12-6-2013

Magnetic Phase Separation and Ordering in SrCoOx

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SrCoO\(_x\) has generated interest due to its high oxygen mobility and unique magnetic properties. Above x = 2.75, SrCoO\(_x\) is a cubic perovskite and orders ferromagnetically. The magnetic ordering temperature is dependent on the oxygen content of the material. Distinct phases have been noted at x = 3.0 (T\(_C\) = 280), x = 2.88 (T\(_C\) = 220) and x = 2.75 (T\(_C\) = 160 K) in bulk samples. At oxygen contents between x = 2.88 and 3.0, the transitions of both end points are seen, though the sample retains a single crystal structure. While magnetic phase separation has been described in a number of similar complex oxides, separation between phases of the same magnetic order is unexpected. Additionally, the oxygen concentrations at which end phases occur (3.0 – n/8, n = 0, 1, 2) imply an ordering commensurate with the lattice.

We explore this system through a series of magnetic and structural investigations, beginning with bulk samples and extending to an extensive investigation of thin films. Using pulsed laser deposition, we have successfully grown epitaxial films of SrCoO\(_x\) and detail a method to select oxygen concentration using an electrochemical cell. We report on the evolution of magnetic properties as a function of oxygen content. A thickness dependent study of these epitaxial films, oriented along the (1 0 0) and (1 1 1) directions, revealed the effects of finite dimensionality and determined a critical length scale for the magnetic regions.
Resonant X-ray diffraction was used to determine the presence of more subtle orderings not detected in standard structural analyses. By tuning to important Co and O absorption edges, arrangements particular to the electric states of those elements are enhanced. We have discovered, for the first time, an ordering commensurate to the lattice at the (1/4 1/4 1/4) position. Incommensurate peaks near this position were also observed. The intensity of these peaks depends on the oxygen concentration of the sample, and can be suppressed at temperatures above 350 K. Regular orderings of charge density which closely match the underlying lattice may help to explain the observed propensity for SrCoO$_x$ to stabilize at particular phases.
Magnetic Phase Separation and Ordering in SrCoO$_x$

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A Dissertation
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy
at the
University of Connecticut

2013
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2013
APPROVAL PAGE

Doctor of Philosophy Dissertation

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2013
ACKNOWLEDGMENT

A work of this type would not be possible without a wide base of help and support. While too many people are owed my thanks to fully list here, I would like express my great appreciation for the contributions of several individuals.

I must begin by thanking my advisor, Dr. Barrett Wells. My advancement as a scientist is the result of his patience, instruction, and support. Barry continually taught me new ways to appreciate our work and his advice has been invaluable both personally and professionally. I am also indebted to my co-advisor, Dr. Joseph Budnick. Dr. Budnick’s wealth of knowledge on most any subject, and particularly condensed matter, has been an amazing resource. My work would never have advanced this far without his guidance. I would also like to thank Dr. Pamir Alpay for his review of this work and input as my associate advisor.

In addition to my committee members, several faculty and staff at the University of Connecticut have aided my advancement through class, research, or administrative assistance. I am particularly grateful to Dr. William Hines. His insights on magnetic measurement and instrumentation have been essential in completing this work. Furthermore, his attention to detail and careful manner continue to serve as my example of proper experimental technique. Beyond UConn, I thank Dr. Bogdan Dabrowski for supplying the samples and targets central to this discussion. I am also grateful to Dr. Feizhou He at the Canadian Light Source for educating me on the process of resonant diffraction and his participation in this research.
Much of my work would have been impossible without the support of my research group. It has been my pleasure to work with and learn from Hashini Mohottala, Changkun Xie, Yuefeng Nie, and Sam Emery. I also much appreciate the support of Lahiru Narangammana, Zhi Hai Zu, and Zhiwei Zhang. I highly value our time together both in and out of the laboratory.

Thanks are also owed to my friends and colleagues in the graduate program. James O’Brien has been a continual source of help and advice, and I am also grateful to Brendan Pratt, John Haga, Adolfo Huet, Rob Fischetti, and Matt Neubelt. Their camaraderie was essential in surviving this process.

I have been blessed to have the backing of exceptional friends and family. Special thanks to Omair Zubairi and Elie Sayegh, who have lent their encouragement and assistance since long before I began this process. Finally, I am forever grateful for the constant support of my family. My parents were the first to inspire me to a career in science, and the realization of that goal has only been possible through their constant enthusiasm and aid.
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1. Introduction

An open question in condensed matter physics is the role of doping in Mott insulators. Traditional band theory would suggest these materials are conductors, but the Coulomb repulsion between electrons inhibits transport. The most common Mott insulators are the transition-metal oxides, where oxygen plays a key role in mediating exchange interactions and determining band structure.\(^1\) Likewise, chemical substitution affects electronic properties by altering both the crystal structure and charge balance. Therefore, even slight changes to either chemical doping level or oxygen content can dramatically influence observed properties like conduction and magnetic order. A common feature to these materials is a spatial variation of electronically ordered regions at different length scales.\(^{2,3}\) A deeper understanding of this aspect may shed light on the underlying physics involved.

In such systems, a competition between various interactions often results in multiple ground states with comparable energy, leading to a rich phase diagram. In particular, perovskite oxides have attracted much attention.\(^4\) The variety of electronic and magnetic states, observed phase transitions, and high oxygen mobility also suggest that these transition metal systems are promising functional oxides for use in devices.\(^4,5\)

Many of the relevant properties of perovskites are influenced by the valence state of the central transition metal ion. This state is determined by the manner in which available electrons occupy the 3d states. That process is influenced by the occupancy of the surrounding oxygen octahedra and valence of the rare-earth cations. Charge doping, through substitution or other means, modifies the valence state, allowing for the spatial
modulation of charge or magnetic order.\textsuperscript{2} As an example, La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} has been observed to separate into ferromagnetic clusters in a nonferromagnetic matrix at low x (x < 0.5).\textsuperscript{6–8} This is due to the effect on the cobalt ion valence by doping with Sr\textsuperscript{2+}, resulting in regions of inhomogeneous hole concentration and the coexistence of ferromagnetic, spin-glass, and paramagnetic regions.\textsuperscript{6} This separation of magnetic regions, where an inhomogeneous chemical composition is not observed, is described as an electronic phase separation.\textsuperscript{3,9–11} Cobalt valence is also affected by the amount of negatively charged oxygen present. Adjusting the oxygen content alters the balance between ground state energies and modifies the crystal structure.

In compounds, Co valence states of +2, +3, and +4 are possible, but Co\textsuperscript{4+} is difficult to obtain and thus rarely studied. Simple charge counting would suggest SrCoO\textsubscript{3} demonstrates Co\textsuperscript{4+}, however, the complicated techniques required to fully oxidize the material has limited its study.\textsuperscript{12} At concentrations less than x = 3.0, one would expect a mixture of Co\textsuperscript{3+} and Co\textsuperscript{4+} We have chosen to investigate SrCoO\textsubscript{x}, altering the Co valence through the filling of oxygen vacancies rather than cation substitution. Standard methods yield as-grown films and bulk samples with x = 2.75 and 2.88, respectively. Using an electrochemical process, we can then further induce oxygen into the samples. This novel method permits the study of a range of oxygen concentrations, up to fully oxidized x = 3.0.

This thesis details the magnetic and structural characteristics of SrCoO\textsubscript{x} epitaxial films as functions of oxygen concentration, crystallographic orientation, and temperature. The work represents a significant survey of the SrCoO\textsubscript{x} system over several oxidations and sample types, with work conducted at the University of Connecticut and national labs in the United States and Canada. Studies were carried out in collaboration with scientists at
those institutions, Northern Illinois University, and the University of Hartford. The following sections provide a background on those concepts central to an analysis of our data. Particular emphasis is placed on their application to the SrCoO$_x$ system.

1.1 Transition Metals

Transition metals and their oxides are especially significant in the study of condensed matter. This is due to the partial filling of the d electron orbital, which are more spatially localized as a consequence of their higher angular momentum. The localization increases the interaction of the orbitals with the surrounding ions of the crystal structure, strongly affecting the energy levels. This interaction couples magnetic and electronic properties of the material with the crystallographic arrangement, which can lead to dramatic transitions with relatively small perturbations or applied fields. Notable examples include colossal magnetoresistance\textsuperscript{13} and the magnetocaloric effect.\textsuperscript{14}

The first group of transition metal elements ranges from from scandium with atomic number 21 to copper at number 29. We may describe the electron configuration of each element by noting the energy level of the constituent electrons, specifying the radial quantum number $n$ as an integer, and the azimuthal quantum numbers $l = 0, 1, \text{ and } 2$ with the letters s, p, and d. A superscript denotes the number of electrons occupying each orbital. This is limited by the available magnetic quantum numbers, which range from $-l \leq m \leq +l$, each of which can contain up to two electrons, one of each spin. Thus each orbital contains at most $2(2l+1)$ electrons.\textsuperscript{15}

In this notation, the first 18 electrons of all elements in this group can be written in the following manner: 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$. As this matches the configuration of argon, a
shorthand form replaces these terms with [Ar]. Each element can then be differentiated by the placement of their remaining electrons. Neutral cobalt, for example, would be written as [Ar]4s^23d^7. The 3d level can hold up to ten electrons, one of either spin in each of five orbitals. In the spherical potential of an isolated atom, these levels would be degenerate. Filling proceeds via Hund’s rule, whereby it is energetically favorable to fill each orbital singly before any orbital is doubly occupied. In a material, coulomb interactions with neighboring atoms must be taken into account. The inhomogeneous electric field which results is known as the crystal field. Depending on the structure producing it, the field may split the orbital degeneracy. The resulting competition between Hund’s rule and crystal field splitting alters the manner in which electrons fill the orbitals. The following sections describe these details for the perovskite SrCoO3.

Figure 1.1 Perovskite Structure. A transition metal ion (B) occupies the center of a cubic cell, surrounded by an octahedral cage of negative oxygen ions (O), with larger radii cations (A) at each corner.
1.2 Perovskite Structure

The materials of this work will form with the perovskite structure. Perovskite is the name for the mineral calcium titanium oxide (CaTiO$_3$) and is used to refer to similar structures of the form ABO$_3$. Here, B represents a transition metal ion surround by six oxygen ions (O$^2-$). The ideal structure is cubic, with A site cations at each corner, B site transition metal at the center, and oxygen ions at the center of each face. In this way, the oxygen ions form an octahedron about the transition metal, as shown in Figure 1.1. Distortions from this ideal are often described as a stretching or rotation of these octahedra.

By treating the ions as point charges, we can approximate the potential acting on a 3d electron as,$^{16}$

$$V(r) = \sum_i \frac{Z_i e^2}{|r - R_i|}$$  \hspace{1cm} (1.1)

where $Z_i e$ is the charge of the $i$-th ion, $R_i$ is its position vector, and $r$ is the position of the electron. In the perovskite structure, the 3d electrons are subject to cubic symmetry. Solving for the eigenfunctions of the Schrödinger equation in this potential reveals the geometric extent of the 3d orbitals. These solutions differ from the case of the free ion, where the eigenfuntions are proportional to the spherical harmonics. In the cubic crystal field, the eigenfunctions are instead given by linear combinations of the spherical harmonics which result in real functions.$^{16}$ The area most likely to contain an electron is mapped for each 3d orbital in Figure 1.2.
Note two orbitals are aligned with the axes, bringing them closer to neighboring oxygen ions than is the case for off-axis orbitals. This results in a stronger Coulomb interaction between those orbitals and the O octahedron, splitting the degeneracy in the 3d orbitals. The 3d orbitals can be classified in terms of this interaction; the \( e_g \) orbitals are \( d_{z^2} \) and \( d_{x^2-y^2} \), while the \( t_{2g} \) orbitals are \( d_{xy}, d_{xz}, \) and \( d_{yz} \). Taking the electrons of the oxygen atom into account, we see the overlap between 3d transition metal orbitals and oxygen p orbitals becomes significant.

![Figure 1.2 Electron probability density for 3d orbitals in a cubic crystal field.](image)

1.3 Magnetism and Spin

The magnetic moment of a free atom arises from the intrinsic spin of the electrons and their orbital angular momentum about the nucleus. The moment is given by the value of \( \mu_B (L + 2S) \). In a crystal field, however, the components of the angular momentum may average to zero. In a classical picture, the plane of an electron orbit for an isolated atom is
fixed, as are the x, y, and z components. In the noncentral field of a lattice, the orbital plane will move, and the components are no longer constants of the motion.¹⁵

Quantum mechanically, one must consider the eigenvalues of the total angular momentum operator $J$ and the z component $L_z$. The orbital angular momentum is quenched when $L_z$ averages to zero. Notice that the orbital angular momentum operator $\mathbf{L} = -i\hbar \mathbf{r} \times \mathbf{\nabla}$ is an imaginary operator. Furthermore, as a Hermite operator, the diagonal elements must be real. So long as the wave functions are also real, as described in the previous section for linear combinations of the spherical harmonics, the matrix elements must be zero to satisfy this condition. The wave functions can be complex when the ground state is degenerate, resulting in only partial quenching of the angular momentum. For the transition metals, interactions with the lattice or the delocalization of electrons often lifts this degeneracy.¹⁶

![Diagram](image)

**Figure 1.3** The symmetry of the electric field in a material leads to a splitting of 3d degeneracy
Therefore, the chief contributor to magnetic moment in these materials is due to the unpaired spins of the transition metal electrons. Each unpaired electron contributes a spin of \( \frac{1}{2} \), from which the total spin magnetic moment can be calculated using equation 1.2, where \( g = -2.0023 \) and \( \mu_B \) is the Bohr magneton.

\[
|\vec{\mu}_S| = g \mu_B \sqrt{s(s + 1)}
\]

The splitting of the 3d degeneracy by the cubic crystal field offsets the \( e_g \) and \( t_{2g} \) orbitals by an amount written as \( 10Dq \). A distortion from the cubic ideal structure may further separate each group of orbitals, as noted in Figure 1.3. Where the Hund’s exchange energy is low compared to \( 10Dq \), electrons will tend to fill the lower \( t_{2g} \) orbitals before the higher \( e_g \) orbitals. In cases where the energies are comparable, a variety of arrangements may be possible, allowing more than one spin state for a particular valence charge.

The magnetic moment per unit volume is defined as the magnetization \( M \), taken to be at thermal equilibrium for a particular temperature \( T \). The magnetic susceptibility per unit volume is defined as the ratio of the magnetization in relation to the macroscopic field intensity \( B \), such that,

\[
\chi = \frac{\mu M}{B}
\]

On application of an external magnetic field, a material with a positive susceptibility will tend to align parallel to the field in an effect known as paramagnetism. For a paramagnetic material, the Curie law gives \( \chi_p = C / T \), where \( C \) is the Curie constant. When the dominant contribution to the moment is due to the effect of the applied field on electron orbitals, \( \chi \) is negative and leads to diamagnetism.
A material which supports a spontaneous magnetic moment even in the absence of an applied field is said to be ferromagnetic. This suggests a regular arrangement of the magnetic moments. In the mean field approximation, we assume this arrangement is due to an internal exchange interaction proportional to the magnetization, $\lambda M$. At high enough temperature, thermal excitations destroy this order. The temperature at which this occurs is the Curie temperature $T_C$.

Consider the adjustment to equation 1.3 due to an additional internal field in a paramagnetic phase. This gives $\mu_0 M = \chi_p (B + \lambda M)$. If we use the Curie law for $\chi_p$ and define $T_C = C\lambda$, we produce the following:

$$\chi = \frac{C}{T - T_C}$$  \hspace{1cm} 1.4

Equation 1.4 is the Curie-Weiss law describing the susceptibility in the paramagnetic region above the Curie point. Below the singularity at $T = T_C$, a spontaneous magnetization exits which persist without an applied field.

