compounds is that the ferrimagnetic ordering temperature for CaMn$_{0.5}$Ru$_{0.5}$O$_3$ remains below room temperature. Furthermore, spin-polarization measurements are still required to verify the theoretical claim that this compound is a half-metal. At this time, it may not be realistic to implement this compound into spintronic devices. However, a search for more magnetically ordered,
chemically disordered materials may reveal new compounds with potentially higher magnetic ordering temperatures.

5.5 Conclusions

CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films were grown on LSAT and SrTiO$_3$ with lattice mismatch values of +1.4% and +2.3% (respectively). Analysis of the lattice parameters and degree of texture demonstrated that the two films are quite similar. In contrast, the magnetic and transport properties are quite different which suggests that the bulk of these films must contain varying amounts of structural defects between the two. The structural impacts manifest themselves also within the conductivity where “bad” metallic to insulating behavior appears as the lattice mismatch increases from LSAT to SrTiO$_3$.

The magnetic properties of the CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ were also probed using SQUID magnetometry. An $M_{\text{sat}}$ of 1.2 $\mu_B$/f.u. was obtained for the film grown on LSAT, which is much greater than the film grown on SrTiO$_3$ (0.5 $\mu_B$/f.u.). The $M_{\text{sat}}$ of the LSAT film agrees well with values obtained for the ferrimagnetic ground state theoretically predicted as well as the bulk. Each CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ film exhibits ferrimagnetic behavior with $T_C$ as high as 185 K and a second transition, potentially antiferromagnetic in nature, near 95 K. The MR of each sample was measured and exhibits a magnetoresistance as large as $-25\%$ and $+150\%$ for the film grown on LSAT and SrTiO$_3$ (respectively).

In summary, we have successfully grown and characterized CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ epitaxial films and studied the structural, magnetic and transport properties as a function of lattice mismatch. From this study, we conclude that CaMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ behaves quite similar to the bulk when the lattice mismatch is minimized.
5.6 References


Chapter 6

Effects of oxygen partial pressure on the structural and transport properties of SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ epitaxial films

6.1 Introduction

The chemically disordered perovskite, SrMn$_{0.5}$Ru$_{0.5}$O$_3$, is a particularly interesting compound for a variety of reasons. One cause for this interest is based on the large contrast of properties in the two end members, SrMnO$_3$ and SrRuO$_3$. The latter is an itinerant ferromagnetic ($T_C = 163$ K$^1$) while the former is an antiferromagnetic insulator ($T_N = 235$ K$^2$). The difference arises in the latter compound due to the weaker overlap between 3$d$ orbitals of Mn ions and oxygen 2$p$ orbitals, resulting in localized t$_{2g}$ electrons.$^3$ Thereby, the introduction of 4$d$ transition metal Ru to form the solid solution, SrMn$_x$Ru$_{1-x}$O$_3$, affects the electronic structure. This results in shifts in the compounds structural, electrical and magnetic properties.$^4,5$

There are several examples in which the properties of SrMn$_x$Ru$_{1-x}$O$_3$ have been investigated. Single crystal studies revealed a nearly 8-fold decrease in resistivity for the range of compositions from $x = 0$ to $x = 0.6$ due to the elimination of itinerant Ru t$_{2g}$ electrons as Mn replaces Ru.$^4$ The transition of ferromagnetism to antiferromagnetism occurs between $x = 0.44$ to $x = 0.59$. Another study completed by Kolesnik et al. demonstrated
the coexistence of competing antiferromagnetic and ferromagnetic phases leading to spin-glass behaviour in polycrystalline samples which suggests a large degree of magnetic inhomogeneity in the SrMn$_x$Ru$_{1-x}$O$_3$ system. As a result of this inhomogeneity an enhanced magnetoresistance (MR) of $-41\%$ at 10 K and 7 tesla was discovered for the nearly 50% Mn substitution. The large MR of the intermediate composition of $x = 0.5$ warrants further investigation in thin films in order to realize their potential in spintronic devices.

Bulk studies have revealed an interesting case of orbital ordering in the intermediate compound of interest, SrMn$_{0.5}$Ru$_{0.5}$O$_3$ and have been previously described in Chapter 1. More detailed studies reveal nearly equal concentrations of Mn$^{3+}$, Mn$^{4+}$, Ru$^{4+}$, and Ru$^{5+}$, equating to average oxidation states of Mn$^{3.5+}$ and Ru$^{4.5+}$. The tendency of the transition metal ions in this compound to have variable oxidation states has led to interest in the influence of oxygen partial pressure ($pO_2$) during film deposition. Since low $pO_2$ can lead to oxygen vacancies, the opportunity to $n$-dope SrMn$_{0.5}$Ru$_{0.5}$O$_3$ is possible which can alter the conductivity.

The role of oxygen vacancies in the end compounds SrMnO$_{3-\delta}$ and SrRuO$_{3-\delta}$ has been investigated. SrMnO$_{3-\delta}$ undergoes multiple phase transitions, exhibiting mixed ion and electronic conductivity in the cubic form, but remains metastable in air. Chang et al. investigated the electrical and structural properties associated with pulsed laser deposited SrRuO$_{3-\delta}$ films grown at different $pO_2$. They observed an expansion of the out-of-plane lattice constant in addition to an increase in electrical resistivity with decreasing oxygen pressure. These results suggest that extraction of oxygen from the SrMn$_{0.5}$Ru$_{0.5}$O$_3$ perov-
skite may be feasible and may lead to new redox pairs which can alter its transport properties.

Studies of oxygen deficient SrMn$_{0.5}$Ru$_{0.5}$O$_3$ thin film materials have not been previously reported and therefore the structural and transport properties are uncertain. Epitaxial films, however, significantly reduce grain boundaries which have been shown to impact the MR of spintronic materials such as Sr$_2$FeMoO$_6$.$^{10}$ In addition, systematically changing the oxygen content of this perovskite will provide insight into how the electronic structure impacts the MR since vacancies will vary the oxidation states of the magnetic ions and hence their magnetic interactions. In this chapter, we investigate the structural and magnetotransport properties of SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ epitaxial films grown by PLD in various oxygen partial pressures in hopes to determine the tunable nature of the electronic structure. The lattice parameters, stoichiometry and microstructure are presented and discussed in addition to the magnetotransport properties of this system.

6.2 Experimental

6.2.1 Target Synthesis

A SrMn$_{0.5}$Ru$_{0.5}$O$_3$ target was synthesized following a traditional solid state synthesis approach. Stoichiometric amounts of SrCO$_3$, RuO$_2$ and Mn$_2$O$_3$ were ground in an agate mortar and pestle until the powder was uniform. The powder was placed in an alumina crucible and heated in a high-temperature box furnace at 1385 °C for 8 hours at a heating and cooling rate of 10 °C/min. Pure-phase powder was obtained and then ground for 3 hours to reduce the crystallite size. The target was formed by pressing a 1-inch × 5 mm disc using a Carver © hydraulic press and then sintering at 1400 °C for 2 hours.
at a heating and cooling rate of 10 °C/min. The $\theta-2\theta$ XRD scan of the as-prepared 
$\text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ target is illustrated in Figure 6.1.

![XRD pattern of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ target.](image)

**Figure 6.1:** $\theta-2\theta$ XRD pattern of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ target.

### 6.2.2 PLD Film Growth

SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films were deposited on 0.29(LaAlO$_3$)0.35(Sr$_2$TaAlO$_6$) (LSAT) 
(100)-oriented substrates using pulsed laser deposition. Films were grown at a substrate 
temperature of 800 °C and in varying degrees of oxygen partial pressure (pO$_2$) in either 
75 mTorr of argon, 75 mTorr of oxygen, or 150 mTorr of oxygen. All films were cooled 
in the same atmosphere used during growth. A laser fluence of 2 J/cm$^2$, repetition rate of 
5 Hz, and 5000 pulses were used. All films were grown when a base pressure of 
$10^{-7}$ Torr was achieved and after the target was pre-ablated with 1000 pulses. The sub-
strate-to-target distance was set to 38 mm.
6.3 Results and Discussion

6.3.1 Impact of varying pO$_2$ on the Structure

The full $\theta$-2$\theta$ XRD patterns for each film grown at different pO$_2$ are illustrated in Figure 6.2 (a)–(c) and high resolution XRD and rocking curves are included in Figure 6.3. A summary of their structural data are listed in Table 6.1.

