2019

Depth dependent atomic valence determination in La_{0.7}Sr_{0.3}MnO₃ thin films using synchrotron techniques

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Depth dependent atomic valence determination in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films using synchrotron techniques

Robbyn Trappen

**Dissertation submitted
to the Eberly College of Arts and Sciences
at West Virginia University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in
Physics – Condensed Matter**

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2019**

**Keywords: Thin film deposition, strongly correlated materials, transition metal
oxides, magnetic dead layers, valence, magnetism, depth profiling, synchrotron
radiation, neutron scattering**

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Abstract

Depth dependent atomic valence determination in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films using synchrotron techniques

Robbyn Trappen

The valence of atoms often has a strong effect on the properties of materials, such as magnetism, conductivity, and superconductivity. The atomic valence is often perturbed at the surface and/or interface and this deviation may play a strong role in many physical phenomena such as interfacial coupling and dead layers, both magnetic and electric. In this dissertation, I present a *non-destructive* approach of combining two X-ray absorption detection modes, electron yield and fluorescence, with very different probing depths in conjunction with theory to map out the layer-by-layer valence of a thin film.

The weighted average Mn atomic valence as measured from the two modes are simultaneously fitted using a model for the layer-by-layer variation of valence based on theoretical model Hamiltonian calculations. Using this model, the Mn valence profile in thin film $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) is extracted and the valence within each layer is determined to within an uncertainty of a few percent. It was found that while the bulk averaged valence hovers around its expected value of 3.3, a significant deviation occurs within several unit cells of the surface and interface. The surface valence increases to up to $\text{Mn}^{3.7+}$, whereas the interface valence reduces down to $\text{Mn}^{2.5+}$. These results were supported by density functional theory calculations. The change in valence from the expected bulk value is consistent with charge redistribution due to the polar discontinuity at the film-substrate interface. The comparison with theory employed here illustrates how this layer-by-layer valence evolves with film thickness and allows for a deeper understanding of the microscopic mechanisms at play in this effect. These results offer insight on how the two-dimensional electron gas is created in thin film oxide alloys and how the magnetic ordering is reduced with dimensionality. Preliminary magnetic depth profiling measurements, discussed in the last section, show an enhancement and suppression of the material's net magnetization at the interface and surface, respectively. This correlation indicates that the observed change in valence may well play a role in the magnetic properties at the film boundaries.

Acknowledgements

The work presented in this thesis was a combined and truly Herculean effort from many scientists and students in groups across the world, who I wish to acknowledge the contributions from here.

In addition to the samples I grew, many samples were provided by Vu Thanh Tra and Ying-Hao Chu from National Chiao Tung University, Taiwan.

Theoretical support came from Shuai Dong (who did the tight binding calculations on which the experimental valence model is based) and Aldo Romero and his students Wilfredo Ibarra Hernandez, Sobhit Singh, and Camillo Garcia Castro who performed the DFT calculations which flushed out much of the underlying physics in our system.

Transmission electron microscopy characterization was done by Prof. James LeBeau at NCSU and his students James Fitch and Aubrey Penn as part of a larger collaboration for a grant.

Polarized neutron reflectivity measurements were carried out at NIST Center for Neutron Research and I wish to thank Brian Kirby and Alexander Grutter for not only helping with the data acquisition and analysis but for being great mentors as well, since I knew little about the subject at our first beamtime.

Synchrotron measurements were taken at Advanced Light Source (ALS) Beamlines 10.3.2 and 6.3.1 as well as Advanced Photon Source (APS) Beamline 4-ID-C. I wish to thank Matthew A. Marcus and Alpha T. N'Diaye of ALS and John W. Freeland of APS for their help in those experiments and beneficial discussions on developing our model, as well as Jinling Zhou for valuable input on the fitting and modeling of our spectra.

I wish to thank the many hands in the Holcomb group who have assisted in growth and characterization as well as helping troubleshoot the problems in our substrate preparation process in earlier years: thanks to Navid Mottaghi, Guerau Cabrera, Chih-Yeh Huang, Ghadendra Bhandari, our post-doc Shalini Kumari, and finally our summer Research Experience for Undergrads (REU) students Allison Haerter, Austin Jantzi, Rainor Connor, and Sebastian Hodge. There is a lot of work that goes into preparing and characterizing a sample, from simply preparing the substrates, the many quality checks via microscopy to verify that the substrate is ok to grow on, X-ray diffraction and reflectivity for thickness characterization, and many other measurements. Your hard work was important for the research to progress at a swift pace.

Thanks to Weiqang Ding, Qiang Wang, and Harley Hart of WVU Shared Research Facilities who conducted trainings, maintained the instruments I used, and provided useful discussions on troubleshooting issues as I conducted the research.

Finally, I want to thank the many professors and post-docs who are and have been at WVU who guided me along the way, answered questions and gave feedback, and gave me a push when I needed one, including Pavel Borisov, Yuri Glinka, David Lederman and his students, Ned Flagg and his students, and Alan Bristow and his students. All of your contributions were invaluable in getting me to the point that I am at now.