The moments will remain aligned so long as the material is kept below the Curie temperature $T_C$. Macroscopically, the magnetic moment observed may be much smaller than expected from a completely parallel alignment. At large scale, a ferromagnet can further reduce its energy by breaking into regions known as domains. Moments are aligned within a domain, but point in different directions compared to neighboring domains. Thus the size of domains and the extent of their boundaries give additional information on the strength of the magnetic interactions. An applied external field of sufficient magnitude can be used to align domains and measure the saturation moment.
For the case of SrCoO$_x$, a variety of Co spin states are possible as the Hund’s exchange energy and the splitting due to the crystal field are comparable. Nominal valence counting would suggest SrCoO$_{2.5}$ has a spin state of Co$^{3+}$, while SrCoO$_3$ displays Co$^{4+}$. For each valence, the spin configuration can be further divided between low, intermediate, and high spin states. For Co$^{3+}$, spin configurations of $t_{2g}^6e_g^0$ (low), $t_{2g}^5e_g^1$ (intermediate), and $t_{2g}^4e_g^2$ (high) are possible. Similarly, Co$^{4+}$ can be configured as $t_{2g}^5e_g^0$, $t_{2g}^4e_g^1$, or $t_{2g}^3e_g^1$.\textsuperscript{17}

1.4 Ordering

In addition to magnetism, there are a number of other types of ordering evident in perovskite systems. A regular arrangement of vacancies, valence charge, or orbital occupancy may or may not match the underlying lattice. If the effect on the charge distribution of surrounding ions is sufficient, these orderings may be detectable through standard laboratory x-ray diffraction analysis. More subtle orderings, however, may require specialized techniques like resonant diffraction to observe. In interpreting our SrCoO$_x$ results, we must consider the possibility of the following types of order.

1.4.1 Vacancy Ordering

So far, we have dealt with the ideal perovskite structure and neglected any discussion on defects or vacancies. Real crystals include various imperfections, including unoccupied lattice sites. Indeed, we make use of this when using electrochemistry to change the oxygen content. In the case of SrCoO$_x$, deficiencies in oxygen content for $x < 3.0$ take the form of vacancies in the oxygen octahedron.

In systems where oxygen is highly mobile, long range interactions may favor a regular arrangement of oxygen vacancies. Z-contrast imaging has been used to study oxygen ordering in the perovskite materials (La$_x$Sr$_{1-x}$)(Fe$_y$Cr$_{1-y}$)O$_{3-\delta}$, SrTiO$_3$, and SrCoO$_{3-\delta}$.\textsuperscript{18}
Vacancy ordering is observed in SrCoO$_x$ at an oxygen concentration of $x = 2.5$. SrCoO$_{2.5}$ is characterized as a brownmillerite structure.\textsuperscript{19} This structure is defined as an ordering of oxygen vacancies along the [1 1 0] direction (See section 3.1).\textsuperscript{20} An orthorhombic structure of oxygen vacancies has also been identified in the related material (La$_{0.5}$Sr$_{0.5}$)CoO$_3$-$\delta$, where the dependence of oxygen ordering in epitaxial films due to strain is examined.\textsuperscript{21}

1.4.2 Charge Ordering

Similarly, a material may display a pattern of the transition metal valence. Doping through substitution or oxygen intercalation alters the number of available electrons or holes. If the electrons are sufficiently localized, the charges can order in real space. This may take the form of stripes or checkered patterns which persist up to a transition temperature known as the charge ordering transition $T_{\text{CO}}$. This electronic ordering can exist in the absence of any specific vacancy ordering.

Charge ordering has been observed in a number of systems, including the layered perovskite manganites and cuprate superconductors. A neutron scattering study on single crystal La$_2$NiO$_{4+\delta}$ found ordering peaks which correspond to charged domain walls between antiferromagnetic domains.\textsuperscript{22} A similar charge stripe ordering has been the focus of much study in the cuprate superconductor La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$,\textsuperscript{23} where superconductivity and charge order are seen to coexist.\textsuperscript{24} An alternating pattern of Mn$^{3+}$ and Mn$^{4+}$ is directly observed in La$_{0.5}$Sr$_{1.5}$MnO$_4$ using the anomalous dispersion of the scattering factor in synchrotron x-ray diffraction. A simultaneous orbital ordering component is also observed.\textsuperscript{25}
1.4.3 Orbital Ordering

Orbital ordering in transition-metal oxides results from an alternating arrangement of 3d orbital occupancy. Local distortions of the oxygen octahedron or lattice structure may further separate the remaining 3d degeneracy. As oxygen ions are shared with neighboring octahedra, all octahedra are similarly distorted resulting in a long range ordering of orbitals. Orbital ordering is often observed concomitant to charge and magnetic order, as seen in Pr$_{1-x}$Ca$_x$MnO$_3$, a schematic of which is given in Figure 1.4.26

The importance of orbital interactions and ordering in transition-metal systems has been discussed in a variety of systems, including V$_2$O$_3$ and YTiO$_3$.27,28 The most referenced example of orbital order, however, is that of LaMnO$_3$.29–31 Goodenough described in detail the ordered arrangements of this system.29 LaMnO$_3$ is a Mott insulating perovskite and a

![Figure 1.4](image.png)

**Figure 1.4** Schematic of simultaneous charge, orbital, and magnetic ordering as described for Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ in Ref [26]. Mn4$^+$ are shown as black points and shaded symbols signify orbital ordering at Mn3$^+$ sites. Magnetic ordering is indicated by arrows. Dotted and solid rectangles detail the charge and orbital unit cells, respectively. The vertical dashed line shows an orbital antiphase domain boundary.
parent material for colossal magnetoresistive materials. An ordering of the $e_g$ orbitals occurs in a-b plane, and can be detected through resonant x-ray scattering.\textsuperscript{32} By tuning the diffraction energy to the K-absorption edge, a core electron is promoted from a 1s to a 4p orbital. Though the 4p states are initially unoccupied, they are split by their interaction with the $e_g$ electrons of the 3d orbitals, allowing a sensitivity to the orbitally ordered sublattice.

### 1.5 Mott Insulators

Conventional band theory derives the energy spectrum available to electrons by considering the allowed wave functions for the regular potential due to the periodic lattice of a solid. This has been highly successful in predicting the electronic transport behavior of a wide range of materials. However, Mott materials are insulating despite band theory predictions of high conductivity. This behavior can be understood by taking into account electron interactions with each other, which band theory treats only in a single particle, mean field manner.

Electrons interactions can be considered between electrons on the same ion and those between electrons of neighboring ions. Ref [16] gives a detailed discussion. The Hubbard interaction describes the interaction between electrons of the same orbital on the same site. Coulomb repulsion creates an additional potential energy term (U) in the Hamiltonian. Because of the overlap of 3d transition metal orbitals with neighboring oxygen 2p orbitals and screening effects, U in transition metal oxides is reduced compared to the isolated ion. Electrons in different orbitals interact through Hund coupling, which energetically favors the alignment of parallel spins.

Interactions between ions are described through exchange mechanisms. In the direct exchange model, the overlap of atomic wave functions is sufficient to allow the exchange
of an electron between ions. This supports ferromagnetic order due to Hund coupling between the exchange electron and the orbitals of each ion. In transition metal oxides, where the metal ions are far enough apart that direct exchange is negligible, indirect interactions dominate. Here, 3d orbitals interact via intermediary oxygen 2p orbitals.

The superexchange interaction, modeled by Anderson, describes this interaction. In transition metal oxides, the filled 2p orbital of the oxygen ion contains two electrons which, through Pauli exclusion, are antiparallel to each other. Through the overlap with the metal ion 3d orbitals, the spin of each oxygen electron will align parallel to those of the metal ion. Thus the system will tend to support an antiferromagnetic alignment between the metal ions. This can be affected by the geometry of the orbitals.

The Hamiltonian describing a simplified system can be written as follows:

$$H = -t \sum_{i,j,\sigma} (c_i^\dagger c_j^\sigma) + U \sum_i n_i \uparrow n_i \downarrow$$

Where t is the hoping integral and U is the Coulomb repulsion described as the Hubbard interaction for two electrons on the same atom. When $t >> U$, the system is described in terms of band theory, as electron interaction are negligible. In the opposite case, the large cost in energy to move an electron to an occupied site makes the system insulating. This is known as a Mott insulator, after Mott explained the insulating properties of nickel oxide. The point between these extremes where the behavior changes from metal to insulator is the Mott transition.

It is possible to induce conductivity in a Mott insulator through the addition of dopants, though their role is not yet well understood. In fact, the parent compounds of the
cuprate superconductors are all Mott insulators, and the dependence of their features on the strong electron correlations of the Mott state is an ongoing problem.\textsuperscript{36} A common occurrence among these materials seems to be a spatial inhomogeneity in spin, charge, or orbital occupation. This separation of distinct phases is often accompanied by interesting phenomena including high temperature superconductivity and colossal magnetoresistance.\textsuperscript{37}

The SrCoO\textsubscript{x} system can be described as a Mott insulator, in that the parent compound at x = 2.5 is an antiferromagnetic insulator which can be made to conducting via charge doping with the addition of oxygen. Some questions remain as to the conducting state of fully oxidized SrCoO\textsubscript{3} or whether the filling of vacant oxygen sites is directly comparable to the lattice substitution in similar material La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3}. These comparisons are developed more fully in the next section and in Chapter 3.

1.6 Phase Separation

Many transition metal oxides exhibit a rich phase diagram as electron interactions result in multiple ground states with comparable energy. In the doped Mott insulators, charge doping can lead to electronic inhomogeneity and in some cases results in clear electronic phase separation. In those cases, particular charge densities are unstable. Instead, the ground state separates into the two regions that bound the unstable range.\textsuperscript{2} It has been proposed that the properties of transition metal oxides should be considered in terms of complex emergent behavior due to the system of strongly correlated electrons. These systems self-organize into structures which vary widely in scale.\textsuperscript{38} The observed properties of the material can be thought of in terms of the physics of each individual phase and that due to the competition between phases.\textsuperscript{37}
In describing colossal properties in the manganites, Dagotto et. al. have suggested that level of disorder plays an important in determining the nature of the phase separation.\textsuperscript{13,37} In this model, a low level of disorder leads to separate regions which do not strongly interact with each other, but rather behave as separate materials. Conversely, a high level of disorder leads to nanoscale domains which are too small to exhibit their own properties. Colossal properties are seen at an intermediate level of disorder, where the separate phases interact strongly and compete to determine the ground state of the system. An external parameter, such as an applied field, can then tip the balance in favor of one phase or another, of particular utility in technological applications. What is not well understood is how one might experimentally control the level of disorder and thus the size of the phase separated regions.

In this thesis, we will explore the role of oxygen doping in phase separation. Previous work by our group has explored the effect of interstitial oxygen in the cuprate superconductor La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4+y}.\textsuperscript{39} The parent compound at x = y = 0 is a Mott insulator, which can be made into a high temperature superconductor through either cation doping or the addition of oxygen. As oxygen is added, the system separates into distinct magnetic and superconducting regions, between stable line phases. At low y, the separation involves a structural component due to oxygen ordering. For y > 0.125, the separation is entirely electronic. Interstitial oxygen is shown to stabilize the formation of larger scale regions (>100 nm) than is the case for Sr doping. In contrast, doping through Sr substitution results in spin-glass behavior and nano-scale phase separation.\textsuperscript{40}

A similar separation occurs in the perovskite La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} (LSCO), where the substitution of Sr\textsuperscript{2+} for La\textsuperscript{3+} leads to a magnetically inhomogenous state and an insulator to
metal transition.\textsuperscript{6-8} An alternative method for controlling the cobalt valence is through the amount of negatively charged oxygen present, altering the balance between ground state energies and modifying the crystal structure. The focus of this work will be the compound SrCoO\textsubscript{x}. Our group has previously described electronic phase separation in this system as a function of oxygen content.\textsuperscript{41} Similar to La\textsubscript{2}CuO\textsubscript{4+y}, the parent compound SrCoO\textsubscript{2.5} can be described as a Mott insulator which is made to conduct through the addition of oxygen. A structural phase separation persist up to x = 2.75, above which the phase separation is also solely electronic.

In both systems, a notable difference exists in the nature of phase separation due to cation versus oxygen doping. It may be the case that the exceptional mobility of oxygen atoms in these materials inhibits disorder and supports the establishment of stable regions of larger scale. The work of this thesis will explore epitaxial films of SrCoO\textsubscript{x}, providing insight on the size of phase regions and the existence of an orderings with the underlying lattice. These topics are discussed at length in Chapters 4 and 5.
2. Experimental Procedures

The electrical, magnetic, and structural properties of these materials were investigated through a variety of techniques. This chapter discusses in detail the methods by which samples are prepared and characterized.

2.1 Pulsed Laser Deposition

The primary focus of this study has been on thin films of $\text{SrCoO}_x$. Thin film samples differ from bulk powders in several key ways. First, alignment with a properly chosen substrate material can affect the lattice constant of the sample material. A thin film will tend to align with the base material, thus a slight mismatch between the lattice constants can induce strain and change the interaction between sites. In addition, the limited thickness in one direction introduces the effects of finite dimensionality. Epitaxial films offer single crystal-like samples which avoid some of the complications of random orientations and grain boundaries inherent to bulk materials. While the lack of material compared to bulk samples can be detrimental to signal intensity, x-ray scattering experiments take advantage of the flat, selectable surface of known orientation inherent to film samples.

To produce such films, we used pulsed laser deposition (PLD). The PLD method uses an Excimer laser to deposit film material on a substrate crystal. Excimer stands for “excited dimer.” A high voltage is used to excite the normally inert krypton gas, allowing a momentary bound state to form with fluorine. The excited compound emits ultraviolet radiation at 248 nm. The high energy and large spot size which results is well suited for laser ablation, though this type of laser has poor collimation and can be difficult to focus properly. Photons pass through a window into the vacuum chamber, where they are
incident upon a target composed of the appropriate ratios of desired film material. The laser is focused to a thin line, and the energy density is high enough to ablate the target material by converting it to a plasma. The disassociated positive ions and electrons create a plume of material which may also interact with the chamber atmosphere to create the film.

Above the plume, a substrate with the desired lattice properties is kept at a temperature which encourages epitaxial growth. The pulse rate of the laser determines the speed at which layers of material are deposited on the substrate. The thickness of the resulting film is a function of the pulse repetition rate and the time of growth. The growth environment can be further controlled by choice of atmospheric gas, typically oxygen. Oxygen incorporation into the film can also be encouraged by slowly cooling from growth temperature in a higher oxygen pressure.
Figure 2.1 Schematic of the pulsed laser deposition chamber. Pulses of 248 nm UV light are focused on a rotating target. This creates an ion plume which condensed on the selected substrate. Temperature and gas environment set to optimize growth.

A diagram of the PLD chamber is shown in Figure 2.1. Vacuum pressure is set through a combination of rough and turbo pump control and gas inlet pressure. The substrate is held at temperature using a high current electric heater, which must be water cooled. The attached chiller also cools a protective stage at the bottom of the chamber protecting the target area. The chamber can hold up to three targets simultaneously, which can be alternated to create layered materials. To foster even target wear and uniform film growth and thickness in a possibly uneven plume, both the target and substrate can be rotated.

2.2 X-Ray Diffraction

The epitaxy and orientation of the films are checked using laboratory x-ray diffraction (XRD). Scans were performed using a Siemens D8 powder diffractometer. The
diffractometer emits K\textsubscript{\alpha 1} radiation of average wavelength 1.5418 Å from a Cu target. The x-ray beam was incident at angle \( \theta \) to a sample slide, and registered by a detector at angle 2\( \theta \) as shown in figure Figure 2.2.

We can describe XRD by considering the interaction of incident radiation at wavelength \( \lambda \) with a crystal lattice of regularly spaced atoms. If the spacing is of a similar order to the incident wavelength, reflected rays will add constructively at particular angles. When the difference in path between rays reflected from planes of the crystal is an integral number of wavelengths, diffraction occurs as described by Bragg’s Law:

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

The spacing between planes in the lattice is given by \( d \), \( n \) can be any integer, and \( \lambda \) is the wavelength of the x-ray photons. As the angle is changed by moving the source and detector, the Bragg condition is satisfied for various spacings present in the lattice. Detector
counts as a function of angle produce a series of peaks that can be analyzed to determine lattice constants. The relationship between spacing observed and the crystal lattice depends on the type of crystal structure. For the cubic case:

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

2.2

Where \( h, k, \) and \( l \) represent the Miller indices and \( a \) is the lattice constant. If multiple phases are present, the resulting pattern is the superposition of the patterns for each phase. For films, the diffractometer can be used to ensure samples are single phase and properly aligned. An XRD analysis of our films is given in section 3.4.