![Graph showing XRD patterns](image)

**Figure 6.2:** Full $\theta$–2$\theta$ XRD patterns of SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ grown on LSAT at 800 °C in (a) 75 mTorr Ar (b) 75 mTorr O$_2$ (c) 150 mTorr O$_2$. 
Figure 6.3: High resolution $\theta$–$2\theta$ XRD patterns showing Laue oscillations (left) and rocking curves illustrating narrow FWHM (right) of $\text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$ grown in (a) 75 mTorr Ar (b) 75 mTorr O$_2$ and (c) 150 mTorr O$_2$.

The rocking curves for the $\text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$ (004) reflections of each film are shown in Figure 6.3(a-c). The narrow FWHM value of 0.02° (comparable to 0.01° for LSAT) for the film grown in the lowest pO$_2$ indicates a high level of texture of the c–axis oriented planes of the film. In fact, small FWHM values are observed for all of the films.
regardless of growth atmosphere. Figure 6.3(a-c) shows the high-resolution XRD patterns of each film containing Laue oscillations, demonstrating their high structural quality at all pO$_2$. From the Laue oscillations, thicknesses for each film were determined to be 60 nm, 90 nm and 80 nm for the 75 mTorr Ar, 75 mTorr O$_2$ and 150 mTorr O$_2$. These values were calculated using the following equation where $\theta_{i+1}$ and $\theta_i$ are the theta angles of two adjacent oscillation maxima or minima:

$$t = \frac{\lambda}{2}(\sin\theta_{i+1} - \sin\theta_i).$$ \[Equation 2.1\]

The pseudocubic lattice parameters of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ in the bulk are $a_p = 3.856$ Å and $c_p = 3.967$ Å.$^7$ The larger lattice parameter of the LSAT substrate (3.867 Å) should induce tensile strain, where expansion of the in-plane lattice parameter accompanied by compression of the out-of-plane lattice parameter is expected for fully strained films. The in-plane lattice parameters are larger than the bulk value for all three films, Table 6.1. Surprisingly, the in-plane lattice parameters are noticeably larger than even the LSAT substrate. The out-of-plane lattice parameter is sensitive to the pO$_2$ in the growth chamber, decreasing as the pO$_2$ increases. The in-plane lattice demonstrates a similar but less pronounced trend. This suggests the formation of oxygen vacancies, SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$, whose concentration increases as the pO$_2$ during growth decreases. The observed variation in lattice parameter can be attributed to a decrease in the oxidation states of Mn and/or Ru as $\delta$ increases, which leads to larger lattice parameters because the lower oxidation state cations have larger ionic radii. Similar conclusions have been made in other reports of oxygen-deficient perovskite thin films.$^{11-14}$
<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Out-of-plane (Å)</th>
<th>In-plane (Å)</th>
<th>Rocking Curve FWHM (°)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
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<td>3.91657(4)</td>
<td>0.02392(26)</td>
<td>60</td>
</tr>
<tr>
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</tr>
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<td>3.8981(1)</td>
<td>0.04902(86)</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 6.1: Structural data for SrMn₀.₅Ru₀.₅O₃₋δ films grown under various pO₂.

To further probe the structural quality, HAADF-STEM measurements of the <110> view were completed as shown in Figure 6.4(a-c) on the film grown in 75 mTorr Ar. Since LSAT is a composite between cubic and rhombohedral phases, disordered regions are visible in the substrate, particularly in (c). It is evident that there is no distinct pattern of B-site ordering of SrMn₀.₅Ru₀.₅O₃ as shown in a previous report of ordered perovskite films. The lack of order of the ruthenium and manganese is not unexpected since SrMn₀.₅Ru₀.₅O₃ is chemically disordered in the bulk. The interface is free from large particulates or linear defects that would contribute to an expanded in-plane lattice parameter, Figure 6.4a. However, areas of bright and dark contrast can be distinguished quite clearly in Figure 6.4(b-c). While defects are not obvious around these areas, the varying contrast could lead to potential local non-stoichiometry of the Ru- and/or Mn- ions. This could be as a result of disorder-induced cluster formation as suspected in the bulk counterpart. Additionally, the inhomogeneity of the substrate near the interface could also lead to some contrast issues.
Figure 6.4: HAADF-STEM images of SrMn$_{0.5}$Ru$_{0.5}$O$_3$-LSAT interface down the <110> crystallographic orientation. (a) large scale image showing dark contrast region at interface and Pt coating at top (b) close-up image showing regions of bright contrast separated by areas of dark contrast (c) Interface image showing contrast clusters and dark contrast at interface. Yellow dotted lines are added to guide the eye in areas of different contrast.

6.3.2 Stoichiometry

RBS was used to further probe the potential for non-stoichiometry of Sr, Mn or Ru cations. From the spectrum illustrated in Figure 6.5, a composition of
Sr\textsubscript{1.00}Mn\textsubscript{0.50}Ru\textsubscript{0.48}O\textsubscript{3–δ} has been determined for the film grown in argon. This composition confirms a very near ideal stoichiometry for the cations. Comparably, the film grown in 75 mTorr O\textsubscript{2} had a stoichiometry of Sr\textsubscript{1.00}Mn\textsubscript{0.50}Ru\textsubscript{0.50}O\textsubscript{3–δ}. The similar stoichiometry implies that variations of the structural or physical properties between the films do not result from cation non-stoichiometry. Since RBS probes a large sample area (~3 × 3 mm\textsuperscript{2}), the stoichiometry calculated is essentially an average and does not take into account potential local non-stoichiometry at the interface. RBS also does not account for disorder-induced Ru- or Mn-rich clusters. Additionally, determining oxygen concentration in films using RBS is a non-trivial process and has not been quantified.

**Figure 6.5:** RBS Spectrum of SrMn\textsubscript{0.5}Ru\textsubscript{0.5}O\textsubscript{3–δ} on LSAT grown at 75 mTorr of Ar.
6.3.3 Transport Properties

6.3.3.1 Electrical Conductivity

The electrical conductivity of bulk SrMn$_{0.5}$Ru$_{0.5}$O$_3$ has previously been described as insulating with a room temperature conductivity of 10 S/cm.$^7$ Ideally, epitaxial films provide an opportunity to probe the intrinsic conductivity of a material since grain boundary resistance will be significantly reduced. In Figure 6.6, the log$_{10}$ conductivity of the three SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ films are shown. Each of the films exhibits insulating behavior, in good agreement with bulk and single crystal studies.$^{3,7}$ There is a noticeably sharper increase in conductivity around 50 K in comparison to the bulk material of nearly two orders of magnitude. However, no distinct transitions are observed near the antiferromagnetic ordering temperature of 200 K observed in the bulk material. If orbital ordering were diminished by the introduction of oxygen vacancies, the conductivity would be expected to behave more like Ca$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ or CaMn$_{0.5}$Ru$_{0.5}$O$_3$ which are more metallic in nature due to the loss of orbital ordering. The enhanced conductivity may instead best be explained by the anticipated reduction in grain boundary resistance.
Temperature dependence of the log conductivity of the films grown at 150 mTorr O$_2$ (filled circles), 75 mTorr O$_2$ (open circle) and 75 mTorr Ar (filled triangles). The inset shows the variable range hopping model for the three films at temperatures up to 300 K.

The initial introduction of oxygen vacancies caused by growing in 75 mTorr of O$_2$ reduces the conductivity by an order of magnitude. Chang et al. reported similar trends in conductivity with the introduction of oxygen vacancies into SrRuO$_3$.9 We suspect that the decrease in film conductivity may be due to a slight increase in the Mn$^{3+}$ ions, whose concentration correlates with more insulating behavior across the Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ solid solution.7 Once oxygen is removed from the growth atmosphere, the conductivity increases to values only slightly higher than SrMn$_{0.5}$Ru$_{0.5}$O$_3$ grown at 150 mTorr O$_2$. This suggests that the oxidation states of the Mn and Ru ions are being affected. As previously mentioned, bulk SrMn$_{0.5}$Ru$_{0.5}$O$_3$ maintains relatively equal concentrations of Mn$^{3+}$, Mn$^{4+}$, Ru$^{4+}$ and Ru$^{5+}$, corresponding to the Mn$^{3+}$ + Ru$^{5+}$ ↔ Mn$^{4+}$ + Ru$^{4+}$ valence
The increase in volume of the film lattice with decreasing pO$_2$ suggests reduction of the Mn and/or Ru ions to a larger cation size. However, there is not nearly as drastic of an increase in the film lattice for the films grown in oxygen as there is for the film grown in argon. The much larger change in lattice parameters observed for the film grown in argon implies a more complex redox situation whose mechanism is not necessarily obvious. Table 2 summarizes the ionic radii of different 6-coordinate Mn and Ru ions. It is likely that the formation of oxygen vacancies in the argon grown film led to the formation of either larger Mn$^{3+}$ and Ru$^{4+}$ ions. Since many different redox pairs are possible within this system, it illustrates a very important point that controlling the precise electronic structure of these materials is heavily dependent upon the atmosphere in which they are grown.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mn$^{3+}$</th>
<th>Mn$^{4+}$</th>
<th>Ru$^{4+}$</th>
<th>Ru$^{5+}$</th>
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<td>0.530</td>
<td>0.620</td>
<td>0.565</td>
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</table>

Table 6.2: Ionic radii of 6-coordinate Mn and Ru ions and the redox potential for the ion pairs.

In order to explain the temperature dependence of the conductivity, we fit the data using the variable range hopping (VRH) mechanism given by the relationship:

\[
\sigma = \sigma_0 (-T_0/T)^{1/4}
\]  

[Equation 2.2]

Here, $\sigma_0$ is the pre-exponential factor and $T_0$ represents the characteristic temperature coefficient (sometimes denoted with the symbol $A$). This is illustrated in the inset of Fig-
ure 6.6. A linear least squares fit was completed to determine the $T_0$ term. This fit provided values of 8.53(8), 9.47(7) and 10.25(4) for the 75 mTorr Ar, 75 mTorr O_2 and 150 mTorr O_2 films, respectively. The VRH mechanism is generally expected at low temperatures, though it models our data well from 5 K to 300 K. The 75 mTorr O_2 film deviates slightly at higher temperature which may suggest that another mechanism such as activated transport is taking over. The agreement between epitaxial films, single crystals and sintered pellets is satisfying and indicates that VRH conductivity is the intrinsic behavior of this compound.

6.3.3.2 Magnetoresistance

The magnetoresistance provides another area in which comparison may be drawn between the SrMn_{0.5}Ru_{0.5}O_{3-δ} films. Zero-field cooled MR measurements were obtained at six different temperatures and are plotted in Figure 6.7a. A summary of the temperature dependence for the three films at 14 tesla are also shown in Figure 6.7b. The temperature dependence of the MR has been defined as $(R_H - R_0)/R_0$, where $R_H$ is the resistance with an applied field and $R_0$ is the resistance at zero-applied field. We see remarkably large MR at 5 K and 14 tesla of $-66\%$ (150 mTorr O_2), $-62\%$ (75 mTorr O_2), and $-46\%$ (75 mTorr Ar). At low temperatures, the MR decreases with decreasing pO_2 as illustrated in Figure 6.7. Once the temperature increases, the films grown in oxygen behave similarly, reaching an MR of approximately $-2\%$ at 300 K. Compared to the bulk MR value of $-43\%$ obtained by Zhang et al. at 7 T, values of $-43\%$, $-39\%$ and $-23\%$ are obtained with decreasing pO_2. The similarity in MR values indicates that the films grown in oxygen behave bulk-like. Therefore, we expect that the MR may be correlated
to the coexistence of ferromagnetic and antiferromagnetic interactions leading to disorder-induced frustration and cluster formation.\textsuperscript{17} The application of a large magnetic field aligns the clusters and reduces the scattering, resulting in large, negative MR.\textsuperscript{18} The reduction of cluster formation in the film grown in 75 mTorr of Ar is supported by the lowest $-\text{MR}\%$ for all temperatures and more narrow coercivity at 5 K.

![Graph](image)

**Figure 6.7:** (a) Normalized magnetoresistance versus field measurements of the films grown at 150 mTorr O\textsubscript{2} (blue), 75 mTorr O\textsubscript{2} (red) and 75 mTorr Ar (black) at 5 K and (b) Temperature dependence of the magnetoresistance for the three films grown at different oxygen partial pressure at applied fields of 14 tesla.
6.4 Conclusions

Epitaxial films of SrMn$_{0.5}$Ru$_{0.5}$O$_{3-\delta}$ have been successfully grown via PLD. Decreasing the pO$_2$ during growth shows an enlargement of the in- and out-of-plane lattice parameters and the overall volume of the unit cell. This implies a sensitivity of the system to the formation of oxygen vacancies since this would promote the reduction of the Mn and Ru ions to lower oxidation states and hence large ionic radii. Despite the formation of oxygen vacancies, a large degree of texture and a high degree of crystallinity is observed for all of the films as indicated by small rocking curve FWHM and the presence of Laue oscillations. In general, the film stoichiometry is maintained during growth in oxygen and argon atmospheres as determined by RBS. Transmission electron microscopy revealed an interface which was free from defects, though a dark and bright contrast regions suggest local areas of non-stoichiometry.

The conductivity and magnetoresistance of the films were larger than bulk and single crystal reports of SrMn$_{0.5}$Ru$_{0.5}$O$_3$. The decrease in oxygen partial pressure led to slight variations in the conductivity, though the temperature dependence for all three films remained semiconducting. A magnetoresistance as high as $-66\%$ was obtained for the film grown in 150 mTorr of O$_2$. This value decreased slightly with decreasing pO$_2$, though the hysteretic behavior and temperature dependence was similar for all three samples. This supports that oxygen vacancy formation and hence electron doping may not play a huge role upon the magnetotransport mechanism of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ films.
6.5 **Acknowledgements**

We would like to thank Dr. Leszek Wiełunski for performing the RBS measurements at Rutgers University and Dr. Michael Susner for assisting with our conductivity measurements. Support for this research was provided by the Center for Emergent Materials at the Ohio State University, an NSF MRSEC (Award Number DMR-0820414).

6.6 **References**


Chapter 7

Compressibility Mechanism of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ determined by

High Pressure Neutron Powder Diffraction

7.1 Introduction

The use of pressure in solid state experiments provides a unique opportunity to create new structural, magnetic and electronic states within a compound. Pressure studies may be achieved in one of two ways: in-situ and ex-situ.$^1$ The in-situ pressure experiment relies on measuring the compressibility of a material while at an applied pressure of interest. The ex-situ experiment is focused on the irreversible changes associated with a material after pressure has been applied and the sample has been removed from the pressure apparatus. Both of these processes provide an understanding of the pressure-temperature phase diagram and phase transitions as well as reveal new physical properties. However, in-situ experiments are generally preferable as many interesting phenomena under pressure are reversible and not observable when external pressure is removed.$^1$ As a result, many techniques including x-ray and neutron diffraction, Raman spectroscopy, and various magnetic and electrical measurements systems may be modified to perform in-situ high-pressure studies.
Perovskites may undergo many different types of structural phase transitions at high pressures. However, there are many conflicting reports as to whether perovskites with applied pressure have a preference for higher or lower symmetry phase transitions. An illustration of octahedral tilting, and hence lower symmetry, being introduced into a cubic perovskite lattice is shown in Figure 7.1. In the case of the double perovskite Ba$_2$YTaO$_6$, the compound transitions from high symmetry $Fm\bar{3}m$ (cubic) to a lower symmetry $I4/m$ (tetragonal) at 5.6 GPa. The GdFeO$_3$-type perovskite CaSnO$_3$ also illustrates a reduction in symmetry up to 7 GPa. In both compounds, the phase transitions are dominated by octahedral tilting at higher pressures due to more compressible $A$–$O$ bonds. In contrast, rhombohedral LaAlO$_3$ exhibits a shift towards higher symmetry at 14 GPa. Kennedy et al. reported a unique phase transition in the rhombohedral perovskite PrAlO$_3$ where an initial increase in symmetry towards cubic was observed followed by a shift to orthorhombic (lower) symmetry at even higher pressures. It is also important to mention that not all compounds exhibit phase transitions with pressure. For example, orthorhombic SrRuO$_3$ and hexagonal SrMnO$_3$ maintain their symmetry up to the highest applied pressure of 34 GPa and 28.6 GPa (respectively), though the lattice parameters and volume exhibit a sensitivity to the pressure. This being said, the preference for perovskites to undergo phase transitions at non-ambient pressures is most likely dependent upon the starting structural parameters of the compound. For example, a perovskite containing octahedral tilting or Jahn-Teller (JT) active ions versus those that have minimal structural distortions may exhibit different compression mechanisms under pressure.
Figure 7.1: High symmetry to low symmetry transition in the perovskite structure where corner sharing B(B')X₆ octahedra are shown with A cation occupying the interstices of the framework. The reduction to lower symmetry occurs via the introduction of octahedral tilting.