2.3 Magnetometry

Magnetic ordering in materials, either spontaneously or in response to an applied field, is a macroscopic expression of the complex interactions which extend beyond a unit cell. Measuring the magnetization of film samples can be difficult, as the detectable signal may be quite small, and one must consider separately any applied field used to generate the response. Their relationship is given by the following equation:

\[
B = \mu_0(H + M)
\]

2.3

\( B \) represents the magnetic flux density, \( H \) is the magnetic field strength, \( \mu_0 \) is the vacuum permeability, and \( M \) is the magnetization, defined as the magnetic moment per unit volume. One can think of these fields in the following way: \( B \) represents the total field measured in a region. This field is composed of any external field present in the space, \( H \), and the response of any material present, \( M \). Magnetization is related to \( H \) by the magnetic
susceptibility $\chi$. In paramagnetic and diamagnetic materials, this relationship is linear, but is nonlinear for ferromagnetism. In general, we can define,

$$\chi = \frac{dM}{dH}$$

2.4

The measurement of $\chi$ is an important indication of the magnetic nature of the material. For this work, we have studied the magnetization of these materials as functions of temperature and applied field.

2.3.1 DC Susceptibility

Magnetization is measured using a Quantum Design superconducting quantum interference device (SQUID). The SQUID uses liquid helium to cool superconducting wire below the critical temperature. This allows the establishment of high applied fields using superconducting magnetic coils. At the University of Connecticut, fields as high as five Tesla can be created.

To measure the response of a sample material, a Josephson junction is used. If two superconductors are separated by a thin insulating layer, a current can quantum mechanically tunnel across the junction. A SQUID makes use of this effect by employing two such junctions on either side of a superconducting loop. As a sample is moved through the pickup coils, the change in magnetic flux induces a current which establishes a voltage across the junctions. This voltage can be used to determine the magnetization to a high degree of accuracy.

A sample heater allows magnetization to be measured as a function of temperature from below 5 K to 350 K. Such M vs T data are used to identify magnetic ordering temperatures and are measured in two ways. In a field-cooled measurement (FC), the
sample in question is cooled below $T_C$ under an applied field. This fosters an alignment of domains with the field and results in a larger total moment. In the zero-field-case (ZFC), the sample is cooled to low temperature with no field applied. The measured moment then reflects the spontaneous alignment of domains. The difference between FC and ZFC measurements imparts information regarding the anisotropy and pinning forces between domains.

The SQUID also allows the measurement of magnetization versus applied field. M vs H scans are used to determine the saturation magnetization and, in the case of ferromagnetic samples, display the magnetic hysteresis and coercivity. A diagram is shown in Figure 2.3. After pumping out ambient air in a load lock, a transfer pole is used to lower the sample into the measurement space, which is isolated from the environment through a grease plug at the top of the device.

For sensitive magnetic measurements, the response of the sample holder must be taken into account. Two options exist for mounting samples at the end of a long transfer pole. The first uses a plastic straw. Powder samples are held in place with small wad of cotton, while film samples are mounted through the walls of the straw with the film surface perpendicular to the applied field. Because the straw is not perfectly symmetric, it can contribute unevenly to the background. In addition, we have found the cotton often contains a small but measurable FM contaminant. The magnetic response from our samples was large enough to easily distinguish the ordering transition despite this. We chose to use the straw mount for irregular shaped or large bulk samples.
Figure 2.3 Diagram of the Magnetic Properties Measurement System. Sensing coils measure the magnetic moment as a sample is moved through an eternal field applied by the superconducting wire. Liquid helium cools the superconductor and sample space.
For the films of this work, an alternative mounting was used. Each sample was attached to a thin quartz rod. The quartz rod has a low magnetic response and contributes evenly to the background of the measurement. Attachment was accomplished either through a Teflon wrap or a small amount of double-sided tape. The Teflon wrap can trap oxygen, resulting in magnetic signal at 52 K. As the transition temperatures for SrCoO$_x$ are above 150 K, this signal was not disruptive to this work. Still, we most often used double-sided tape to avoid the issues. For the quartz rod setup, the film surface is parallel to the applied field, minimizing the effects of demagnetization. The film signal must be separated from the response of the material on which it is grown. The applied field is chosen to maximize the film response without swamping the signal with that of the often diamagnetic substrate. An expanded discussion of this for our work is given in section 3.6.3.

### 2.4 Three-Wire Electrochemical Cell

In order to adjust the oxygen content of our samples, we made use of a three-wire electrochemical cell. The cell operates by immersing the material in an electrolyte solution and applying a voltage to the sample. Negatively charged oxygen ions are induced to flow into the sample. A schematic is shown in Figure 2.4.

Samples of SrCoO$_x$ were held at 0.8v in a 5% solution of NaOH. 0.8 v was chosen to maximize oxygen incorporation while minimizing surface reactions, as described in section 3.5. The sample is wrapped in a platinum mesh to ensure a consistent voltage across the surface, and attached to the working electrode (WE). The voltage is measured with respect to a reference electrode (RE), in this case a platinum wire in contact with the
solution. Current is monitored at the counter electrode (CE). The reaction at each electrode is expressed as:\(^{42}\)

\[
\text{WE:} \quad \text{SrCoO}_x + 2y\text{OH}^- \rightarrow \text{SrCoO}_{x+y} + y\text{H}_2\text{O} + 2ye^- \tag{2.5}
\]

\[
\text{CE:} \quad 2y\text{H}_2\text{O} + 2ye^- \rightarrow 2y\text{OH}^- + y\text{H}_2(\text{g}) \tag{2.6}
\]

The cell is elevated above room temperature by a water bath at 80° C. This procedure was used effectively to raise the oxygen content of both bulk and film samples. For film samples, oxidation times of as little as 5 minutes produced noticeable changes. In the case of bulk samples, a period of several days was required.

Figure 2.4 Schematic of the electrochemical cell. A constant voltage is maintained between the working and reference electrodes. The sample is wrapped in a Pt mesh and attached to the working electrode. Current is measured at the counting electrode.
2.5 Scanning Electron Microscopy

A scanning electron microscope (SEM) was used to examine features of the film surface and as a spot check of film thickness. To image the surface of films, a JSM-6335F SEM was used. The SEM generates images by rastering a focused electron beam over a small area. The interaction of the beam with the atoms of the sample surface produces secondary electrons which are detected to form the image. Because of this injection of electrons, the sample surface must be at least partially conductive and electrically grounded, or charging will blur the image. In addition, this instrument can determine the composition of the sample at selected points by analyzing the x-rays produced in the interaction, a process known as energy dispersive x-ray spectroscopy (EDXS). In our case, SCO films were insulating, making SEM imaging difficult. See section 3.7 for additional details.

The Strata 400 DualBeam SEM is a similar device that includes focused ion beam technology (FIB). In this work, FIB was used as a check of film thickness. After laying down a protective platinum coating, a trench can be milled using the ion beam. The platinum protects the edge of this trench, which is then imaged by the SEM in profile. In this configuration, differences in contrast can be directly measured at several points, allowing a rough average thickness to be calculated.

There are two notable disadvantages to this method of determining film thickness. First, SEM images rely on an interpretation of visible contrast in the image. One cannot be certain that the film-substrate interface will be visible, or that the contrast seen represents that boundary. Second, the FIB method spot checks a random location with may or may
not be representative of the film as a whole. A secondary method of determining average thickness through analysis of saturation magnetization is given in section 3.6.3.

2.6 Resonant X-Ray Diffraction

We investigated the possibility of a superlattice structure in these materials using resonant soft x-ray diffraction (RSXS), which can reveal subtle ordering not discernible in ordinary Bragg diffraction.\textsuperscript{25} Additionally, absorption data was taken at significant O and Co energies. This work was performed at the Resonant Elastic and Inelastic X-ray Scattering 1OID-2 beamline at the Canadian Light Source, in collaboration with beamline scientist Feizhou He.

The technique is similar to the previously described XRD in that incident x-ray radiation is detected at particular angles to give information on lattice structure. However, conventional hard x-rays, near 10 keV, scatter through interaction with the electron cloud of the atoms, resulting in a scattering cross-section proportional to the square of the atomic number. Any charge or orbital ordering which may exist in the SrCoO\textsubscript{x} system is determined by slight changes in valence shell occupancy, representing a small percentage of the total electron number and making detection through standard diffraction unlikely. Similarly, while conventional XRD is sensitive to magnetic structure, the scattering cross section is reduced by $(\hbar \omega/mc)^2$, making observation above the background difficult.\textsuperscript{43} RSXS makes use of an enhancement of the scattering cross-section which occurs at key atomic absorption edges. This process excites a core electron to a higher intermediate state, usually an unoccupied valence site. As the electron decays back to the ground state, a photon is emitted with the same energy as the incident radiation. Because the absorption
energy necessary to promote the electron depends on the element involved, RSXS offers an element specific probe of magnetic and electronic order in transition metal systems.

An comprehensive review of resonant diffraction is given in reference [44]. A short summary is given here. The change in amplitude and phase which occurs during scattering is given by the scattering length, or form factor $f_n$, of a crystal site $n$ as follows:

$$f_n = f_n^T + f_n^M + \Delta f$$  \hspace{1cm} (2.7)

The terms $f_n^T$ and $f_n^M$ represent the charge (Thomson) and magnetic scattering, respectively. $\Delta f$ is the dispersion correction, which depends on the photon energy and polarization. In the kinematic approximation, the intensity detected is proportional to a unit cell structure factor, which includes $f_n$, describing the interference of scattered waves within a unit cell, and the lattice sum entailing the interference due to different unit cells. The cross section for scattering of a photon with an atomic electron is given by the Kramers-Heisenberg formula. The first-order term of the interaction Hamiltonian describes the Thomson, non-resonant scattering. The enhancement due to the resonant process is seen in the second-order term.\textsuperscript{44} At energies close to an absorption edge, the second-order term can dominate the scattering.

The high flux and energy selectivity required for RSXS necessitate a cyclotron source. The term “soft x-ray” refers to the fact that diffraction is done at energies lower than 2000 eV. For SrCoO$_x$, the energy is tuned to match the cobalt L$_3$ and L$_2$ edges at 779 eV and 795 eV. The L-edge excitation promotes a 2p electron to an unoccupied 3d orbital. In practice, the detector can operate through detection of the emitted photon in total fluorescence yield (TFY) or by monitoring the necessary ground current to keep the sample
neutrally charged, thus measuring the electrons produced which do not recombine. This channel is the total electron yield (TEY). TEY gives a more surface sensitive result, while TFY probes more deeply into the sample.

The availability of 3d orbitals is a function of the Co site valence. As such, x-rays tuned to the L edge are the best choice for resonant experiments on these materials. RSXS at L edges probes the partially filled valence shell of the material, allowing a means to detect contrasts in occupancy or orbital ordering. K edge diffraction, for example, would promote a 1 s electron to an empty 4 p orbital, giving no information on electronic ordering. In addition, because the 3d orbitals overlap neighboring oxygen p orbitals, vacancies in the oxygen octahedra affect the excitation through the hybridization of Co d and O p orbitals. In this way, RSXS at L edges can be sensitive to orderings due to spin states, electron orbitals, or oxygen vacancies. One drawback, however, is the smaller range in q due to such low energies. This makes detection of such peaks much more difficult, as standard Bragg peaks must be detected for alignment at the higher energies available, while regions of interest remain within the q space that can be scanned at the lower absorption energies. The details of our efforts and results are given in Chapter 5.
Figure 2.5 Absorption process occurring in Resonant Soft X-Ray Diffraction. An incident photon excites a core electron to an unoccupied valence level, resulting in an intermediate excited state. The core hole and excited electron recombine and emit a photon with the same energy as the incident radiation.
3. SrCoO$_x$ System

SrCoO$_x$ undergoes structural and magnetic transitions with the addition of oxygen. At high concentrations, we have identified SrCoO$_x$ as a candidate material exhibiting magnetic phase separation. This chapter discusses the details of this system. We begin with a detailed background as reported in the literature. We include an explanation of the previous work by our group which first identified phase separation in bulk samples.

The fact that the unique magnetic states appear for oxygen concentrations of 2.75 (3-1/4) and 2.88 (3-1/8) and 3.0 indicates a commensurate ordering on the scale of four or eight unit cells. This order may be attributed to a pattern of oxygen vacancies, valence charge, or orbital order. Determining its source may shed light on the mechanism responsible for phase separation. In order to investigate that possibility, crystallographic ally well-ordered samples were required. The work of this thesis has focused on epitaxial films of SrCoO$_x$, with characteristics most similar to single crystals.

The creation of epitaxial thin films at the appropriate oxygen concentration can be challenging. This chapter relates the details of sample preparation and characterization.

3.1 Structural Evolution with Oxygen (Bulks)

The structural evolution of this system with oxygen content has been examined in the literature (2.5 ≤ x ≤ 3.0). The structure observed is dependent on the oxygen level of the sample. SrCoO$_{3.0}$ orders with the ideal perovskite arrangement, but the presence of oxygen vacancies at lower concentrations distorts the structure. At x = 2.5, vacancy ordering results in an orthogonal structure. This is observed in neutron diffraction studies.
on bulk samples, where $\text{SrCoO}_{2.5}$ is arranged in the brownmillerite-type structure and orders antiferromagnetically at $T_N = 570$ K.\textsuperscript{46} The ideal perovskite and brownmillerite structures are compared in Figure 3.1. Note the position of vacancies in the brownmillerite structure alternates between rows of fully occupied octahedra, creating a larger unit cell than in the perovskite case.

Oxygen can be added to $\text{SrCoO}_{2.5}$ via electrochemistry. As oxygen is incorporated, a second cubic structure develops, corresponding to $\text{SrCoO}_{2.75}$. This has been identified as a ferromagnet with ordering temperature $T_C = 160$ K.\textsuperscript{41} For the range $2.5 \leq x \leq 3.0$, the two phases coexist in bulk samples, and both crystal structures are evident in diffraction. The perovskite phase grows at the expense of the orthorhombic phase until the sample is completely $\text{SrCoO}_{2.75}$.\textsuperscript{20} Above $x=2.75$, the material remains cubic and the lattice constant decreases smoothly with oxidation, with the exception of a slight tetragonal distortion near $x=2.88$.\textsuperscript{20,45} At $x=3.0$, $\text{SrCoO}_x$ is a ferromagnet with $T_C=280$ K.\textsuperscript{19}
Figure 3.1 A schematic of the cubic perovskite (left) and orthorhombic brownmillerite (right) structures. Oxygen ions are shown in red, with vacancies as black dots. The central cobalt ion is in blue. Strontium atoms are not shown for clarity. Taken from [20]
Figure 3.2 Evolution of crystal structure as oxygen content is increased from $x = 2.5$ in bulk samples. An orthorhombic and cubic structure coexist until $x = 2.75$, above which the lattice is pseudo-cubic and evolves smoothly. Adapted from [20]
3.2 Phase Separation in Bulk Materials

Recently, our group reported a magnetic phase separation in bulk samples of SrCoO$_x$ for oxygen content $2.88 < x < 3.0$.\textsuperscript{41} Beginning with $x = 2.88$, samples were electrochemically oxidized to $x = 3.0$, while magnetic measurements were made at stages along the process. At the endpoints, the $x = 2.88$ and $x = 3.0$ compounds show single ferromagnetic transitions at $T_C = 220$ K and 280 K, respectively. At intermediate concentrations, both magnetic transitions are seen, while high resolution x-ray diffraction (XRD) shows only a single pseudo-cubic crystallographic phase.

Figure 3.3 shows the evolution of the magnetic ordering and structure for bulk samples as taken by Xie et al.\textsuperscript{41} The mixed phase sample in panel (b) shows two magnetic transitions. Le Toquin et al. have shown two crystallographic phases coexist between $x = 2.5$ and $x = 2.75$. A logical assumption might be that a similar process results in the mixture of end point phases, each ordering at a different temperature. If this were the case, XRD analysis should show separate peaks particular to each lattice structure. Panel (d) shows high resolution XRD data taken at Brookhaven National Laboratory. A single peak is noted, representing the (222) Bragg peak. For comparison, vertical lines are placed at the known positions for $x = 2.88$ and $x = 3.0$. A cumulative fit due to a summation of peaks set at each end point position does not match the data. Therefore, the observed magnetic phase separation is not explained by a mixture of the end point structures.