In addition to affecting the octahedral tilting and bond lengths and angles, high pressure may also impact the occupation and ordering of orbitals within a material. This in turn may influence the electrical properties and magnetic ordering of the system. Perhaps one of the best illustrations of this behaviour is within perovskites containing JT active ions such as Mn³⁺. The compound LaMn³⁺O₃ is an interesting case of how orbital order corresponds to magnetic ordering and its structure has previously been described in Section 1.1.3.1.¹⁰ Orbital ordering of this compound as a function of applied pressure has been previously studied. Using high-pressure synchrotron radiation, the “critical pressure” for complete quenching of the JT distortion and orbital ordering was found to be 32 GPa.¹¹ The crystal structure above this pressure exhibited no JT distortion or orbital order which corresponded to an insulator to metal transition. The magnetic structure of LaMnO₃ may also be tuned with pressure. Pinsard-Gaudart et al. performed high pressure neutron diffraction experiments on this compound up to 7 GPa. It was shown that the A-type AFM ordering temperature increased, but the magnetic moment was severely dimin-
ished in conjunction with a compressed $b$ lattice parameter (the largest lattice parameter).\textsuperscript{12} While this pressure regime is lower than other reports\textsuperscript{11}, the hypothesis is that suppression of the JT distortion oriented along the $b$ axis is responsible for the decrease in magnetic moment and larger ordering temperature. Physical pressure also has the capability of changing the magnetic order. When orbitally-ordered LaMnO$_3$ is substituted with 25\% calcium for lanthanum to form La$_{0.75}$Ca$_{0.25}$MnO$_3$, the material becomes an orbitally disordered, ferromagnet at ambient pressure.\textsuperscript{13} Above an applied pressure of 23 GPa, the compound undergoes a uniaxial compression of the MnO$_6$ octahedra along the $b$ axis which signals orbital order. The orbital order destabilizes the ferromagnetism and creates an A-type AFM ground state similar to un-substituted LaMnO$_3$. In-situ pressure experiments on other AFM and orbitally-ordered oxides can provide new means to study and create new exotic ferromagnetic states.

\subsection*{7.1.1 SrMn$_{0.5}$Ru$_{0.5}$O$_3$, a compound for high-pressure studies}

Previous work on LaMnO$_3$ illustrates a key point that suppression of the orbital order and JT distortion using pressure may impact both the magnetic and electronic states of orbitally ordered compounds. The related perovskite SrMn$_{0.5}$Ru$_{0.5}$O$_3$ also demonstrates orbital ordering and a C-type AFM structure that is consistent with the pattern of orbital ordering.\textsuperscript{14,15} The structure of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ can be described as tetragonal ($I4/mcm$) with elongation along the $c$-axis due to the cooperative JT distortion and exhibits anti-phase tilting ($a'^0a'^0c^-$) about the $c$-axis.

This compound is particularly interesting due to the sensitivity of the material to chemical pressure.\textsuperscript{15} Substitution of the smaller Ca$^{2+}$ ion to a value of $x = 1$ causes com-
plete loss of orbital ordering as well as the JT distortion. This is also evidenced by a decrease in cell parameters and unit cell volume and increase in octahedral tilting with calcium substitution, Figure 7.2. A detailed look at the bond lengths and angles indicate the presence of large amounts of octahedral tilting and a reduction of symmetry to an orthorhombic (Pnma, $\bar{a}b^+a^-$) structure type.

The application of chemical pressure by substituting strontium with calcium drives the structure to an orthorhombic, ferrimagnetic conducting state. Additionally, Ca-rich samples exhibit ferrimagnetism ($T_C = 230$ K) and metallic conductivity that has been predicted to be highly spin polarized (half-metallic). The variation in the structural, transport and magnetic properties illustrates that chemical pressure directly impacts the exchange interactions between the Mn- and Ru-ions. It is logical to assume that application of external pressure to one of the Sr-rich orbitally ordered, AFM phases ($x = 0$) could drive a transition to half-metallic ferrimagnetic phase.
Figure 7.2: Pseudocubic lattice parameters derived from the following relationships: $(Pnma- a_p = a/\sqrt{2}, b_p = b/2, c_p = c/\sqrt{2}; I4/mcm- a_p = b_p = a/\sqrt{2}, c_p = c/2)$ and the unit cell volume plotted as a function of increasing calcium content. Plot was recreated from reference [15].

To the best of our knowledge, no studies on the SrMn$_{0.5}$Ru$_{0.5}$O$_3$ system have been obtained by high-pressure neutron powder diffraction (NPD). The most compelling question is whether application of physical pressure will lead to similar changes in orbital and magnetic ordering that mimic those caused by chemical pressure. The behaviour will not necessarily be the same because the size mismatch between Sr$^{2+}$ and Ca$^{2+}$ leads to local strains that are known to impact physical properties. The magnetic behaviour will be dependent on how much of the volume reduction is taken up by compression of the elongated Mn–O bonds and how much is taken up by rotations of the octahedra. Since SrMn$_{0.5}$Ru$_{0.5}$O$_3$ is disordered and the bond lengths are determined by NPD as an effective average of the structure, it is plausible to assume any compressibility observed along the c-axis is due predominantly to changes in shape of the MnO$_6$ octahedra rather than the
RuO$_6$ octahedra. A pictorial representation of the distorted MnO$_6$ octahedra is shown in Figure 7.3. The question remains as to whether the compression of the MnO$_6$ would lead to a change in symmetry and if so, would it lead to a more symmetric or a less symmetric structure.

High pressure NPD provides an excellent opportunity to find one or more new magnetic phases, as well as to explore the similarities and differences between the effects of chemical pressure versus external pressure. To understand how the magnetic, orbital and structural properties of these compounds are impacted by pressure and answer the aforementioned questions, high pressure NPD experiments were performed on SrMn$_{0.5}$Ru$_{0.5}$O$_3$ at pressures ranging from 0.4 GPa to 8 GPa and at temperatures above and below the magnetic ordering temperature.

**Figure 7.3:** Perovskite containing two different the distorted MnO$_6$ octahedra (elongated bonds) and the undistorted RuO$_6$. The symmetry of this system under pressure is determined based upon either octahedral tilting or anisotropic compression of the lattice parameters.
7.2 Experimental

7.2.1 High Pressure Neutron Diffraction

Individual time-of-flight (TOF) data were collected at the Spallation Neutron and High Pressure (SNAP) diffractometer at Oak Ridge National Laboratory, USA. For this experiment, a total of six detector banks were used and a bandwidth chopper was used to define a wavelength range between 0.5–4.2 Å for detector banks 1–4 and 0.99–7.4 Å for detector banks 5–6. Data were measured using a highly pixelated Anger camera centered on a scattering angle of 42.16º (Banks 1–4) and 84.53º (Banks 5–6). Therefore, each pressure-temperature data point will have two histograms, histogram 1 and histogram 2, for banks 1–4 and banks 5–6 (respectively). The data were converted to neutron counts versus d-spacing and summed to give a measured intensity averaged across the entire detector bank.

A SrMn$_{0.5}$Ru$_{0.5}$O$_3$ sample was prepared for neutron diffraction experiments as described in Chapter 3. Approximately 225 mg of sample was pressed into a toroid shape using a standard hydraulic press. The sample was placed in TiZr gasket with a small amount of methanol to serve as a pressure medium. Pressure was applied externally to the compound using a Paris-Edinburgh (PE) pressure cell. Pressures of 0.4 GPa, 0.8 GPa, 1.3 GPa 2 GPa, 3 GPa, 4.6 GPa, 6 GPa, and 8 GPa were applied and the temperature was varied from 90 K (lowest attainable temperature) to 300 K. The pressure of 0.4 GPa is the value obtained when the sample is placed in the PE cell and serves as the base-line for zero-applied pressure. No structural changes due to pressure are anticipated for the data collected at 0.4 GPa. An initial 300 K data set was collected prior to cooling down to
90 K to verify the structural integrity of the sample between each pressure-temperature (PT) data set. A typical experiment is described in the following way:

1. Pressure cell temperature is set to 300 K
2. Desired pressure is applied.
3. Preliminary 300 K data is collected (approximately 2.5 hour scan).
4. Pressure cell is cooled to 90 K at desired pressure and first PT data point is collected (approximately 2.5 hour scan).
5. Sample is heated to next temperature at desired pressure.
6. Final PT at desired pressure is 300 K. [this data set is compared to preliminary 300 K to ensure no degradation of the sample].
7. Repeat measurement process for next desired pressure data set.

All of the nuclear and magnetic structures were refined using the software GSAS. The magnetic moment models were imaged using DRAWXTL.

7.3 Results

7.3.1 Nuclear Structure

The refinements of the ambient pressure dataset are illustrated in Figure 7.4 and Figure 7.5 for the low temperature (90 K) and room temperature (300 K) data. These datasets serve as the base-line ambient pressure conditions. The lower set of tick marks denote the nuclear structure reflections, whereas the upper set mark the possible magnetic reflections.

While the SrMn$_{0.5}$Ru$_{0.5}$O$_3$ structure has previously been solved using NPD, different experimental conditions and gasket materials required for high-pressure NPD may
contribute to variations between the reported data. For example, one of the notable features in histogram 2 is the slight offset in the fit for the (100) magnetic peak near 5.4 Å collected below 190 K. The offset is attributed to the initial calibration of the sample which did not include peaks extending to this high of d-spacing. For this reason, the lattice parameters are best illustrated by histogram 1 (d-spacing 0.51 Å–4.23 Å) and the magnetic structure by histogram 2 (d-spacing 1 Å–7.4 Å). The crystal structure is described by the tetragonal space group $I4/mcm$ and Glazer tilt system $a^0a^0c^-$—in good agreement with previous studies by Woodward et al.$^{14}$

The pressure dependent NPD data collected at 90 K and 0.4, 0.8, 1.3, 2, 3, 4.6, 6, and 8 GPa are illustrated in Figure 7.6. Several regions (labeled I, II, III) exhibit tetragonal peak splitting at 0.4 GPa which is reduced upon an increase in pressure. It is important to note that while peak splitting becomes less obvious, tetragonal symmetry is retained up to 8 GPa as determined from Rietveld refinement. This will be discussed further in subsequent sections.

For all of the refinements, the chemical disorder was taken into consideration by constraining the site occupancy of the B-site cation to be 0.5 for both Mn and Ru ions. All previous reports demonstrate no long range order of the Mn and Ru ions.$^{14,15,19}$ The quality of the fit was not improved for any of the PT points if the occupancy was refined. This indicates that the $B$-site order is not affected by changes of the compressibility of the lattice or octahedral tilting induced by pressure.
Figure 7.4: Rietveld refinements of NPD patterns collected at 90 K and 0.4 GPa. The top figure represents histogram 1 and the bottom figure represents histogram 2. In each diagram, the observed data is shown in black, calculated in red, and the difference curve between these two data sets in gray. The black tick marks in each figure represent reflections corresponding to the magnetic phase (top) and nuclear phase (bottom). The most prominent magnetic peak near 5.4 Å is specified with an arrow.
Figure 7.5: Rietveld refinements of NPD patterns collected at 300 K and 0.4 GPa. The top figure represents histogram 1 and the bottom figure represents histogram 2. In each diagram, the observed data is shown in black, calculated in red, and the difference curve between these two data sets in gray. The black tick marks in each figure represent reflections corresponding to the nuclear phase as no magnetic phases were detected at 300 K.
Figure 7.6: NPD patterns collected at 90 K and several pressures. The top figure represents histogram 1 and the bottom figure represents histogram 2. The prominent magnetic peak is illustrated with a black arrow. The gray arrows highlight regions (I, II, III) where the splitting is less pronounced.
NPD patterns at temperatures surrounding 190 K were collected to achieve a more precise gauge of the impact of pressure upon the magnetic ordering. The pressure dependence of the lattice parameters, volume, $c/\alpha$ ratio and $\chi^2$ are listed in Table 7.1 and Table 7.2 for several temperatures. The temperatures were chosen based upon the magnetic ordering temperature of 190 K observed in SrMn$_{0.5}$Ru$_{0.5}$O$_3$. Additionally, the bond lengths for the three different Sr–O bonds, Mn/Ru–O$_{eq}$ and Mn/Ru–O$_{ax}$ are illustrated in Table 7.3.
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<th>Temperature</th>
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<th>190 K</th>
<th>240 K</th>
<th>300 K</th>
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<td>0.8</td>
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<td>5.4301(4)</td>
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<td>7.9808(1)</td>
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<td><strong>χ²</strong></td>
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Table 7.1: Structural information obtained from Rietveld refinement of NPD patterns for each PT data point from 0.4 to 2 GPa. *Data point collected at 250 K.
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**Table 7.2:** Structural information obtained from Rietveld refinement of NPD patterns for each pressure-temperature data point from 3 to 8 GPa.
Table 7.3: Bond lengths obtained for Sr and Mn/Ru cations as a function of pressure. Both 90 K and 300 K data are included for comparison.

7.3.1.1 Estimating the Bulk Modulus

In an effort to quantify the compressibility of SrMn$_{0.5}$Ru$_{0.5}$O$_3$, the bulk modulus, $B_0$, has been determined. This value is a measure of a material’s ability to retain its volume while under an applied physical pressure. For example, a compound with a large bulk modulus is difficult to compress. The bulk modulus was found by fitting the pressure-volume data using the Birch-Murnaghan equation of state\textsuperscript{20}, defined by the following:

$$P(V) = \frac{3}{2}B_0\left(\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V}{V_0}\right)^{5/3}\right)\left[1 + \frac{3}{4}(B_0' - 4)\left(\left(\frac{V}{V_0}\right)^{2/3} - 1\right)\right]$$

[Equation 6.1]
Where $B_0$ is the bulk modulus, $B_0'$ is the bulk modulus pressure derivative, $V$ is the volume at a specific pressure, and $V_0$ is the unit cell volume at $P = 0$. A fixed $B_0'$ of 4 was used as this is the standard for many oxides. From this fit, a $B_0$ of $\sim 140$ GPa at 300 K was obtained. Since the pressure range spans only to 8 GPa, this value is presented with caution. However, our $B_0$ is similar to other perovskites (both with and without JT ions and orbital order present) including SrRuO$_3$ at 192 GPa$^{21}$, Sr$_2$MgWO$_6$ at 128(4) GPa$^{22}$, Sr$_2$CuWO$_6$ at 185(14) GPa$^{23}$, and Sr$_2$CoMoO$_6$ at 152(9) GPa$^{23}$.

7.3.1.2 **Compressibility of $BO_6$ octahedra and $AO_{12}$ dodecahedra**

The propensity for a perovskite to undergo a phase transition under pressure is influenced by the compressibility of the $AO_{12}$ or $BO_6$ polyhedra (or the $A$–$O$ and $B$–$O$ bonds).$^{24}$ If the $AO_{12}$ dodecahedra are more compressible than the $BO_6$ octahedra, volume reduction due to increased $BO_6$ octahedral tilting is expected in order to maintain the coordination of the A-site. Bond valence calculations are often used to predict which of these polyhedra are more likely to compress under non-ambient pressures.$^{24,25}$ However, many of these methods are inaccurate when describing disordered perovskites containing JT ions such as Mn$^{3+}$ in SrMn$_{0.5}$Ru$_{0.5}$O$_3$ as the bond lengths are averages and do not take into account local distortions. Furthermore, recent studies on EuO at non-ambient pressures revealed that the estimated valence states calculated from the traditional bond valence method—which takes into account the atomic structure only—deviated significantly from the measured valence states.$^{25,27-29}$ This implies that the structural distortions induced by pressure in materials with a complex electronic structure do not behave predictably. Therefore, a blend of chemical intuition and careful data analysis are the best means to gauge the compressibility of the SrMn$_{0.5}$Ru$_{0.5}$O$_3$. 
The most direct method to determine the compressibility of the lattice is to investigate the lattice parameters and metal–oxygen bond lengths (metal = Sr, Mn/Ru) as a function of pressure. Figure 7.7(a) shows the pressure dependence of the pseudocubic lattice parameters, $a_p$ and $c_p$, at different temperatures. A decrease in the $a_p$ and $c_p$ lattice parameters occurs for the whole pressure range. However, the $c_p$ lattice parameter decreases by approximately 2.2% while the $a_p$ lattice parameter by only 0.9% at 90 K from 0.4 GPa to 8 GPa. The large difference indicates a preference for anisotropic compression of the BO$_6$ octahedra along the $c$-axis. However, the decrease in the $a_p$ lattice parameters suggests that contributions from both bond compression and octahedral tilting may be occurring simultaneously.