This implies an electronic separation which may be due to an ordering of either oxygen vacancies or valence electrons. Additionally, removing oxygen through electrochemical reduction produced a phase with $T_C = 160$ K, identified as $x = 2.75$.\textsuperscript{41} The occurrence of stable phases at the oxygen contents $x = 2.75 (3.0 - 1/4)$, $2.88 (3.0 - 1/8)$, and
3.0 further suggests an ordering with the lattice related to a periodicity of four or eight unit cells. Moreover, while separation between phases of different magnetic order can be explained as a consequence of slight variations in their ground state energies, a separation of two ferromagnetic phases is unexpected.
Figure 3.3 (a-c) Change in magnetic ordering temperature as oxygen is incorporated. (d) High resolution XRD shows the mixed phase sample is of a single crystal structure. Adapted from Ref [41]
3.3 Bulk vs Film Samples

The best choice of one type of sample over another depends on the measurement being made. Bulk samples are composed of pressed powders annealed at high temperatures. Films are grown on a crystalline substrate, in our case through PLD. Each method presents certain advantages and disadvantages which must be considered carefully.

Bulk samples are created by mixing stoichiometric amounts of constituent powders. Microscopically, they are made up of numerous crystallites randomly oriented with respect to one another. The boundaries of each crystal grain denote a transition to an inter-granular matrix within which the ratio of materials may differ from that of the crystals.

Bulk samples of SrCoO$_x$ were prepared for our work from SrCO$_3$ and Co$_3$O$_4$. Pressed powders were fired several times in air at increasing temperatures from 900 to 1150 °C, followed by intermittent grinding. A subsequent high pressure oxygen anneal could reach final oxygen concentrations of $x = 2.88$. This work was done by the group of Professor Bogdan Dabrowski at Northern Illinois University.

General characterization of the lattice through XRD can be made easier by the large quantity of material created in this method. Additionally, the large number and random orientation of the crystals means effectively all crystallographic directions are sampled in a single scan. Magnetization measurements see a larger signal and sharper transitions when measuring bulk samples. Techniques relying on weakly interacting probes, like muon spectroscopy, are also benefited by a larger sample amount. On the other hand, grain boundaries can be problematic for experiments like resistivity measurements, where the inter-grain matrix may inhibit charge transport. The random orientations of the crystals
make the investigation of long range ordering more difficult. The diffraction signals for subtle shifts in lattice arrangement are usually quite weak. A large single crystal sample improves signal-to-background, with the caveat that the single crystal must now be properly aligned to allow the desired peak to be detected.

The oxygen concentrations corresponding to stable magnetic phases hinted at an ordering of every four or eight unit cells, and a RSXS survey of powder samples (see section 4.1) showed what appeared to be a weak peak at (¼ ¼ ¼). To more fully examine the prospect of superlattice ordering, we required single crystal-like samples. Single crystals of SrCoO$_X$ can be prepared with high pressure oxygen anneals,$^{12}$ but this process was unavailable at the University of Connecticut. Epitaxial films offer many of the same advantages and can also be used to apply strain or investigate finite dimensional effects. Crystallographic orientation is selected through proper choice of substrate. A major concern, however, is in developing the proper growth technique to produce such films. The majority of this work focuses on the preparation and measurement of epitaxial films, though powder samples were also investigated.

3.4 Film Growth

Films were grown using pulsed laser deposition (PLD) from a SrCoO$_{2.5}$ target. Dense polycrystalline targets were prepared in the same manner as has been described for bulk materials. After the annealing and grinding of the pressed powders, a final firing of a d = 24 mm target was done as follows: 24 h at 1150 °C, slowly (1 deg/min) cooled to 900 °C, followed by quenching to room temperature on a copper plate. The resulting material was single-phase brownmillerite with oxygen content near 2.5.
A 248 nm KrF excimer laser operated at 4 Hz was used to deposit the films on SrTiO$_3$ (STO) substrates of (0 0 1) and (1 1 1) orientation. The substrates were held at 700 °C in an atmosphere of 300 mTorr O$_2$ and cooled slowly after growth in 300 Torr O$_2$. The resulting films were not well aligned with the substrate, and XRD data showed the presence of multiple phases. To achieve epitaxial films of single phase, a secondary annealing and quenching process was required.

The films were annealed in the PLD chamber for 30 min at 750 °C in 300 Torr O$_2$, then quickly cooled in vacuum to ambient temperature through contact with an internal, water cooled stage. This process resulted in well-ordered films of nominal oxygen concentration $x = 2.75$, with $T_C = 160$ K. It should be noted that a variety of quick-cool techniques were attempted without success. This included simply shutting off the heater after the annealing step and moving the sample holder away from the heater. We also attempted to anneal in a high temperature oven. Quenching was accomplished by removing the sample from the oven and placing it in contact with a steel heat sink or liquid nitrogen. Neither method could replicate the results from the in-chamber process.

Figure 3.4 demonstrates the improvement in film quality by annealing. XRD data of the same film is compared before and after the process. Because of the close match in lattice constants, film peaks lie close to substrate peak positions, and can be difficult to discern. In panel (a), multiple additional peaks reveal that the film is not single-phase. After the anneal process, panel (b) shows sharper film peaks and the elimination of the extra phases.
Figure 3.4 (001) SrCoO$_{2.75}$ film before and after post growth annealing process. (a) Multiple peaks are noted in the as-grown film. STO substrate peaks are labeled in blue. (b) After annealing, extra phases are reduced and film peaks become more noticeable on the shoulder of substrate peaks. These are labeled in red.
Without the secondary anneal, the resulting films were not well aligned with the substrate, regardless of substrate orientation. However, for the case of (111) orientations, as-grown films tend to align in the (110) direction. See Figure 3.5. While such films were not used for this work, this result may supply another orientation for future study.

A shift in peak positions can be caused by slight misalignments in mounting. The shift seen is greater at higher two theta position. The lattice constants for the SrTiO$_3$ substrates are well documented$^{47}$ and can be used to correct our calculations for the films. The difference between the theoretical and actual position is noted for each substrate peak.

**Figure 3.5** XRD of SCO film on (111) STO substrate. Before post growth anneal treatment, films tend to align along (110) direction. The additional peaks represent extra phases typically reduced in the anneal process.
visible in a single XRD scan. These are plotted as delta versus two theta position. A linear
fit then gives an equation for the amount of shift for a particular angular position. Using
the measured position of the film peaks, one can calculate the necessary correction in two
theta position. The corrected value can be used to determine a spacing d for each of the
observed film peaks, starting with a plausible assumption for their (h k l) values and using
Bragg’s law as explained in section 2.2. If the measured film peaks are along the same
lattice direction (i.e. (100), (200), (300)) the computed lattice constants for each position
should be in close agreement. The average of these measurements is taken to represent the
lattice constant of the film. For the films used in this work, only the out-of-plane lattice
constant was measured. For a symmetric cubic structure, all lattice constants are equivalent.
It should be noted, however, that film samples may distort slightly from cubic symmetry,
particularly if in-plane strains are induced by the substrate. We measured an out-of-plane
lattice constant of 3.83 Å. This agrees closely with reports for bulk SrCoO$_{2.75}$, where the
constant a measured as 3.842 Å and 3.845 Å.$^{20,45}$ This demonstrates our films are not thin
enough to significantly strain the lattice. As Chapter 4 will discuss further, finite thickness
effects may play a more important role than strain.

It should also be noted that, even under identical growth conditions, the PLD growth
and annealing process did not consistently produce high quality film samples. High quality
is here defined as samples which are well aligned, exhibit easily identifiable XRD peaks
with no extra phases, and show a clear magnetic transition at $T_c = 160$ K. This would
suggest a maximum amount of SrCoO$_{2.75}$ over other phases. Visually, samples of highest
quality were dark black in appearance with a shiny, smooth surface. In roughly two thirds
of the attempts, these criteria were not met. For borderline cases, where film peaks or
magnetic transition were only partially discernible, the electrochemical oxidation process could result in acceptable samples at the next magnetic phase. This suggests that the quality of the film is highly dependent on oxygen absorption during the growth and anneal process. Slight variations in laser power, chamber pressure, or thermal conductivity can therefore have appreciable effects. To produce several films of like characteristics, samples were often grown in batches of two to four. So long as the substrates were kept well within the plume, substrate position was not seen to affect outcomes.

### 3.5 Oxidation

Solid materials through which oxygen can easily permeate are desirable for a variety of technological devices, including oxygen monitors, pumps and solid oxide fuel cells. In many such materials, current can flow through the movement of the oxygen ions, which hop from one available lattice site to another. In device applications, these materials are often employed in extreme conditions of temperature and pressure, requiring a sufficiently durable material and complex device design. Fuel cell design, an area of renewed focus due to energy concerns, highlights the requirements for working materials. Perovskite oxides show promise as potential functional oxides for these purposes. In particular, La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ has been noted for its high ionic conductivity.

Solid solutions based on SrCoO$_{3-\delta}$ are among the highest oxygen flux materials, and have been investigated for their catalytic properties as oxygen electrodes. Karvonen et. al. have described the process by which oxygen ions are first absorbed at the surface and eventually fill vacant lattice sites in the oxygen octahedra. We make use of this high oxygen mobility to fully oxidize SrCoO$_x$ films, in a process similar to that described by
Nemudry et. al. and Le Toquin et. al,\textsuperscript{20,45} and our group’s previous work on bulk samples\textsuperscript{17,41} While the chemical oxidation of SrCoO\textsubscript{x} films has been reported\textsuperscript{55} this work represents the first electrochemical study of film samples. Details of the electrochemical cell itself are described in 2.4.

![Cyclic voltammetry of a SrCoO\textsubscript{x} film. Sample current was measured as the applied voltage was cycled between 1 and -1v in the indicated direction. The sharp increase in current at approximately 0.8 v denotes unwanted surface reactions. Voltage was kept at or below 0.8 v using the electrochemical cell circuitry.](image)

**Figure 3.6** Cyclic voltammetry of a SrCoO\textsubscript{x} film. Sample current was measured as the applied voltage was cycled between 1 and -1v in the indicated direction. The sharp increase in current at approximately 0.8 v denotes unwanted surface reactions. Voltage was kept at or below 0.8 v using the electrochemical cell circuitry.
The electrochemical cell employed an operational amplifier to keep a steady voltage applied between the working and reference electrodes. To determine the proper voltage, we performed cyclic voltammetry on a sample film. In this procedure, the voltage is cycled between -1 v and 1 v in 1 mv steps at a rate of 10 mv/s. Figure 3.6 shows the resulting graph. Note the large increase in current at approximately 0.8 v. This indicates surface reactions are occurring, including the disassociation of water. At higher voltages, bubbles can be seen rising from the electrodes. The possibility surface reactions at the smaller peaks observed between ±0.5 v, perhaps due to a degradation of wire surfaces, cannot be discounted. However, to keep the oxygen incorporation as high as possible while avoiding visible bubbles, we kept the cell voltage at or slightly below 0.8 v.

Ideally, the cell would keep the set voltage constant despite changes in the sample resistivity as oxygen is incorporated. In practice, the cell was unstable, particularly over short intervals. This may be attributed to the fact that these home built potentiostats were constructed with bulk samples in mind, where oxidation times of several days were expected.\cite{17,42} In this work, high quality films could be completely oxidized in approximately 20 minutes. Thus, fluctuations in voltage which may settle over several hours become more problematic for film work. Another thought is to set a fixed current and monitor the fluctuations in voltage. While the necessary apparatus was not constructed for this work, this method may offer a solution to the stability issue.

Voltage is monitored using a meter between the WE and RE terminals, while current is measured through a meter at the CE. A voltage can only be read after the sample is immersed in the electrolyte solution. A user must then adjust the cell to the desired voltage. Typically, a large spike in the magnitude of the cell voltage is seen over the first minute,
after which the voltage will climb slowly over time. To keep a desired value, the cell must be adjusted periodically. The intent was to identify the development of new phases through jumps or inflections in the current, and accurately predict the phase proportions in the sample based on time in the oxidation cell. These manual adjustments are somewhat imprecise, and care must be taken not to confuse features caused by the adjustments with those due to phase changes in the sample.

Figure 3.7 shows a typical current vs time graph for a SrCoOx film, oxidized in two five-minute steps. This can be compared to Figure 3.8, which shows the oxidation of a large bulk sample over a total of 30 hours. On this larger time scale, the initial drop in current occurs relatively quickly, and the current stabilizes to a more constant value.
Figure 3.7 Current vs time during oxidation of a SrCoOx film. This film was oxidized for five minutes in two separate sessions. The initial spike in current corresponds to immersion of the sample in the electrolyte solution.
Figure 3.8 Oxidation current vs time of a bulk SrCoOx sample over 30 hours. The sample was oxidized in three successive sessions of 1, 5, and 24 hours. Measured current was relatively stable on the scale of hours.
Even in the case of bulk samples, the cell voltage must be periodically monitored and adjusted. Efforts are underway to improve the stability of the cell and include computer control and measurement with Labview programming. Because of the cell fluctuations, the current graphs are used only as a qualitative measure of the electrochemical process.

Phase changes due to oxidation where tracked by measuring the ferromagnetic transition temperature using SQUID magnetometry, discussed further in section 3.6. In general, film samples could be oxidized to the intermediate magnetic phase \((x = 2.88)\) after 3 to 5 minutes of oxidation. Full oxidation \((x = 3.0)\) could be achieved with a cumulative total of 15 to 20 minutes of oxidation. While achieving high quality films could be difficult, once made, oxidation was typically not problematic. However, as a result of variations in sample quality and the oxidation process, not all films responded in this manner. These issues seemed to be more prevalent when several weeks had passed between sample growth and oxidation, though older films were successfully oxidized. The next section outlines some of the difficulties encountered in the oxidation process.

### 3.5.1 Film Damage and Repeatability

Over time, the general quality of film samples is negatively impacted by the electrochemical process. Surface damage is expected for a sample in a chemical cell, but becomes especially problematic for film samples over bulks. The oxidation process occurs much more quickly in film samples due to smaller amount of material present. After the first oxidation session of one to five minutes, an initially smooth, dark, and shiny film surface becomes clouded and marked. Because the samples are oxidized in several steps, the issue is compounded.
As such, the effects of oxidation damage are more apparent in film samples. In fact, the number of phases which can be observed are more limited for film samples. For example, additional phases can be attained in bulk samples by reversing the polarity of the electrochemical cell, which show evidence of a phase matching $x = 2.50$.17 This process draws ions from the sample and lowers the oxygen concentration. In film samples, however, reversing the flow of current removes material from the substrate. This damage makes these film samples unusable.

Furthermore, the variability inherent to the process means even oxidation steps of the same duration are not completely equal. The spacing of the electrode wires, contact between the sample and the Pt mesh, fluctuations of the cell voltage, and differences in the sample quality introduce irregularities which become more apparent for films.

### 3.5.2 Effects on Lattice Constant (Films)

The following study gave some puzzling results. It is described here for completeness and to illustrate some of the difficulties in preparing high quality film samples. Section 3.1 describes the structural evolution noted for bulk samples. To date, no such survey has been completed with film samples. We have attempted to track the effects of oxidation on the lattice constant of film samples, noting the additional challenges discussed in the preceding section.

Figure 3.9 collects XRD data after 12 successive oxidation steps. The progression of magnetic phase as a function of time in the oxidation cell for films in this study differed from those of previous attempts. These measurements were performed several months after the films were first prepared. Experience has shown the SrCoO$_x$ films are time sensitive, and their quality will degrade over time. The stability of the magnetic phases is discussed.
further in the next section. While the TC = 160 K phase seems to be most stable, it may be true that films exposed to atmosphere for an extended period are less likely to respond similarly to films oxidized directly after growth.