In order to verify anisotropic compression of BO$_6$ octahedra, the Mn/Ru–O equatorial (eq) and axial (ax) bond lengths have been plotted together in Figure 7.7(b). Here, the axial bonds along the $c$-axis exhibit a much greater degree of compression than the equatorial bonds. The similar behavior in lattice parameters and bond-length reduction along the $c$-axis supports anisotropic compression. It is noteworthy that a depression in both $c$ lattice parameters and axial bond lengths occurs at 2 GPa. This will be discussed further in subsequent sections.
Figure 7.7: (a) Pseudocubic lattice parameters for $\text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ determined using the following relations for $I4/mcm$: $a_p = b_p = a/\sqrt{2}$ (dashed) and $c_p = c/2$ (solid) (b) $\text{Mn/Ru-O}_{\text{eq}}$ (dashed) and $\text{Mn/Ru-O}_{\text{ax}}$ (solid) bond lengths. The error bars for each point are the same size as the data point itself.

In order to verify the compressibility of the lattice, several compressibility factors, $\kappa$, were determined. The linear axial compressibility factors of the $a$-axis and $c$-axis ($\kappa(a)$ and $\kappa(c)$, respectively) were determined using a least squares fit to extract the pressure dependence. The following equation was used to do so:

$$a(P) = a_0 (1 - \kappa(a, c)P) \quad \text{[Equation 7.2]}$$

Where $a(P)$ is the lattice parameter at a given pressure, $a_0$ is the initial lattice parameter, and $P$ is the pressure. Since the lattice parameter data shown in Figure 7.7 reveal nonlinear behavior between 2 and 4.6 GPa, two linear regions, 0 to 2 GPa and 4.6 to 8 GPa, were used for the compressibility determination. The data are summarized in Table 7.4. The data all illustrate that $\text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_3$ is more compressible in the pressure region of 0 to 2 GPa than at higher pressures 4.6 to 8 GPa. Furthermore, anisotropic compression is
further illustrated by the larger $\kappa(c)$ values. At the higher pressures, $\kappa(a)$ and $\kappa(c)$ begin to converge which indicates an increase in octahedral tilting.

<table>
<thead>
<tr>
<th>Compressibility, $\kappa$</th>
<th>0 to 2 GPa</th>
<th>4.6 to 8 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa(a) \times 10^{-3}$</td>
<td>3.2</td>
<td>1.6</td>
</tr>
<tr>
<td>$\kappa(c) \times 10^{-3}$</td>
<td>6.6</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Table 7.4: Linear axial compressibility factors, $\kappa(a)$ and $\kappa(c)$ determined using least square fit. Two regions where the data were linear were used to calculate each value.

It was previously mentioned that bond valence sums may not provide the most accurate depiction of the polyhedral environment or the valence state of the cations involved, particularly the JT distorted ions. However, the bond valence method may provide a qualitative picture of the pressure effects upon the valence state of the Sr ion since this would not take into account the distorted Mn–O bonds. The individual bond valence, $v_i$, describes the distribution of the central cation valence to the coordinated anions (in this case oxygen). The $v_i$ is calculated by the following equation:

$$v_i = \exp \left( \frac{R_0 - R}{b} \right)$$  \hspace{1cm} [Equation 7.2]

Where $R_0$ is a standard bond length value obtained for Sr$^{2+}$, $R$ is the measured bond length at a given pressure and temperature, and $b$ is a constant of 0.37. For example, a Sr cation equally bonded to 12 oxygen atoms would yield a $v_i$ of $\sim$0.167 valence units/bond and a Sr valence state of +2. The three different Sr–O bond lengths listed in Table 7.3 were used to calculate the $v_i$ for each bond and valence state of strontium assuming 12-fold co-
ordination at 300 K. The Sr valence was then plotted as a function of pressure in Figure 7.8. From the figure, the Sr valence increases with increasing pressure. Consistent with data previously illustrated, the slope of the line at pressures from 0–2 GPa is steeper than in the other pressure regimes. This behavior is caused by the shortening of the metal-oxygen bond lengths. While compression of the lattice occurs at all pressures, the bond valence analysis further supports anisotropic compression as the dominant mechanism below 2 GPa.

![Graph showing Sr valence state at 300 K versus pressure](image)

**Figure 7.8:** The calculated Sr valence state at 300 K versus pressure.

7.3.1.3 **Octahedral tilting in SrMn$_{0.5}$Ru$_{0.5}$O$_3$ under pressure**

The reduction of the unit cell volume in the solid solution Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ is correlated with increased tilting of the (Mn/Ru)O$_6$ octahedra upon substitution of the
smaller Ca ion. This is verified by a reduction in the unit cell volume from ~235 Å³ to ~220 Å³ and bond angle from 166° to 159°. In order to determine the mechanism associated with the reduction of the unit cell volume of SrMn₀.₅Ru₀.₅O₃ at non-ambient pressure, octahedral tilting must be considered in conjunction with bond compression. In high pressure studies, octahedral tilting dominates when the AO₁₂ dodecahedra is more compressible than the BO₆ octahedra. In the previous section, it was evident that anisotropic compression along the c-axis occurs. If only this behavior is considered, it would appear that volume reduction due to compression of the B–O bonds is the primary mechanism. However, the notable change in the Sr–O and Mn/Ru–O bonds, particularly at 2 GPa, suggests octahedral tilting is also playing a role.

The presence of octahedral tilting may be determined by investigating both the Mn/Ru–Oeq–Mn/Ru bond angle (depicted as a dashed yellow line in Figure 7.10) and the octahedra tilt angle, ψ. Here, Oeq represents the equatorial oxygen in the (Mn/Ru)O₆ octahedra. The influence of pressure upon the Mn/Ru–Oeq–Mn/Ru bond angle is illustrated in Figure 7.9(a). For all temperatures, a notable increase in the bond angle near 2 GPa is present. This suggests that the metal-oxygen-metal bond angle is driven closer to 180°, an angle associated with a more symmetrical crystal structure.
Figure 7.9: (a) Mn/Ru−O_{eq}−Mn/Ru bond angles (b) Octahedral tilt angle, $\psi$ determined from Equation 6.2. Temperature key is located at the bottom right hand corner. The error bar for the bond angle data is the same size as the data point itself.

In comparison, the tilt angle has been determined using the following equation:

$$
\psi = \frac{180 - (M-O_{eq}-M)}{2}
$$

[Equation 6.3]

where $M-O_{eq}-M$ represents the Mn/Ru−O_{eq}−Mn/Ru bond angle. The tilt angle is plotted in Figure 7.9(b) versus pressure. The pressure dependence of the octahedral tilt angle is opposite of the Mn/Ru−O_{eq}−Mn/Ru bond angle. Here, the tilt angle decreases until 2 GPa, increases up to 6 GPa, and then stays pretty flat on increasing the pressure to 8 GPa. The minimum in the tilt angle suggests a decrease in the octahedra rotation due to compression of the Mn/Ru−O bonds dominating. Following 2 GPa, anisotropic compression is less pronounced and increased octahedral tilting is observed. While the structure remains tetragonal for the whole pressure range measured, this behavior suggests that a
phase transition driven by octahedral tilting may occur at pressures exceeding 8 GPa. An increase in octahedral tilting would be necessary in order to mimic chemical pressure. A diagram illustrating the behavior of the bond angle and bond length compression at 0, 2, and 8 GPa is illustrated in Figure 7.10.