**Figure 3.9** XRD measurement of film peak at various stages of oxidation. The film peaks, where visible, are seen at right. The largest two peaks at left correspond to the Kα1 and Kα2 peaks for the (0 0 2) STO substrate. Magnetic transition temperatures are shown for steps where SQUID data were taken. Counts are normalized to the maximum value of the STO peak and scans are shifted for clarity.
Figure 3.10 Measurement of current as a SrCoO$_x$ film was oxidized in stages for up to 45 minutes. While cell fluctuations obfuscate any subtle features due to phase changes, three general plateaus are evident (the dashed line is a guide to the eye).
Figure 3.10 shows the current measurements taken during the oxidation steps which correspond to the XRD scans in Figure 3.9. Even after 45 minutes of oxidation, this film did not reach $x = 3.0$, as measured by $T_c$. At this point, the film was too far damaged to make further oxidation reasonable. The instability in the cell current measurements mean they cannot be used to identify when the sample shifts to the next phase or to identify the amount of oxygen induced into the sample. However, comparison of Figure 3.10 with the change in lattice constant calculated from the film peak positions shows a possible correspondence between the current flow at each step and size of the unit cell. This relationship should be explored further as the electrochemical cell is improved.

![Graph showing lattice constant vs time](image)

**Figure 3.11** Out-of-plane Lattice constant vs time for film samples.

Each point is calculated based on the film peak position in the XRD scans. A higher value seems to correspond to a larger current during the oxidation stages.
3.6 Magnetization

Measuring the oxygen content of oxide films is difficult, especially because the substrate used is most often also an oxide. Methods to detect the oxygen content of the film, such as thermo-gravimetric analyses, would be difficult to separate from the much larger contribution of the substrate. In our work, the Curie temperature of the magnetic transition ($T_C$) from paramagnetism to ferromagnetism is used to characterize our samples. By comparing the $T_C$ observed to those reported in the literature, we can estimate the oxygen content of the sample. In the case of films, where the current measurements of the previous section suggest the oxygen level is changing continuously, it may be more precise to report that the sample behaves magnetically in a similar manner as bulk samples of the noted oxygen level.

In order to identify $T_C$, a clear transition must be evident in the associated magnetization versus temperature data obtained through SQUID magnetometry. With bulk samples, transitions are relatively sharp and can be easily noted (See Ref [41]). Film samples are often more varied, and depending on growth conditions may exhibit little or no response. Magnetization measurements can be used in this manner to select films of appropriate quality for additional research. It is therefore important to discuss what factors are considered in assessing the quality of samples.

This section addresses the selection process by outlining our evaluation of film quality through the interpretation of magnetization data. The data shown represents field-cooled magnetization versus temperature scans unless otherwise noted. Certain stable phases are seen after sample growth and electrochemical oxidation. The stability of those phases is
examined here. Finally, an analysis of magnetization as a function of applied field (H) is included.

Because of the small amount of material inherent to films, an applied field must be chosen which maximizes response while limiting the diamagnetism of the substrate. For most films, an applied field of $H = 300 \text{ Oe}$ was used. A much larger signal is seen for bulk samples. Care must be taken to avoid responses much higher than 1 emu in order to limit inaccuracies in the SQUID measurements. For bulk samples, an applied field of $H = 50 \text{ Oe}$ was typical.

3.6.1 Film Quality

The magnetic response of the films could be used to characterize samples and determine their quality for the purposes of this investigation. Film samples chosen for additional study were those which, after the anneal process, showed a clear transition near 160 K. Two examples are shown in Figure 3.12 for a film of (1 0 0) and (1 1 1) orientation. These samples transition from relatively high magnetizations below $T_C$ to near-zero values at higher temperatures. The transition temperature $T_C$ is defined as the point of intersection between linear extrapolations of the sloped region and the near-zero plateau at high temperatures. In films defined as high quality, the transition temperatures are easily identifiable.

Figure 3.13 shows an example of three films of insufficient quality. In approximately two thirds of cases, films grown through the PLD process do not show clear transitions. This result is likely due to insufficient absorption of oxygen during the anneal process. Figure 3.14 supports this conclusion. Here, an as-grown film of low quality is oxygenated
Figure 3.12 Magnetization data showing ideal as-grown transitions for films of each orientation. (1 0 0) is shown on left, (1 1 1) on right. Both display $T_c = 160$ K.
Figure 3.13 Magnetization vs temperature for three films of low sample quality. No clear transition is seen at any temperature.

Figure 3.14 Magnetization vs temperature for a film of low sample quality before and after oxidation for five minutes. Before oxidation, no clear transition is seen. Afterwards, an obvious transition is seen near $T_C = 225 \, \text{K}$. This suggests oxygen absorption is a central issue during film growth.
for 5 min. This results in a clear transition at the next phase, near $T_c = 225$ K. For similar films, the structure and properties are particularly dependent on oxygen pressure,\textsuperscript{56} and Le Toquin \textit{et al.} have stressed the necessity of quenching in stabilizing SrCoO$_{2.5}$.\textsuperscript{20}

Considering the in chamber anneal and quenching processes required for epitaxial alignment, it is likely that oxygen content is a determining factor in the quality of our film samples.

To increase the chance of producing proper samples of appropriate quality, samples were often grown in batches of two to four films. Even within a batch, some variability is seen among samples. Figure 3.15 demonstrates the differences in the character of the transition for three as-grown films. The inconsistencies underscore the critical nature of oxygen absorption during the growth and anneal stages.

\textbf{Figure 3.15} Three films grown at the same time show differences in magnetization data. Though a transition is seen in each case near $T_c = 155$ K, the magnitude of the response and sharpness of the transition differ.
3.6.2 Stability of Phases

The oxidation of film samples has highlighted particularly stable phases which match those reported for bulk samples at transition temperatures of $T_C = 160, 220$ and $280$ K.\textsuperscript{41} Though the transitions occur at slightly different temperatures, it is clear the system tends to stabilize at certain phases. Figure 3.16 shows magnetization data taken for a batch of three (1 0 0) films oxidized for various amounts of time. To better illustrate the difference in transition temperatures, the data in this figure are normalized for each sample.

![Normalized magnetization data](image.png)

**Figure 3.16** Films A, B, and C of a (1 0 0) film batch. Each film was oxidized for a different amount of time, from 10 min to one hour. Transitions are notable near $T_C = 170$ K, 255 K, and 275 K. The inconsistencies in transition temperature when compared to oxidation time indicated phase stability is an issue.
One initial source of confusion was the lack of correspondence between transition temperatures and times of exposure in the oxidation cell. In most trials, three transitions were apparent; an as-grown transition near 160 K, an intermediate transition above 220 K, and a fully oxidized transition near 280 K. However, the time of oxidation necessary to produce each phase seemed inconsistent. The issue was resolved by considering the time between oxidation runs and magnetization measurements. Unlike in bulk samples, higher concentrations of oxygen are not stable in films over a period of days. A delay between oxidation and magnetic measurements allowed the films to deoxidize to the environment, confusing coordination of sample oxygen content with time in the oxidation cell.

Figure 3.17 tracks the same (1 1 1) film as it is oxidized in stages. Times shown in minutes represent cumulative exposure to the oxidation cell. In parenthesis, the delay in days between oxidation and magnetic response measurement are noted. At first, no clear pattern between oxidation time and transition temperature was evident. Further investigation showed that films oxidized above $x = 2.75$ were not stable for more than 24 hours. As oxygen is released back to the environment, the transition temperature moves to lower $T_c$. Furthermore, the surface of the films degrade each oxidation cycle. It is therefore important that transition temperatures be measured as quickly as possible after oxidation. In doing so, transition temperatures are observed to increase with longer oxidation time, indicating a greater oxygen content for the films.

Figure 3.18 shows the magnetic transition temperatures for a (1 0 0) film where care has been taken to make such measurements directly after oxidation. Here, an initial $T_c = 170$ K is increased to 230 K after five minutes of oxidation. An additional five minutes of oxidation shifts the transition temperature to $T_c = 282$ K. Finally, after seven days of
Figure 3.17 Magnetization data for a single (1 1 1) film, oxidized in stages. Transitions are seen close to $T_C = 155$ K, 210 K, and 235 K. Times represent cumulative exposure to the cell, with days between oxidation and measurement in parenthesis. The transition at $T_C = 235$ K underscores the instability of fully oxidized SrCoO$_3$.

Figure 3.18 Magnetization data for a (1 0 0) film taken directly after oxidation. Times represent cumulative exposure to the cell. Distinct transition are seen at $T_C = 170$ K, 230 K, and 282 K, representing stable phases which match those reported in bulks. After one week, the system settles at the intermediate temperature transition.
exposure to atmosphere, the transition temperature is measured again, displaying a $T_c$ near 220 K.

Two key results are evident. First, the high temperature ferromagnetic transition, associated with fully oxidized SrCoO$_3$, is unstable over a period of a few days. Our experiments have shown the fully oxidized phase decays to the more stable intermediate phase in approximately three days. Secondly, the intermediate phase near $T_c = 220$ K is stable for a comparatively longer period, and may represent a relatively stable phase for films of this thickness. Note also that at no point in this cycle are two simultaneous phases seen, in sharp contrast to the behavior of bulk samples. In (1 1 1) films of 300 nm thickness, however, two phases are observed. This discovery has significant implications on the size of the magnetic regions central to phase separation, and is discussed more fully in Chapter 4.

Additional oxidation work was performed on new bulk samples provided by Dr. Bogdan Dobrowski at Northern Illinois University. As in previous cases, these samples began with a transition at $T_c = 220$ K, indicating an oxygen content of $x = 2.88$. Figure 3.19 demonstrates the change in magnetic behavior as oxygen is added. The time required to fully oxidize bulk material depends on the size of the sample, in this case 143 mg and 238 mg. At that size, a noticeable fraction of the sample transitions near $T_c = 280$ K after about six hours of oxidation, with full oxidation requiring upward of 30 hours. In some cases, a high temperature transition for bulk samples is seen at $T_c = 300$ K, as in the second panel of Figure 3.19. Figure 3.20 tracks the change in transition temperature of this sample and a similar bulk example. Over the course of several days, the samples stabilize at a transition at $T_c = 280$ K.
Some variation has been reported in the ordering temperature of fully oxidized SrCoO$_3$. High pressure synthesis of bulk SrCoO$_x$ with $2.6 \leq x \leq 3.3$ reports $T_C = 258$ K for the fully oxygenated composition. A recent study involving high pressure synthesis of a single crystal of SrCoO$_3$ yielded $T_C = 305$ K, while a single-crystalline SrCoO$_3$ thin film prepared using liquid oxidants showed $T_C = 300$ K. In some of our $(1 0 0)$ film cases, a small amount of ferromagnetic behavior extends above room temperature for the fully oxidized phase. These variations may indicate the presence of a higher $T_C$ phase above 300 K, or it may be that some time is required to homogenize the distribution of oxygen. It may also be the case that, once lattice sites are full, oxygen atoms begin to occupy interstitial sites, bringing the oxygen content above $x = 3.0$. The slight

**Figure 3.19** Magnetization data of bulk samples, oxidized in stages. Fully oxidized SrCoO$_3$ could be obtained after approximately 30 hours, depending on sample size. The bulks shown here are 238 mg (left) and 143 mg (right). A transition at $T_C = 300$ K, seen at right, it sometimes evident in bulk samples.
Variations in ordering temperatures between the films of different orientation and with the bulk samples can be ascribed to minor differences in detailed film morphology.

### 3.6.3 Saturation Magnetization

The maximum magnetic response of the sample can be used to calculate the contribution per cobalt site. If the response per site can be assumed to be the same as that observed for bulk samples, the saturation magnetization can be used to estimate the magnetically active part of the film. Figure 3.21 shows the magnetic behavior as a function of applied field at 10 K and 310K for a (1 0 0) film immediately after oxidation for 20 minutes. In this sample, the magnetic transition occurs at $T_C = 280$ K, corresponding to an oxygen concentration of $x = 3.0$. The hysteresis loops are characterized by a ferromagnetic contribution from the SrCoO$_3$ film along with the diamagnetic contribution of the STO substrate. The data approach linear behavior with negative slope as the applied magnetic field is increased, reflecting the diamagnetic response of the substrate. The film samples

Figure 3.20 In some bulk samples, a higher temperature transition at $T_C = 300$ K is seen after oxidation. The system equilibrates over several days to a transition at $T_C = 280$ K.
are oriented in the SQUID with the surface parallel to the direction of the applied field, minimizing demagnetization effects.

Extrapolation from the linear regions back to the vertical axis (H = 0) yield values for the film saturation magnetic moment, while the slopes give the substrate diamagnetic susceptibility. From the slopes, an average value of $\chi = -1.3 \times 10^{-7}$ emu/g is obtained, consistent with measurements for a blank STO substrate. Accounting for the substrate, an average value of $2.0 \times 10^{-3}$ emu is measured for the saturation magnetic moment due to the film. Using the measured value of $a = 3.83$ Å, the film density was estimated to be $\rho = 5.7$ g/cm$^3$. Assuming that the saturation magnetization of the film is the same as that for bulk

![Figure 3.21](image)

**Figure 3.21** Magnetic response as a function of applied field for a 200 nm thick film of (1 0 0) orientation. Data are taken below and above $T_C = 280$ K at 10 K (squares) and 310 K (circles). Saturation magnetization are measured by extrapolation of the linear region to $H = 0$. Some FM response persists above $T_C$. 
SrCoO$_3$ ($\sigma = 63.5$ emu/g or $2.2 \mu_B$/Co),$^{17}$ film thicknesses of 200 nm and 300 nm ($\pm$ 20 nm) are estimated for the films described in this study. These estimates are consistent with spot checks via scanning tunneling electron microscopy of film profiles, described in section 3.7. Moreover, while the spot checks can be taken as an indication of film thickness, they measure only a particular point and cannot account for variability over the surface of the film. This magnetic technique, however, averages over the magnetically active region. The relatively large deposition thickness of greater than 200 nm and concurrence with the bulk lattice constant suggest strain is not significant in these films.

The appearance of a $1.2 \times 10^{-4}$ emu saturation moment in the hysteresis loop at $T = 310$ K only occurred for the SrCoO$_3$ film which was fully oxidized. As-quenched films of those with shorter oxidation times, and therefore lower values of $\chi$ and $T_C$, did not show the same remnant moment above 300 K. This behavior cannot be attributed to the substrate and may be an indication in film samples of an unstable phase at higher $T_C$.

### 3.7 Surface and Thickness Characterization

The surface features and thickness of select films were examined using scanning electron microscopy available through the Institute of Material Science. We found these films to be insulating. This poses a problem for the purpose of electron microscopy, as the electron beam charges the sample and eventually causes blurring of the image produced.

Figure 3.22 shows a (001) oriented film at 10,000 magnification. Surface features are blurred slightly due to charging, particularly evident in the central region where several measurements were performed. Noticeable features include spherical surface deposits and a cracked and fissured background. These features were typical of all films studied. On the
order of 0.25 μm, the spherical features are too small to be identified by EDXS analysis. The ability of oxygen to move into the films may be improved by the presence of surface fractures. These serve as additional pathways to oxygen absorption and effectively increase the surface area of the films.

SEM analysis was also used to spot check the thickness of films. To improve image quality, a thin (~10nm) Pt coating was applied to the surface of the film. A focused ion beam was then used to mill a 4 μm deep trench, which allowed the profile of the film to be imaged. In order to produce a clean edge, a 2 μm thick Pt strip was applied before milling took place. Differences in contrast were measured to give an average value for film thickness. Examples of the milling process and film profile image are shown in Figure 3.23. Comparing these measurements to growth times, we estimate films grown for 30 minutes to be 200 nm thick, while films grown for 45 minutes are likely 300 nm thick.
**Figure 3.22** SrCoO$_{2.75}$ (0 0 1) as-grown film at x10,000 magnification. The surface displays fissures and spherical deposits. The central region shows the effects of charging on the image quality.
Figure 3.23 SEM images of selected films. (top) A Pt strip was used to protect the edge of a focused ion beam milled trench. (bottom) The trench allowed an image of the film profile to be taken, where differences in contrast can be measured to find an average film thickness.
4. Suppression of Magnetic Phase Separation

We have examined the effect of film thickness on the establishment of phase separation in SrCoO$_x$. Epitaxial films of 200 nm and 300 nm thickness were prepared on SrTiO$_3$ substrates. As electrochemical oxidation increases the oxygen content from $x = 2.75$ to 3.0, the films tend to favor the discrete magnetic phases seen in bulk samples for the homologous series SrCoO$_{(3-n/8)}$ ($n = 0, 1, 2$). Unlike bulk samples, 200 nm thick films remain single phase throughout the oxidation cycle. 300 nm films remain single phase during oxidation, but can show two simultaneous phases during deoxidation. These results are attributed to finite thickness effects and imply the formation of ordered regions larger than approximately 300 nm.

4.1 Background

Previously, our group reported on magnetic phase separation in bulk samples of SrCoO$_x$ for oxygen content $2.88 \leq x \leq 3.0$. Beginning with $x = 2.88$, samples were electrochemically oxidized to $x = 3.0$, while magnetic measurements were made at stages along the process. At the endpoints, the $x = 2.88$ and $x = 3.0$ compounds show single ferromagnetic (FM) transitions at $T_C = 220$ K and 280 K, respectively. At intermediate concentrations, both magnetic transitions are seen, while high resolution x-ray diffraction shows only a single crystallographic phase. This implies an electronic mechanism of separation, where the stable phases may be related to an ordering of either oxygen vacancies or Co ion valence. In this chapter, we describe the suppression of phase separation in films below a critical thickness of 200 nm. The films tend to stabilize with ferromagnetic transitions at similar temperatures as in the bulk, indicating that the same
phases are most stable. In 300 nm thick films, phase separation reemerges and two phases are seen simultaneously. Taken together, this implies phase separation is related to the formation of distinct magnetic regions stabilized at dimensions larger than 300 nm.

The evolution of the SrCoO$_x$ crystal structure with oxygenation for bulk materials is detailed in Chapter 3. Above $x = 2.75$, the material remains cubic and the lattice constant evolves smoothly, with the exception of a slight tetragonal distortion near $x = 2.88$. At $x = 3.0$, SrCoO$_x$ is a ferromagnet with $T_C = 280$ K.

Single crystalline samples can provide more detailed information concerning crystalline orientation and mitigate the effects of grain boundaries. While such crystals have been prepared, the growth process makes analysis with oxygen evolution difficult. Epitaxial films offer a practical alternative. One report describes the growth of SrCoO$_{2.5}$ films which can be fully oxidized through a wet chemical process.

We have used a post growth anneal and quenching technique to produce metastable films of SrCoO$_{2.75}$. Electrochemical oxidation is used to increase oxygen content up to $x = 3.0$. In an effort to identify the effects of sample ordering and dimensionality in this system, we performed magnetic measurements on epitaxial films of SrCoO$_x$ grown on SrTiO$_3$ (0 0 1) and (1 1 1) substrates. The results of this study were submitted for publication in Applied Physics Letters, and published in volume 102, page 152402 (2013).

### 4.2 Sample Preparation

Films were grown using pulsed laser deposition from a SrCoO$_{2.5}$ target, detailed in section 3.4. After the in-chamber quenching process, films of (1 0 0) and (1 1 1) orientation were prepared of both 200 nm and 300 nm thickness. Structural characterization was
carried out by conventional Cu Kα XRD using a Siemens D8 θ-2θ powder diffractometer. XRD analysis showed the films were well-ordered with the substrate, shown for the samples of this study in Figure 4.1. Electrochemical oxidation was performed using the home built potentiostat and three-wire electrochemical cell detailed in section 2.4. We produced a number of film samples with oxygen $2.75 \leq x \leq 3.0$. Magnetic ordering temperatures were measured at various oxidation intervals using the Quantum Design MPMS SQUID magnetometer.
Figure 4.1 X-ray diffraction pattern of (a) a 200 nm thick, (0 0 1) oriented film and (b) a 300 nm thick, (1 1 1) oriented film. (*) Represents Cu K$_{\beta}$ radiation. Film peaks correspond to a pseudo-cubic lattice constant of $a = 3.83$ Å. No other phases are observed.
4.3 Sample Characterization

Figure 4.1 shows typical XRD patterns for films used in our oxidation studies. The films are oriented in the (0 0 1) (panel a) and (1 1 1) direction (panel b), with no other orientations evident. Though partially obscured by the much stronger substrate peaks, the observed film peaks are indexed as a perovskite pseudo-cubic lattice. Using the known SrTiO$_3$ substrate as a reference (a = 3.905 Å), the film peaks for both films are fit to an out-of-plane lattice constant of a = 3.83 Å. This agrees closely with the bulk and previous reports.$^{12,19,20,45,57}$

Film thickness is estimated through an analysis of magnetic behavior as a function of applied field. The data approach linear behavior with negative slope as the applied field is increased. The details of this calculation are given in section 3.6.3. Assuming that the saturation magnetization of the film is the same as that for bulk SrCoO$_3$ ($\sigma = 63.5$ emu/g or 2.2 $\mu_B$/Co)$^{17}$, an estimated film density of $\rho = 5.7$ g/cm$^3$, and using the measured lattice constant of a = 3.83 Å, film thicknesses of 200 nm and 300 nm ($\pm$ 20 nm) are estimated for the samples described in this study. These estimates are consistent with spot checks via scanning electron microscopy of film profiles shown in section 3.7. The relatively large deposition thickness of greater than 200 nm and concurrence with the bulk lattice constant suggest substrate induced strain is not significant in these samples.

Samples were electrochemically oxidized in stages to reach SrCoO$_3$. We could achieve full oxidation ($x = 3.0$) after approximately 20 minutes at 0.8 V, in contrast to the 24 hours or longer required for bulk samples. Oxygen content is estimated by comparing the sample ordering temperature to the observed $T_C$ of the bulk,$^{41}$ correlated with the electrochemical literature$^{20,45}$ by XRD measurements of lattice constant. Magnetization data shows
ordering temperatures for the as grown samples are \( T_c = 160 \text{ K (0 0 1)} \) and 180 K (1 1 1), indicating an oxygen content of approximately \( x = 2.75 \) when compared to the bulk materials.\(^{41}\)

**4.4 Phase Progression with Oxygen**

To track possible changes in magnetic phase as the electrochemical process progressed, magnetization versus temperature data were taken at stages up to full oxidation. Figure 4.2 a shows field cooled data for a 200 nm thick (0 0 1) film as-grown and after 3, 10, 15, and 20 minutes of cumulative exposure to the oxidation cell. Stable magnetic phases are notable at \( T_c = 160 \text{ K}, 230 \text{ K}, \) and 270 K, roughly matching the phases described by Xie et al.\(^{41}\) However, unlike in the bulk, no two-phase behavior is seen during oxidation. Figure 4.2 b shows comparable phases for a set of (1 1 1) ordered films. Transition temperatures of \( T_c = 180 \text{ K}, 210 \text{ K}, \) and 270 K are measured for as grown, intermediate, and fully oxidized samples, respectively, also in close agreement with the noted bulk phases. The variation in transition temperatures indicates a small range over which each phase is stable.

Beginning with the as-grown films, oxidation raises the moment, with a significant increase in magnitude at full oxidation. Though the transition temperature also increases, the coexistence of two magnetic phases was not observed for films of any orientation or thickness during oxidation. Rather than the growth of one phase at the expense of the
Figure 4.2 (a) Field-cooled magnetization vs. temperature for a 200 nm thick (0 0 1) film. Three transitions are evident at $T_C = 160$ K, 230 K, and 270 K. Times describe the cumulative minutes of oxidation. (b) Field-cooled magnetization for a series of (1 1 1) oriented films at different stages of oxidation. Similar phases are noted at $T_C = 180$ K, 210 K, and 270 K. No two-phase behavior is seen for either orientation. Curves are scaled as indicated for clarity.
previous, as reported for the bulk, the film samples tend to remain at particular stable phases until, with the addition of enough oxygen, the sample transitions to the next $T_C$ phase. As seen in Figure 4.2 a, although the data for oxidation of 10, 15, and 20 min were taken at equal increments, a transition to a higher ordering temperature only occurred after the final stage. While the oxygen absorbed between 10 and 15 minutes was insufficient to effect a change in $T_C$, an equal increment of further exposure results in the shift noted at 20 minutes. Thus oxygen absorption occurs throughout the process, but the transition to the next phase is dependent on the necessary electronic balance.

SrCoO$_3$ is oxidized well past equilibrium and not stable in ambient conditions. Thus we can also follow the magnetic phase behavior during natural deoxidation. This process is dependent on the thickness of the film. The stability of the fully oxidized phase for (0 0 1) and (1 1 1) films of 200 nm thickness is shown in Figure 4.3. In contrast to the bulk, the $x = 3.0$ phase loses oxygen relatively quickly. For the (0 0 1) film (Figure 4.3 a), after two days the sample is no longer fully oxidized, and decays to the more stable $T_C = 220$ K ($x = 2.88$) phase. Similarly, the (1 1 1) film (Figure 4.3 b) transitions to $T_C = 210$ K over the same time frame. For both orientations, a two-phase state was not observed after deoxidation.

The magnetic response of a batch of (1 1 1) oriented films of 300 nm thickness is shown in Figure 4.4. Though there are slight differences between transition temperatures of each films, the normalized data demonstrates a trend in behavior which differs from the 200 nm films. Film A represents the as-grown film, with a single transition at $T_C = 180$ K. Film B was oxidized for 15 minutes and shows a transition at $T_C = 268$ K.
Figure 4.3 Field-cooled magnetization vs. temperature as oxygen leaves the films for (a) (0 0 1) and (b) (1 1 1) oriented films of 200 nm thickness. Times denote number of days since full oxidation. Throughout the process, all films of 200 nm thickness remain single phase.
**Figure 4.4** Magnetization vs temperature for three (111) films of 300 nm thickness. Data is normalized to the maximum moment per scan. The inset shows a detail of the high temperature regime. Transitions are noted near $T_C = 180$ K and 285 K. After three days of exposure to atmosphere, two phase behavior begins to reappear.
After three days of exposure to atmosphere, the film has mostly shifted back to a transition near $T_C = 180$ K. However, as seen in the inset, a second transition can be seen near $T_C = 285$ K. Film D was also fully oxidized for 15 min. The data shown here was taken 15 days after full oxidation. Here, two phases are more clearly seen.

Figure 4.5 compares the data for film D with the transitions noted in bulk materials. Unlike the 200 nm case, two coexisting phases are observed in this film, with $T_C = 175$ K and 285 K. The inset of Figure 4.5 reproduces the phase diagram from Ref. 41 for bulk samples. It appears that, for films of this thickness, the $x = 2.88$, $T_C = 220$ K phase is less likely to appear than those with higher or lower $T_C$. Nevertheless, only in 300 nm thick films does the two-phase magnetic behavior characteristic of the bulk begin to reappear.
**Figure 4.5** Field-cooled magnetization vs. temperature of 300 nm thick, (1 1 1) oriented film after 15 days of deoxidation in atmosphere. As in the bulk, two magnetic phases are evident with $T_C = 175$ K ($x = 2.75$) and $T_C = 285$ K ($x = 3.0$). The inset shows the phase diagram described for bulk samples, reproduced from Ref. 41.
4.5 Conclusions

Generally, there can be several differences between bulk samples and well-ordered epitaxial films. The most commonly discussed film-specific issues are finite size effects on magnetism or strain caused by lattice mismatch with the substrate. For similar La$_{0.5}$Sr$_{0.5}$CoO$_3$ films these effects are typically significant for films thinner than about 60 nm. A kind of phase separation has been reported in the near-interface region of some LSCO films, though the effect is only for regions on the order of 10 nm. Strain has been calculated to result in a metal to insulator transition for SrCoO$_3$, however the match in lattice constant between our samples and that reported for the bulk imply our films are fully relaxed. Thus, both the 200 and 300 nm films used in this study should be considered as bulk-like in most respects, but with a limited size in one dimension.

The symmetry of the cubic structure and lack of significant strain suggest the suppression of phase separation for 200 nm films is not due to classic film effects such as interactions at the interface or the compression of the lattice. The suppression is observed for films of both (0 0 1) and (1 1 1) alignment, making orientation an unlikely cause. Instead, we conclude the ground state energy of the magnetic phases is affected by thickness. At 200 nm, the films tend toward a metastable $T_C = 240$ K phase, whereas the 300 nm films stabilize at the $T_C = 175$ K and 285 K end points. In contrast to the single phase observed for 200 nm thick films, the two phases seen in the 300 nm thick film indicate a size dependent effect with a critical thickness of approximately 300 nm.

The coexistence of magnetically distinct phases within a single chemical composition has been described in the related material La$_{1-x}$Sr$_x$CoO$_3$. In that system, hole-rich FM clusters form within a hole-poor matrix, with correlation lengths on the order of 10 nm.
It may be that the cause of phase separation is similar but that the larger length scale noted in this work is a result of the type of dopant introduced, i.e., mobile oxygen ions rather than substitutional cations.\textsuperscript{63}

SrCoO\textsubscript{x} and La\textsubscript{1-\textit{x}}Sr\textsubscript{\textit{x}}CoO\textsubscript{3} form a system with similarities to the cuprate superconductors LaCuO\textsubscript{4+y} and La\textsubscript{2-\textit{x}}Sr\textsubscript{\textit{x}}CuO\textsubscript{4}. For the cuprates, there are many reports of nanoscale phase separation in the well-studied La\textsubscript{2-\textit{x}}Sr\textsubscript{\textit{x}}CuO\textsubscript{4} system,\textsuperscript{40,64} including magnetically glassy behavior for a wide doping region.\textsuperscript{65,66} However, doping with excess oxygen results in larger phase separated regions with characteristic lengths larger than 100 nm and clear two-phase behavior.\textsuperscript{39,67,68} The larger length scale of the phase separation is associated with the presence of mobile oxygen dopant atoms, which have been shown to take part in ordering transitions of La\textsubscript{2}CuO\textsubscript{4+\delta} down to 200 K.\textsuperscript{69} Thus we find that the nature of the dopant ion may play a major role in the varying types of phase separation reported in doped Mott insulator oxides. Another unusual aspect of this system is that we are reporting phase separation between two different FM phases, rather than completely different electronic states. Phase separation between two FM states, while unusual, has been reported for the cobaltite Pr\textsubscript{1-\textit{x}}Ca\textsubscript{\textit{x}}CoO\textsubscript{3}.\textsuperscript{70} In that study, two distinct FM regions form at different temperatures, distinguished by short and long range order. The dependence of magnetic ordering on the size of FM clusters underscores the possible role of finite dimension effects in this work.

In summary, we prepared and characterized epitaxial thin films of SrCoO\textsubscript{x} with 2.75 \( \leq x \leq 3.0 \), on (0 0 1) and (1 1 1) STO substrates. Electrochemical oxidation produced FM phases similar to those in the bulk, but two simultaneous phases were only observed after several days of deoxidation in atmosphere for thicker (1 1 1) films. The agreement
between the measured c lattice constant and that reported for the bulk implies the films are relaxed; meaning the lack of two-phase behavior is not a result of strain. In the bulk materials, the presence of two FM transition temperatures at intermediate oxidation levels implies simultaneous regions of different hole or charge concentrations. Furthermore, the observed phases in both systems correspond to the magnetic phases reported for oxygen contents of $x = (3 - n/8)$, with SrCoO$_{3.0}$ ($n = 0$), SrCoO$_{2.88}$ ($n = 1$), and SrCoO$_{2.75}$ ($n = 2$). This suggests the presence of a long-range ordering commensurate with the lattice. As the oxygen content in the films is altered, the finite dimensionality normal to the surface may inhibit the formation of an electronically distinct region smaller than 200 nm. In contrast, the thicker (1 1 1) films allow the establishment of large scale, separate regions which phase separate in a similar way as observed in the bulk. This further implies a connection between long range interactions and electronic phase separation in this system.
5. Commensurate and Incommensurate Ordering

SrCoOₙ has been shown to exhibit magnetic phase separation for 2.75 ≥ x ≥ 3.0, as described for bulk samples in Chapter 3 and for films in Chapter 4. The oxygen content for which stable ferromagnetic phases are documented in bulk samples can be described by 3.0 − n/8, for n = 0, 1, 2. This suggests a possible ordering of either oxygen vacancies or the holes they introduce with the underlying lattice. Simple valence counting would suggest a cobalt valence of Co³⁺ (3d⁶) in partially oxidized SrCoO₂.₅. The introduction of electron holes as oxygen ions fill vacant lattice sites should raise the valence to Co⁴⁺ (3d⁵). Therefore, an arrangement of the Co charge or the occupied orbitals may be expected on the order of every four or eight unit cells, depending on oxygen content. Fully oxidized SrCoO₃, following this argument, should not exhibit superlattice ordering, as all vacancies are filled and the sample is homogeneous.