Figure 7.10: Illustrated of the tilted perovskite octahedra from 0 to 8 GPa. The yellow dotted line illustrates the Mn/Ru–O$_{eq}$–Mn/Ru bond angle. Shortening of the $c$-lattice parameters are illustrated in the top portion of the figure.
7.3.1.4 Pressure effects on the Jahn-Teller Distortion

Another notable feature is the expansion of the \( c \) lattice parameter with decreasing temperature for all pressures. This implies that the JT distortion is enhanced at lower temperatures, in good agreement with previous studies.\(^{14}\) From 0.4 GPa to 8 GPa at 90 K, the \( c \) lattice parameter decreases by nearly 2.2\%. This decrease is much larger than the temperature dependent \( c \) lattice expansion of 1\% from 300 K to 90 K. Presuming the behavior under high-pressure is similar to temperature, the decrease is representative of a diminishing JT distortion.

The coherent JT distortion may be quantified by calculating the JT distortion parameter, \( \sigma_{JT} \).\(^{30}\) This function determines the extent of structural rearrangement due to loss of JT distortion as a function of pressure and is described by the following equation:

\[
\sqrt{\frac{1}{3} \sum_i [(M - O)_i - \langle M - O \rangle]^2}
\]

[Equation 6.4]

where \((M - O)_i\) represents the 2 axial and 4 equatorial bond lengths of the \((\text{Mn/Ru})\text{O}_6\) octahedra and \(\langle M - O \rangle\) is the average Mn/Ru−O bond length. The \( \sigma_{JT} \) as a function of pressure and temperature is illustrated in Figure 7.11. The \( \sigma_{JT} \) exhibits a very similar decrease as the \( c \) lattice parameter when plotted versus pressure. In the same way, depression in the \( \sigma_{JT} \) at 2 GPa is visible. This is a strong indicator that 2 GPa is a critical pressure for structural rearrangement due to a decrease in the JT distortion.

To this point, physical pressure has illustrated significant effects upon the structure of \( \text{SrMn}_{0.5}\text{Ru}_{0.5}\text{O}_3 \). In particular, an applied pressure of 2 GPa has decreased the \( c \) lattice parameters, lowered the JT distortion parameter, increased the Mn/Ru−O\(_{\text{eq}}\)−Mn/Ru
bond angle and finally lowered the octahedral tilt angle. All of these phenomena show that at pressures up to 2 GPa, the effect of pressure is primarily to compress the long bonds of the Mn–O octahedra. Above 2 GPa, the long bonds become less compressible and the volume contraction is taken up by an increase in the octahedral tilting, and a smaller compression of the size of the octahedra.

**Figure 7.11:** The JT distortion parameter of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ as a function of temperature (top) and pressure (bottom) as defined by Radaelli et al.$^{24}$
7.3.2 Magnetic Structure

It is clear from the previous sections that a structural dependence with external pressure exists, but the question remains as to how the magnetic structure is impacted. The initial goal of this work was to discern whether high pressures could eliminate the JT distortion and orbital order along the c-axis, destroy the C-type antiferromagnetism and introduce new magnetic order. From the NPD patterns illustrated in Figure 7.6, it is clear that C-type AFM ordering remains up to 8 GPa due to the presence of the strong magnetic peak (highlighted with an arrow). However, a significant decrease in the intensity of the magnetic peaks is visible and suggests a decrease in the total magnetic moment, \( u_B \). In order to gauge this decrease, magnetic refinements have been completed.

The magnetic structure was refined using a \( P\bar{T} \) unit cell while the lattice parameters and atomic positions were defined in the space group, \( I4/mcm \). The four unique fractional positions of the magnetic ions are listed in Table 7.5. The magnetic unit cell of SrMn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) with the magnetic ions labeled is shown in Figure 7.12. Due to the disorder of the Mn and Ru ions, reliably determining the individual magnetic moment (\( \mu_B \)) per transition metal site is challenging. Using several different methods during the refinement process, the best fit of magnetic moment as a function of pressure was when the coherent scattering length of the Mn\(^{3+} \) ion was used and it was assumed that each of the sites listed in Table 7.5 were fully occupied by Mn\(^{3+} \) for the magnetic refinement.
\begin{table}
\centering
\begin{tabular}{ll}
\hline
Atom & Fractional Positions \\
\hline
1 & (0,0,0) \\
2 & (½, ½, ½) \\
3 & (0,0, ½) \\
4 & (½, ½, 0) \\
\hline
\end{tabular}
\caption{Fractional coordinates for magnetic ions under the \textit{I4/mcm} space group in the SrMn$_{0.5}$Ru$_{0.5}$O$_3$ structure.}
\end{table}

\textbf{Figure 7.12:} C-type antiferromagnetism of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ with the fractional coordinates of the magnetic ions labeled from Table 7.5. Green arrows represent the direction of the magnetic moment.

The magnetic moment per transition metal site is plotted in Figure 7.13. After 190 K, no magnetic ordering was present. Therefore, only 90 K, 150 K, and 190 K data were used for the magnetic refinements. As expected, the magnetic moment was greater
at 90 K than at 190 K which corresponds well with the increase in the (100) peak intensity at lower temperatures. One of the more important features of Figure 7.13 is how the magnetic moment decreases with increasing pressure. This effect is more dramatic at the lowest temperature of 90 K. While a slight dip in the magnetic moment is observed at 2 GPa at 150 K and 190 K, more data points are required to determine whether this is due to the structural distortions at this pressure.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$\mu_B$/transition metal ion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>90K</td>
</tr>
<tr>
<td>0.4</td>
<td>1.62(3)</td>
</tr>
<tr>
<td>0.8</td>
<td>1.61(3)</td>
</tr>
<tr>
<td>1.33</td>
<td>1.62(3)</td>
</tr>
<tr>
<td>2</td>
<td>1.60(4)</td>
</tr>
<tr>
<td>3</td>
<td>1.49(3)</td>
</tr>
<tr>
<td>4.66</td>
<td>1.38(4)</td>
</tr>
<tr>
<td>6</td>
<td>1.09(5)</td>
</tr>
<tr>
<td>8</td>
<td>1.01(4)</td>
</tr>
</tbody>
</table>

**Table 7.6:** Summary of magnetic moment per transition metal ion at 90 K, 150 K, and 190 K and pressures ranging from 0.4 to 8 GPa.
Figure 7.13: Magnetic moment per transition metal ion in SrMn$_{0.5}$Ru$_{0.5}$O$_3$ versus pressure at 90 K, 150 K, and 190 K.

7.4 Discussion

The results from the nuclear and magnetic structural refinements revealed that pressure does impact the nuclear and magnetic structure of SrMn$_{0.5}$Ru$_{0.5}$O$_3$. It was determined that below 2 GPa, compression of the Mn/Ru−O bonds (as opposed to increased octahedral tilting) contributes mostly to the reduction of the unit cell volume. Above pressures of 2 GPa, octahedral tilting and compression of the Mn/Ru−O bonds contribute to a decrease in the unit cell volume. However, neither of these behaviors were enough to facilitate a phase transition to the $Pnma$ symmetry expected if external pressure mimicked chemical pressure.