With this motivation, we investigated the possibility of superlattice ordering through resonant x-ray diffraction performed at the Canadian Light Source. Tuning the incident energy to the cobalt L₂ and L₃ edges promotes a core electron to the d orbital, probing the valence shell of the material. The enhancement in scattering as this electron is reemitted allows the detection of charge or orbital ordering, and may also highlight oxygen vacancy ordering through the hybridization of oxygen p and cobalt d orbitals.

Our resonant x-ray diffraction study on epitaxial films observed strongly resonant peaks near the (¼ ¼ ¼) position at similar oxygen concentrations to those noted in the previous work on bulk materials. This represents the first report of superlattice ordering in this system, and may provide a motivation for the stability of key magnetic phases. The
intensity and position of the resonant peaks shifted with oxygen content. Two incommensurate peaks were evident at an oxygen concentration of $x = 2.75$. A single, strong commensurate peak was seen at $x = 2.88$. At full oxidation of $x = 3.0$, all peaks were suppressed. The sharp energy dependence of the peaks precludes an ordering due directly to an arrangement of oxygen vacancies. The implication is that each phase represents a particularly stable arrangement of valence shell electron occupancy. A match between electronic ordering and the underlying lattice periodicity may explain the tendency of this material to separate toward particularly stable phases.

This chapter discusses the results of our resonant soft x-ray scattering work, performed at the Canadian Light Source in collaboration with Dr. Feizhou He.

5.1 Sample Preparation

Both bulk and film samples were characterized at the 10ID-2 REIXS beamline using the RSXS endstation. The beam energy can range from 80 to 3000 eV, with full polarization control. Defined at 1000 eV, the beamline has an energy resolution of $\Delta E/E = 10^{-4}$ and a flux of $5 \times 10^{12}$ photons/s/0.1% bandwidth. The spot size is $\sim 250 \mu m$ by $\sim 150 \mu m$ at the sample position. For our diffraction measurements photon energy was tuned through the Co L absorption edges. Absorption profiles were also taken at oxygen K edge energies. Scans were taken at various temperatures between 20 K and 400 K.

As previously detailed, bulk samples were prepared at Northern Illinois University with an oxygen level of $x = 2.88$, and subsequently oxidized to higher levels at the University of Connecticut. Epitaxial films of SrCoO$_{2.75}$ were grown on SrTiO$_3$ (STO) substrates at (1 1 1) orientation using pulsed laser deposition (see section 3.3-3.5). A KrF
eximer laser deposited films of approximately 300 nm thickness on the substrates, following the anneal and quenching process described previously. Initial structural analysis was carried out using a conventional Cu Kα powder diffractometer. X-ray diffraction (XRD) analysis showed the resulting films were of single phase, with a pseudo-cubic lattice constant of 3.83 Å, indicating the films are fully relaxed. The magnetic ordering temperature was measured using a MPMS SQUID magnetometer (section 3.6). As grown, the films ordered ferromagnetically at $T_C = 160$ K, indicating a nominal oxygen concentration of $x = 2.75$. The three-wire electrochemical cell described in section 2.4 was used to further oxidize both types of samples.

5.2 Cobalt Absorption and Ordering

We began with an assessment of bulk samples. Although the intensity of potential peaks is reduced in a pressed powder as compared to an oriented crystal, the random orientation of grains allowed a survey of important q space positions without the difficulties of sample alignment. Figure 5.1 shows the absorption profile of SrCoO$_x$ measured as the incident energy is swept over the L$_3$ and L$_2$ energies. As expected, peak absorption occurs at those positions, 778.1 eV and 793.2 eV. The profile is reminiscent of the related material La$_{1-x}$Sr$_x$CoO$_{3-\delta}$, which has also been described as a mixed Co$^{3+}$/Co$^{4+}$ system. Orikasa et al. ascribe the shoulder on the low energy side of the L$_3$ peak as due to Co ions in the intermediate or high spin state.\textsuperscript{72}
Figure 5.2 shows the result of a wide angle diffraction scan at the L₃ energy. The sample is a pressed powder as-received from Dr. Dabrowski, with an oxygen content of x = 2.88. A peak is observed with low intensity compared to the background. Because the position of the peak is near the limit detectable at the REIXS line, artifacts due to internal chamber geometry are sometimes seen. As a check, the movement of the peak was monitored as the incident energy was changed. The angular positions of artificial effects due to beam line occlusions are constant as the energy is shifted. For the observed ordering in Figure 5.2, the peak is only present near the L₃ energy, and its position shifts when the energy is deviated slightly from L₃. These suggest the peak is the result of an ordering with the lattice. The position of this peak corresponds closely to (¼ ¼ ¼), indicating an ordering matching the lattice every four unit cells.

![Graph showing absorption of SrCoOₓ powder](image)

**Figure 5.1** Absorption of SrCoOₓ powder as measured through total fluorescence yield. Dotted lines represent the cobalt L₃ and L₂ binding energies.
To further explore this result, we required single crystal-like samples. With the PLD system, we could produce epitaxial films offering many of the benefits of single crystals. We can control sample orientation through choice of substrate direction and produce a relatively smooth surface. Well-ordered films could improve the intensity of the peaks by limiting the spread in q, though the lack of material and alignment issues could complicate their detection. While the sample amount is less than in bulk samples, it was felt that the limited penetration depth of soft x-rays lessens this issue for films of sufficient thickness. To properly orient our samples, we needed to align on a known Bragg peak detectable at the upper energy limit of the REIXS line (~3 kev). We found that the q space of interest

![Graph](image)

**Figure 5.2** Wide angle diffraction of a SrCoO$_{2.88}$ powder sample, taken off (773 eV) and near the L$_3$ energy (773.3 eV). An ordering peak is observed at approximately ($\frac{1}{4} \frac{1}{4} \frac{1}{4}$) on resonance.
could not be reached at the L-edge energies for films aligned in the (1 0 0) direction. This was the motivation in choosing STO substrates of (1 1 1) orientation for film growth.

The (1 1 1) Bragg peak of the substrate was used at 2780 ev for alignment before searching for ordering peaks at the L-edge energies. We expected relatively weak peaks due to the lack of material inherent to films and the nature of the ordering. We attempted to improve the intensity of the ordering peak by growing for a longer amount of time, resulting in films of 300 nm thickness.

As discussed in section 3.4, the PLD growth process resulted in films with a transition at $T_C = 160$ K, suggesting an oxygen content of $x = 2.75$. As our first detection of an ordering peak was in bulk samples of $x = 2.88$, we oxidized our film sample for 15 minutes in the laboratory at the University of Connecticut. While this amount of exposure to the oxidation cell likely resulted in a fully oxidized film, the delay due to travel to the light source and experimental set-up allowed to sample to release oxygen to the environment. Keeping in mind the discussion in 3.6.2, it is probable the film was at the intermediate oxygen concentration at the time of the resonant diffraction measurement.

Figure 5.3 shows the result of wide angle diffraction scans taken along the (1 1 1) direction of the described film. Scans were performed at six energies on and off the cobalt L$_3$ and L$_2$ positions. An intense resonant peak is observed at a position corresponding to $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$. The peak is surprisingly strong on resonance, is not present off resonance, and is not detected in standard diffraction at higher energy. This critical dependence on energy suggests the peak is not the result of oxygen vacancy ordering. The relatively large change in charge density due to the lack of an oxygen ion would likely be detectable at a synchrotron source, and the associated peak would persist off the L$_3$ or L$_2$ resonance.
energies. Thus, we surmise the ordering observed is electronic in nature, representing charge, orbital, or magnetic order.

It should be noted that, due to the instability of the film samples after oxidation, we cannot say with certainty what level of oxidation or which magnetic phase best described the films at the time the resonant diffraction took place. Moreover, the absorption of x-rays at this energy in the vacuum chamber of the REIXS line may also affect the state of the sample. For these reasons, it was preferable to oxidize the samples on site at the light source. This experiment was performed on a subsequent trip the Canadian Light Source, and is described in the next section.
Figure 5.3 Wide angle diffraction of a (1 1 1) oriented SrCoO$_x$ film, of 300 nm thickness. Incident energies are selected about cobalt L$_3$ and L$_2$ values. An ordering peak corresponding to (¼ ¼ ¼ ) is evident on resonance, but is not present off resonance.
5.3 Resonant X-Ray Diffraction and Oxidation

In order to investigate the changes in ordering as a function of oxygen content, electrochemical oxidation was performed on site at the beamline. The same three-wire cell was sent to the Canadian Light Source and a resonant diffraction scans similar to those in the previous section were taken. Since the $x = 2.75$ samples are stable over a number weeks, we could confidently assume the initial characterization of the as-grown samples represented that phase. The sample was then removed from the beamline, fully oxidized, and immediately returned to the RXSXS chamber. The results of these experiments more closely correlate the observed ordering features with the oxygen content of the sample.

RXSXS measurements were taken before and after oxidation, along the (1 1 1) direction. After the initial characterization, the film was oxidized for 20 minutes. Previous work had shown this to be a sufficient interval to achieve full oxidation in films of this thickness (300 nm). Diffraction peaks were evident at superlattice positions when the incident energy was tuned to the Co L$_3$ edge at 779 eV. Significant changes in intensity and position of the diffraction peaks were noted over time with exposure to the x-ray beam.

Panel (a) of Figure 5.4 shows wide angle XRD scans at 779 eV for the same sample at different stages of oxidation. Initially, the as-grown ($x = 2.75$) film showed two incommensurate peaks; a small peak near ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$) (low q) and a more intense peak at a slightly higher q position (high q). The sample was then placed in the electrochemical cell and fully oxidized to $x = 3.0$. Immediately afterward, the film was placed in the RXSXS chamber and quickly cooled to $T = 20$ K. The subsequent XRD scan showed both peaks
Figure 5.4 (a) Wide angle XRD scan showing position of ordering peaks for oxygen concentrations $x = 2.75, 2.88, \text{ and } 3.0$. (b) Oxygen K edge absorption profile for each scan.
Table 1 Position and peak width (full width at half maximum) of the ordering peaks in figure Figure 5.4 (a).

<table>
<thead>
<tr>
<th>Position in H</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 2.75 low q</td>
<td>0.243</td>
</tr>
<tr>
<td>x = 2.27 high q</td>
<td>0.268</td>
</tr>
<tr>
<td>x = 2.88 (¼ ¼ ¼)</td>
<td>0.248</td>
</tr>
</tbody>
</table>

were suppressed, with only a very low intensity evident at the high q position. This is likely a result of the filling of oxygen vacancies eliminating the contrast responsible for the ordering. Over the course of approximately three hours at 250 K, a surprisingly intense commensurate peak at (¼ ¼ ¼) was seen to develop. Table 1 lists the positions of the ordering peaks and their full width at half maximum (FWHM), found by performing a Gaussian fit on each peak. Of the three, the commensurate peak is sharpest, implying the associated arrangement of charge is better ordered. Figure 5.4 (b) shows the corresponding oxygen absorption over the k edge energies for the samples in panel (a). While not quantitative, this may be the best measure of the oxygen content of our sample. The change evident in prominent features is consistent with our interpretation that the oxygen content has evolved in the sample. For example, the sharp feature near 527 eV becomes more pronounced with increasing oxygen content, in agreement with the trend in the absorption spectra reported by Karvonen et. al. for x = 2.5 to 2.82. However, we cannot determine the oxygen content definitively by these means.

The progression of the commensurate peak with time at 250 K is shown in Figure 5.5. It is likely that exposure to the beam and the vacuum of the chamber induced oxygen to leave the sample during that time. Considering the next stable phase reported in our
work,\textsuperscript{17,60} we believe this phase corresponds to an oxygen content of $x = 2.88$. This conclusion is further supported by the match between the new peak’s position and that of the commensurate peak noted in section 5.2. Both film and bulk samples in that case were oxidized to $x = 2.88$ and showed resonant peaks near $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$.

As we have discussed, the stable magnetic phases correspond to key oxygen levels ($3.0 - n/8$ for $n = 0, 1, 2$). SrCoO$_x$ has been noted for especially high oxygen mobility and vacancies are known to order in the brownmillerite phase.\textsuperscript{20} Therefore, one possibility is that the ordering peaks we have seen are the result of an arrangement of the oxygen

![Figure 5.5](image)

**Figure 5.5** Progression over time of the commensurate peak intensity for the $x = 2.88$ phase. The position corresponds to $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$. The peak developed as the sample equilibrated at $T = 250$ K, likely corresponding to the removal of oxygen from the sample.
vacancies. The suppression of any peaks in the fully oxidized case would be expected as all available vacancies are filled. However, we do not believe vacancy ordering is responsible for these results. First, as mentioned in the preceding section, the loss of the charge density due to the missing oxygen atom, or the resulting shift in the lattice, should be seen in standard XRD. Even if the vacancy ordering were subtle enough to require RSXS, one would expect a larger shift in peak positions between various n than noted here.

Figure 5.6 (a) shows the Co L\textsubscript{3} and L\textsubscript{2} absorption profile taken at T = 250 K, after the development of the (¼ ¼ ¼) peak. For each of the energies noted by the dotted lines, a wide angle XRD scan was taken. These are shown in panel (b). The peak is only evident at the L\textsubscript{3} and L\textsubscript{2} edges. Again, that no peak is seen off resonance implies the ordering observed is due to an arrangement of valence charge rather than lattice vacancies.

The intensity of the (¼ ¼ ¼) peak persists over a wide temperature range. Maximum intensity is seen at T = 250 K, but once developed, the peak is clearly present down to T = 20 K. Figure 5.7 tracks the intensity of the commensurate peak as the temperature is raised from 20 K to 360 K. Even at 250 K, the commensurate peak develops slowly over time. At lower temperatures, this development progresses more gradually. As such, the intensities noted in Figure 5.7 likely do not represent the equilibrium values. Still, a clear ordering temperature is seen at T = 350 K. Above that temperature, the commensurate peak is suppressed. Note this temperature exceeds the ferromagnetic ordering temperature for x = 2.88 films at T\textsubscript{C} = 220 K and, as far as we know, this q vector is not associated with ferromagnetism. Taken together, this suggests the ordering seen is not magnetic in origin.
Figure 5.6 (a) Absorption profile of $x = 2.88$ film taken at $T = 250$ K. (b) Wide angle XRD measurement for each of the energies noted in panel (a). Peaks are evident only at the $L_3$ and $L_2$ edges.
Figure 5.7 Intensity of the commensurate peak for the 300 nm thick \( x = 2.88 \) film as a function of temperature. \( T = 350 \) K represents an ordering transition above which the peak is suppressed.
On cooling, the \((\frac{1}{4} \frac{1}{4} \frac{1}{4})\) peak reestablishes itself, meaning the transition at 350 K is the result of ordering rather than a loss of oxygen. \(T = 350\) K therefore represents a critical ordering temperature for this material. This ordering is distinct from the ferromagnetic order at lower temperature. The most plausible explanation is a charge ordering of \(\text{Co}^{3+}\) and \(\text{Co}^{4+}\) which persists to high temperature. This represents the first direct observation of such ordering in this system. As we will discuss below, this may also provide a plausible explanation for the stability of particular states discussed in Chapter 4. In the next sections, we will describe the energy dependence and polarization analysis of the ordering peaks which further support this conclusion.

5.4 Energy Dependence

The energy dependence of the ordering peaks was measured before and after oxidation. This was done by setting the detector to remain at fixed \(q\) while the incident energy is scanned through the cobalt \(L_1\) and \(L_2\) energies. Two scans are taken, one with the detector fixed on the peak and another at an off peak position to measure background absorption. The difference between the two gives the energy profile of the ordering peak.

The absorption profiles are shown in Figure 5.8. Panel a. was measured for the as-grown film, before oxidation \((x = 2.75)\). In that case, two incommensurate peaks are seen; a low \(q\) position near \((0.24 0.24 0.24)\) and at a high \(q\) position near \((0.27 0.27 0.27)\). After full oxidation, no peaks are evident, so there is no equivalent energy scan. Panel b. was measured for the peak which develops over time at \(T = 250\) K, identified as the \(x = 2.88\) phase. The background absorption is shown in each figure for comparison.
A notable difference occurs near 778 ev. For the $x = 2.75$ phase, the absorption maximum occurs at a prepeak feature for the low $q$ position, while the maximum for the high $q$ peak occurs at the $L_3$ edge. A similar phenomenon occurs at the $L_2$ edge. The absorption behaviors of the two peaks at this phase are the inverse of each other. At the $x = 2.88$ phase, no such feature exists in the absorption. The lack of correspondence between the absorption profiles for the near commensurate positions of each phase may indicate a fundamental difference between the types of ordering in each instance and implies different valence states are involved.