According to Angel et al., the potential for perovskites to undergo phase transitions at non-ambient conditions may follow several general “rules”. For example, phase
transitions in which a high symmetry structure goes to a lower symmetry may be associated with changes in the tilt of rigid octahedra. Assuming the octahedra are very rigid, an increase in the magnitude of octahedral tilting must be accompanied by a decrease in the unit cell volume. Alternately, the unit cell volume may decrease due to compression of elongated bonds. A summary of the percent volume changes for several compositions in the \( \text{Ca}_x \text{Sr}_{1-x} \text{Mn}_{0.5} \text{Ru}_{0.5} \text{O}_3 \) solid solution are shown in Table 7.7. Considering only the lattice parameters, the change in unit cell volume in \( \text{SrMn}_{0.5} \text{Ru}_{0.5} \text{O}_3 \) as a function of pressure was calculated to be approximately 4.8%. If this value is compared to the change in unit cell volume going from full Sr to full Ca in the solid solution, the best match would be the ferrimagnetic \( x = 0.7 \) composition, \( \text{Ca}_{0.7} \text{Sr}_{0.3} \text{Mn}_{0.5} \text{Ru}_{0.5} \text{O}_3 \) (unit cell volume = 4.9%). However, the latter composition is orthorhombic (\( \text{Pnma} \)) with a tilting scheme similar to \( \text{CaMn}_{0.5} \text{Ru}_{0.5} \text{O}_3 \) (\( a-b+a^- \)).\(^{15}\) Since no phase transition or changes in magnetic order are observed up to 8 GPa, compression of the B-site lattice appears to be the more dominant mechanism rather than octahedral tilting. The composition in the solid solution at the boundary of antiferromagnetism and ferrimagnetism, \( \text{Sr}_{0.8} \text{Ca}_{0.2} \text{Mn}_{0.5} \text{Ru}_{0.5} \text{O}_3 \), has an octahedral tilt angle near 7.5° at 300 K.\(^{15}\) This value is greater than the tilt angle of ~6.6° determined for \( \text{SrMn}_{0.5} \text{Ru}_{0.5} \text{O}_3 \) at 8 GPa. It is likely that higher applied pressure to \( \text{SrMn}_{0.5} \text{Ru}_{0.5} \text{O}_3 \) is needed to exceed the tilt angle of 7.5° and shift to a less symmetrical crystal structure. In the same way, a phase transition or change in the magnetic order might be observed if a composition closer to the phase boundary such as \( \text{Sr}_{0.8} \text{Ca}_{0.2} \text{Mn}_{0.5} \text{Ru}_{0.5} \text{O}_3 \) were measured.
Table 7.7: Percent volume change associated with $x = 0$ to $x = 1$, 0.7, and 0.5 compositions in the Ca$_x$Sr$_{1-x}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ solid solution compared to volume change of SrMn$_{0.5}$Ru$_{0.5}$O$_3$ at ambient pressure and 8 GPa. The values obtained for the solid solution were determined from reference [15].

<table>
<thead>
<tr>
<th>$x$</th>
<th>% Volume Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td></td>
</tr>
<tr>
<td>$x = 0$</td>
<td>6.75%</td>
</tr>
<tr>
<td>$x = 0.7$</td>
<td>4.88%</td>
</tr>
<tr>
<td>$x = 0.5$</td>
<td>3.167%</td>
</tr>
<tr>
<td>(0.4$\rightarrow$8 GPa)</td>
<td>4.78%</td>
</tr>
</tbody>
</table>

Since it appears that the unit cell volume change as a function of pressure is due more so to compression rather than octahedral tilting, a closer look at the the compressibility of the BO$_6$ versus AO$_{12}$ dodecahedron must be considered. Lufaso et al. demonstrated the effects of pressure on double perovskite systems with and without JT distortions such as the B-site ordered $A_2$CuWO$_6$ ($A =$ Ba, Sr) and Sr$_2$CoMoO$_6$ perovskites. In the Cu-containing compounds, the $c$ lattice parameter decreased in conjunction with the JT distortion oriented along the same axis. This behavior was attributed to the preferential compression of the Cu–O bonds. Interestingly, both Ba$_2$CuWO$_6$ and Sr$_2$CuWO$_6$ exhibited greater compressibility along the $c$-axis, though the anisotropic compressibility was greater for the Ba-analogue. This implies that the Sr–O bonds were more compressible than the Ba–O bonds giving way to more octahedral tilting. In contrast, Sr$_2$CoMoO$_6$, which contains undistorted octahedra, exhibited increased octahedral tilting and uniform bond compression as the primary mechanism for reduction of the unit cell volume. This behavior suggests that the compression mechanism for Sr$_2$CuWO$_6$ lies in a region where neither anisotropic compression (Ba$_2$CuWO$_6$) nor octahedra tilting (Sr$_2$CoMoO$_6$) dominate. It is true that SrMn$_{0.5}$Ru$_{0.5}$O$_3$ is a chemically disordered perovskite, but the orbital
order and JT distortion are not all that dissimilar from ordered Sr$_2$CuWO$_6$. In this regard, it is not surprising that a phase transition did not occur with SrMn$_{0.5}$Ru$_{0.5}$O$_3$ at 8 GPa as none was observed for the Cu-based compounds up to 6 GPa. It is worth noting that the compressibility of the (Mn/Ru)O$_6$ octahedra under pressure does not appear to be influenced by B-site order.

Finally, it may be plausible to assume that SrMn$_{0.5}$Ru$_{0.5}$O$_3$ is simply a very challenging system to induce a phase transition to lower symmetry. In part, this is due to the long Mn–O bonds which compress more readily than the Ru–O bonds. It is also due to the fact that the mechanism for volume reduction is swayed by both anisotropic compression and octahedral tilting. However, studies of Ba$_2$YTaO$_6$ have shown that higher pressures may break the barrier which prevents octahedral tilting from dominating over BO$_6$ octahedra compression.\textsuperscript{3} Below pressures of ~4 GPa, Y–O and Ta–O bond compression dominates. Above 6 GPa, octahedral rotation takes over and induces a phase transition from \textit{I4/m} to \textit{Fm}$\overline{3}$\textit{m}. That being said, pressures exceeding 8 GPa in SrMn$_{0.5}$Ru$_{0.5}$O$_3$ may increase the propensity for octahedral tilting and lead to a lower crystal symmetry.

### 7.5 Conclusions

The compressibility mechanism of the disordered perovskite SrMn$_{0.5}$Ru$_{0.5}$O$_3$ was investigated using high-pressure NPD. The goal of this work was to use high pressure to simulate the effects of chemical pressure in the SrMn$_{0.5}$Ru$_{0.5}$O$_3$–CaMn$_{0.5}$Ru$_{0.5}$O$_3$ solid solution where a shift in the magnetic ordering from antiferromagnetic to ferrimagnetic is observed. Pressures were applied up to 8 GPa and the crystal structure and magnetic ordering were monitored at temperatures ranging from 90 K to 300 K.
The compression mechanism of SrMn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) may be broken down into two regions: 0 to 2 GPa and 2 GPa to 8 GPa. From 0 to 2 GPa, anisotropic compression dominated as indicated by decreases in the \(c\) lattice parameters and axial bond lengths. Further support for anisotropic compression was shown by the overall decrease of \(c\) lattice parameters by 2.2\% for the whole pressure range in contrast to a decrease of only 0.9\% for the \(a\) lattice parameters. The lower pressure region also illustrated a slight increase in the (Mn/Ru)−O−(Mn/Ru) bond angles and corresponding decrease in the octahedral tilt angle, indicating that anisotropic compression, not octahedral tilting, is dominating. At pressures greater than 2 GPa, the decreases in \(c\) lattice parameters and axial bond lengths were not as significant, but the (Mn/Ru)−O−(Mn/Ru) bond angles began to decrease and octahedral tilt angle increased. While the bond lengths and lattice parameters continued to compress, the behavior of the bond and tilt angles clearly shows an increase in the degree of octahedral tilting. It is concluded that up to 2 GPa, anisotropic compression dominates the unit cell volume reduction. Above 2 GPa, octahedral tilting and (Mn/Ru)−O bond compression are both present. In spite of the increased octahedral tilting, the structure of SrMn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) remained tetragonal for all pressures and temperatures.

The C-type AFM structure was studied at all pressures and temperatures up to 190 K. The total moment per transition metal site was reduced from 1.62(3) \(\mu_B/\text{transition metal site}\) to 1.01(4) \(\mu_B/\text{transition metal site}\) at 90 K at 0.4 GPa and 8 GPa (respectively). This indicates that the magnetic order is only mildly suppressed at 8 GPa.

From this study, it was determined that SrMn\(_{0.5}\)Ru\(_{0.5}\)O\(_3\) is sensitive to the effects of physical pressure, though not enough to reduce the symmetry of the structure and fully disrupt the JT distortion and orbital order. As a result, the tetragonal distortion and AFM
order is retained. This suggests that physical pressure up to 8 GPa and applied pressure
do not have the same effect as chemical pressure. Future studies will require either a
composition closer to the phase boundary such as Sr$_{0.8}$Ca$_{0.2}$Mn$_{0.5}$Ru$_{0.5}$O$_3$ or pressures
greater than 8 GPa.

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