Features in the absorption spectrum have been related to the local symmetry of the Co ion and the Co spin state. For SrCoO$_3$, Potze et. al., compared experimental Co absorption spectra to theoretical multiplet calculations, taking into account crystal field energy, hybridization with oxygen $p$ orbitals, and three possible spin states. For the Co$^{4+}$ ion, these are high spin ($s = 5/2$), intermediate spin ($s = 3/2$), and low spin ($s = 1/2$). The authors concluded SrCoO$_3$ could best be described by the intermediate state, noting that the split between the main peak and a prepeak at the $L_3$ edge decreases as the spin is increased. In fact, for the low spin case, the position of the prepeak roughly matches the low energy feature of our incommensurate peaks near 778 eV. Thus one interpretation of our data is that the distinct features for each peak represent different ground state spin arrangements, with the incommensurate peaks more closely related to the low spin state. On the other hand, only a slight prepeak is observed in the background absorption off peak, shown as the dotted line in each panel of Figure 5.8.
Figure 5.8 Absorption profile of the ordering peaks, taken at $T = 250$ K. (a) Measurement of the incommensurate peaks for $x = 2.75$ at low and high $q$ positions. (b) Profile for the $x = 2.88$ phase at the commensurate peak. The dotted lines show the background absorption taken off the peak and scaled for comparison.
At the same time, we must note our ordering peaks are observed at oxygen concentrations below $x = 3.0$, implying a mixture of $\text{Co}^{4+}$ and $\text{Co}^{3+}$. X-ray absorption spectra were analyzed by Hu et al., in the related system $\text{Na}_x\text{CoO}_2$, which also exhibits a spin state degree of freedom between high, intermediate, and low spin, and has been described as a $\text{Co}^{3+}/\text{Co}^{4+}$ charge ordered system. The authors compare experimental polarization dependent absorption data for the $x = 0.5$ and $x = 0.75$ cases to simulated spectra and the individual $\text{Co}^{3+}$ and $\text{Co}^{4+}$ contributions.\(^{76}\)

In that work, the prepeak feature is associated with contributions from $\text{Co}^{4+}$ in each case. The general shape of our absorption profile for the high $q$, $x = 2.75$ peak most closely resembles the reported $\text{Co}^{4+}$ contribution. One could interpret this as an indication that the high $q$ peak is associated with an ordering pattern based on $\text{Co}^{4+}$ ions. However, there are some notable differences between that work and our results. First, the absorption peaks for $\text{Na}_x\text{CoO}_2$ occur at slightly higher energies than our work. Secondly, the $\text{Co}^{3+}$ contribution does not match the shape of our low $q$ data, and does not appear to be an inversion of the intensities at each peak feature.

No noticeable prepeak exists for the absorption profile of the commensurate peak. Panel b of Figure 5.8 shows this profile is most similar to the background absorption. The commensurate data can be described in one of two ways. Either this peak represents a third, distinctly different arrangement or ordering than the previous two incommensurate peaks, or alternatively, the two incommensurate peaks have merged to produce a single peak at a commensurate position in $q$. Figure 5.9 addresses this possibility by comparing the absorption profile of the commensurate peak to the sum of the incommensurate peak patterns. The commensurate peak does not appear to be a simple sum of the two. Instead,
the commensurate peak seems most similar in nature to the main peak of the high \( q \) case. This is surprising, considering the position of the commensurate peak in \( q \) is much closer to that of the low \( q \) peak. As such, the commensurate peak can also not be described as a simply a more intense or well-ordered version of the low \( q \) peak. Rather, the source of the ordering in the commensurate case is likely similar to that of the high \( q \) peak, but at a periodicity which more closely matches that of the lattice. To more specifically relate the absorption features we have observed to a particular ordering will require a theoretical model from which calculated spectra could be compared.
Figure 5.9 Absorption profiles for the commensurate peak ($x = 2.88$) and the sum of the two incommensurate peaks ($x = 2.75$). The profiles are normalized for comparison. The commensurate peak profile does not display a prepeak feature.
5.5 Polarization Effects

Another method to identify the nature of the ordering responsible for the diffraction peaks is the analysis of RSXS as a function of polarization. In section 2.6, we explained the dependence of scattering intensity on the form factor $f_n$. The form factor is composed of terms describing the charge and magnetic scattering, and is the dispersion correction $\Delta f$, which depends on the photon energy and polarization.\textsuperscript{44} With the proper experimental set-up, it may be possible to distinguish between charge, orbital, and magnetic orderings.

The incident and scattered wave vectors define a scattering plane. The incoming or outgoing beam polarization directions are defined as parallel ($\pi$) or perpendicular ($\sigma$) to this plane. Because of the polarization dependence of $\Delta f_n$, a shift in the polarization direction of the incoming and scattered beam contains information on the symmetry of the ordering.\textsuperscript{44} To study this effect, experimental control of the polarization for the incoming beam is required. At the Canadian Light Source, the beamline can be set to circular left and right, linear vertical, linear horizontal, and linear 45° polarizations.\textsuperscript{71} In addition, an analyzer is needed before the detector to determine the polarization of the scattered beam. Typically, the analyzers used are graded multilayers created to optimize reflectivity for the energy range of interest. Mounted at the Brewster angle, the analyzer suppresses polarizations in the analyzer scattering plane.\textsuperscript{77} At the time of our measurements, no analyzer was available for the Co L\textsubscript{3} and L\textsubscript{2} edges. For this reason, we did not focus our efforts on the collection of polarization data. However, we did observe a difference in intensity and features of an ordering peak as a function of incoming polarization.

The polarization dependence of the absorption profile for the low q peak at the $x = 2.75$ phase was taken at $T = 200$ K, and is shown in Figure 5.10. A difference is notable between
horizontal and vertical polarizations. Though additional data is needed, this suggests the possibility of an orbital ordering component to the observed periodicity. To further interpret this data, additional runs with a Co analyzer are necessary. As Staub et. al. describe, such data can be separated into cases where the polarization is unchanged after scattering, \( \pi-\pi' \) or \( \sigma-\sigma' \), or rotated, \( \pi-\sigma' \) or \( \sigma-\pi' \). For charge scattering, no rotation occurs and the \( \pi-\pi' \) and \( \sigma-\sigma' \) channels differ by a factor \( \cos(2\theta) \). For magnetic scattering, the \( \pi-\pi' \) channel is proportional to \( \sin(2\theta) \), the \( \sigma-\sigma' \) channel has zero intensity, and the rotated cases have opposite phase. All four polarization channels are allowed, but the \( \pi-\sigma' \) and \( \sigma-\pi' \) channels will generally not equal each other. With the proper analyzer, future work making use of this information could pinpoint the type of ordering we have observed.
5.6 Conclusions

We have discovered a previously unreported charge ordered state in SrCoO$_x$ thin films. The nature of this ordering is dependent on the oxygen content of the film. At $x = 2.75$, two incommensurate peaks are observed. At $x = 2.88$, a surprisingly intense commensurate peak develops at $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$ position. For fully oxidized $x = 3.0$, no ordering peaks are observed. The implication is that oxygen vacancies introduce holes which are particularly mobile in this system. The mobility of these holes supports longer range interactions than...
in similar systems, and allows the establishment of ordered Co\textsuperscript{3+} and Co\textsuperscript{4+} arrangements which match or come close to the periodicity of the crystal lattice.

As oxygen is incorporated into vacancy sites, the overlap between oxygen p and cobalt d orbitals is affected, as is the overall charge balance. Simple charge counting suggests a mix of Co\textsuperscript{3+} and Co\textsuperscript{4+} at oxygen concentrations less than x = 3.0. Our analysis suggests it is a regular arrangement of these species which is detectable on resonance. The observed polarization dependence indicates the ordering may also include an orbital ordering contribution.

The as-grown film, corresponding to a phase of x = 2.75, shows two ordering peaks. Though the less intense low q peak appears near to the (1/4 1/4 1/4) position, close comparison to the commensurate peak which develops at x = 2.88 indicates a conspicuous shift in position. Taking into consideration the difference in behavior of the absorption profiles, it is likely this peak represents a different ordering than that observed at x = 2.88. For the incommensurate peaks at x = 2.75, the low q and high q absorption profiles seem to be inversely related to each other. The low q peak has most of its intensity in the pre-edge feature, with a smaller intensity at the L\textsubscript{3} edge. Conversely, the high q peak is most intense on the L\textsubscript{3} edge with a less intense, but still significant, prepeak feature. It is likely that the two incommensurate peaks represent differing, but closely related, sources of order. For example, two distinct types of orbital ordering or two incommensurate arrangements of each valence type. As we have discussed, spin degrees of freedom may also play an important role. Another possibility is that the two peaks represent a single, more complicated ordering by a combination of these sources. The next step will be to develop
a theoretical model which can be used to predict absorption profiles and compare to our
data to those calculations.

Experimentally, a logical extension of this work is a more complete polarization
analysis. Already, we have seen that the intensity of the peaks depends on polarization,
which itself implies an orbital contribution to the ordering. Polarization analysis of the
scattered beam may settle this question. Future work should focus on creating or otherwise
obtaining a multilayer analyzer optimized for the Co L₃ and L₂ which is compatible with
the REIXS beamline.

Even with an analyzer in place, an important unknown factor in our RSXS work is the
exact oxygen content of our sample at the time that ordering is observed. Measuring the
oxygen content of film samples in any case is already notoriously difficult. The most
feasible option would be to continue characterizing oxygen content by noting the magnetic
transition temperature, as we have detailed in Chapter 3. To better detail our RSXS
samples, we would require a method of doing so in the REIXS chamber. One idea is to use
Magnetic Circular Dichroism. The sample could be mounted on a magnetic stage, and the
difference in the absorption of left and right hand circularly polarized light would be
proportional to the sample magnetization. Rather than measuring the magnitude of the
magnetization, one could increase the temperature until a clear transition is observed.
While the REIXS line is equipped for such an experiment, it has yet to be seen whether the
transition of our samples would be detectable.

As we have pointed out in preceding arguments, the sharp energy dependence of the
peaks is not consistent with oxygen vacancy ordering. On the other hand, the
commensurate peak at x = 2.88 develops somewhat slowly and arises at the relatively
elevated temperature of $T_c = 250$ K. Likewise, the ordering persists to high temperature ($T = 350$ K), and some time is required to reach equilibrium intensity, on the order of 3 hours. These qualities are more consistent with the mobility of oxygen ions than merely a rearrangement of charge. This is somewhat surprising, considering our conclusion that vacancy ordering is not responsible for the ordering. Therefore, although variations in charge need not match the position of vacant oxygen sites, an association between the two persists. The nature of that association remains an open question.

The ordering peak persists well above the highest magnetic ordering temperature for this system. While the ordering itself cannot be magnetic in origin, the arrangement may give rise to a particular magnetic ordering at lower temperature. Therefore, the orderings observed represent arrangements of charge distribution which support certain magnetic phases. This indicates a potential answer to a critical question which arises following the analysis presented in chapter 4; namely, why some phases appear to be particularly stable. We have shown that a charge ordering with a periodicity matching the lattice exists at $x = 2.88$. Even at lower oxygen concentration, an ordering exits, though it is not commensurate. We conclude that a charge ordering corresponding to the underlying crystal lattice exists in this material for certain oxygen levels, and that ordering supports the establishment and stability of the key magnetic phases.
6. Conclusion

This work represents a detailed study of the magnetic and electronic characteristics of SrCoO$_x$. Through pulsed laser deposition and electrochemical oxidation, we have prepared samples of various oxygen concentration, film thickness, and magnetic order. Building upon previous work identifying magnetic phase separation in bulk materials, we were able to successfully prepare epitaxial films which also exhibit a separation of magnetic regions. Further, our analysis identified a size dependent effect, whereby phase separation was suppressed below a critical thickness of 200 nm. This novel result established the relatively large dimension of the phase regions as compared to similar materials such as La$_{1-x}$Sr$_x$CoO$_3$.

Our next investigation used resonant soft x-ray scattering to explore the possibility of commensurate ordering in this system. This search was motivated by the key oxygen concentrations at which stable magnetic phases form, $x = 3.0 - n \times \frac{1}{8}$ ($n = 0, 1, 2$). Both commensurate and incommensurate ordering peaks were found on and about the ($\frac{1}{4} \frac{1}{4} \frac{1}{4}$) position in q, revealing a previously unknown hidden ordering in this material. This implies an arrangement on the order of every four unit cells.

Our goal is to understand the nature of this ordering. Further analysis showed a dependence of peak intensity on incoming beam polarization. This suggests an orbital ordering component. The limitations of our experimental set-up prohibited analysis of the scattered beam, which could more readily identify the source of ordering. However, we could examine the energy dependence of the diffraction peak, and noted several interesting features.
The absorptions of the incommensurate peaks \((x = 2.75)\) appear to mirror each other. A prepeak feature before the \(L_3\) edge dominates the intensity of the low \(q\) peak. For the high \(q\) peak, while the prepeak is distinct, the main peak is more intense. Similar behavior is seen at the \(L_2\) edge. For the commensurate peak \((x = 2.88)\), no prepeak feature is observed. Comparing our results to similar reports in the literature, we can infer this dependence is a reflection of either a difference in the spin state (high, intermediate, or low) of the Co ions involved in the ordering, or is due to differing contributions of \(\text{Co}^{3+}\) and \(\text{Co}^{4+}\) in each arrangement.

The persistence of the ordering peak with temperature was also noted. The ordering can be melted above \(T = 350\, \text{K}\), but returns on cooling. The relatively long time needed to reach equilibrium suggests that this ordering is connected with the movement of oxygen in the sample. However, because of the sharp dependence on energy, we do not believe this ordering is due to an arrangement of oxygen vacancies. Rather, the electronic ordering we observe is itself dependent on the mobility of the oxygen ions.

This connection is related to the description of this material as a Mott insulator. Comparing our work to the literature on doped Mott materials, we conclude the mobility of the dopant ions plays a large role in the size of phase-separated regions. Highly mobile dopants seem to support regions of longer extent. It is also likely that the superlattice orderings reflect long-range interactions that are sensitive to the concentrations and placement of oxygen throughout the region.

While the magnetic phases and orderings observed are clearly related, the ordering persists above the Curie temperature. Different ordering of charges likely support different ferromagnetic states. In our film thickness study, we saw that films below 200 nm thickness
do not allow the establishment of two simultaneous phases. This is most likely a result of
the finite dimension of the film normal to the surface, which inhibits the required
arrangement to stabilize a particular phase. This relationship between ordering and the
magnetic phase may explain why the noted oxygen concentrations correspond to key
magnetic phases. An underlying ordering which to some degree matches that of the crystal
lattice is particularly stable, as are the corresponding magnetic phases.

There are several directions for future work that could further explore these issues.
The most pressing is to definitively associate an oxygen content with the orderings we
observe in RSXS. We suggest a method to do so using Magnetic Circular Dichroism. Next,
a direct measure of the type of ordering observed is needed. The production of an analyzer
multilayer tuned to the Co L$_3$ and L$_2$ edges is required to perform full polarization analysis
which could reveal the type of ordering in more detail. Methods to observe the size and
magnetic response of the individual magnetic phases are also of interest. Muon
spectroscopy may offer a means to do so, though their use is mostly limited to bulk samples.
Finally, an increased understanding of the ordering parameters may be gained through an
investigation of the effects of strain on this system. Our PLD station is well suited to
produce strained samples through thin film growth.

The phase diagram of this system as a function of dopant type and mobility can be
mapped through similar analysis of A$_2$Sr$_{1-y}$CoO$_x$. Substitution of Sr with Ba or La can
underscore which effects are related to mobility. Altering the oxygen content of these
cation doped samples would add another dimension to the phase space and clarify the
relationship of this material to the wider issue of doped Mott insulators.
REFERENCES