Synchrotron and electron microscopy measurements were supported by NSF (DMR-1608656). The layer-by-layer fit to experimental data and DFT calculations were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0016176. The double exchange model simulation by Shuai Dong was supported by the NSFC (Nos. 11274060 and 51322206). Synchrotron and electron microscopy measurements were supported by NSF (DMR-1608656). The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under Contract No. DE-AC02-05CH11231. Partial funding support for students was provided by the WV Higher Education Policy Commission

(grant HEPC.dsr.12.29). We acknowledge the use of the WVU Shared Research Facilities. We acknowledge the computational support from XSEDE which is supported by National Science Foundation under grant number ACI-1053575 with the Bridges and Stampede supercomputers. The authors also acknowledge the support from the Texas Advances Computer Center and the DMREF-NSF 1434897. Thanks to all of the funding agencies that supported this work.

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Abbreviations and nomenclature

AFD: Antiferrodistortive rotations

AFM: Atomic force microscopy

ALS: Advanced Light Source

APS: Advanced Photon Source

DFT: Density functional theory

EDS: Energy dispersive spectroscopy

EELS: Electron energy loss spectroscopy

EXAFS: Extended X-ray absorption fine structure

FY: Fluorescence yield

LAO: LaAlO_3

LMO: LaMnO_3

LSMO: $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

NCNR: NIST Center for Neutron Research

NCSU: North Carolina State University

OV: Oxygen vacancies

PLD: Pulsed laser deposition

PNR: Polarized neutron reflectivity

RHEED: Reflection high energy electron diffraction

SLD: Scattering length density

SMO: SrMnO_3

STO: SrTiO_3

TB: Tight-binding model

TEM: Transmission electron microscopy

TEY: Total electron yield

u.c.: Unit cell

$V(z)$: Modeled Mn valence as a function of depth in the film

$V_{\text{exp}}(N)$: Experimentally obtained valence as a weighted sum of N layers

WVU: West Virginia University

XAS: X-ray absorption spectroscopy

XMCD: X-ray magnetic circular dichroism

XRD: X-ray diffraction

XRMS: X-ray resonant magnetic scattering

XRR: X-ray reflectivity

1. Introduction

With semiconductor technology reaching its physical size limits, alternatives to conventional electronics have been explored. One proposed alternative lies in non-volatile magnetic memory. In this scheme, rather than using the presence or absence of current in a semiconducting transistor as either the “0” or the “1,” the spin of the electron in magnetic materials (or similarly, the magnetic direction of a magnetic domain) could be used. The advantage is that because the magnetic field of the electron is always on (as opposed to a constant flow of current being necessary in semiconductor electronics), power would only need to be consumed to read something in memory rather than maintaining it.

The family of materials known as manganites has received considerable attention for magnetic device applications such as magnetic tunnel junctions and magnetic sensors¹. Manganite materials are part of the so-called strongly correlated materials, meaning strong electron-electron interactions. As a result, they exhibit a rich spectrum of physics such as ferromagnetism², metal-to-insulator transitions³, spin glasses⁴, and ferroelectricity⁵ that makes them desirable for a wide variety of applications.

However there is a roadblock to this appealing route to new device applications. Magnetic thin film materials will begin to lose their magnetism (this has been shown to happen at the surface⁶ and/or interface⁷) as they are made thinner and thinner until a thickness is reached where the magnetism is lost entirely and electrical conductivity is replaced by an insulating state. Regions of suppressed magnetization can even occur in thicker materials⁶. This phenomenon is known as the magnetic dead layer, shown as a cartoon in Figure 1. This term can be a little misleading, as the layer is not typically devoid of magnetic order.

Figure 1. Cartoon of the magnetic dead layer. While this diagram indicates that the layer is interfacial, these layers have been shown to occur at surfaces as well.

Naturally, the loss of ferromagnetism in devices that require it poses a problem for device miniaturization. Unfortunately the cause is not yet clear. This material also exhibits a conductive dead layer, which has been explained by Liao *et al.* in terms of increased carrier localization with reduced film dimensionality augmented by scattering from defects⁸. However density functional theory (DFT) calculations by the same group indicate that films of 1 u.c. thickness should remain ferromagnetic. The predicted existence of magnetism despite loss of conductivity implies that the magnetic dead layer is not (at least primarily) electrical in origin. Various suggestions have been put forth for the cause of the dead layer and include interdiffusion⁹, strain^{8,10}, oxygen defects^{8,11}, cation non-stoichiometry¹¹, and others, but no consensus has been reached on the factor(s)

responsible, and more than one may be at play here as shown by some disagreement in experimental results. For example, Peng et al. studied the effect of cation stoichiometry in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and find that by heavily Sr-doping the interfacial layer (i.e. $x = 1$), the magnetization is improved¹². However, other studies report optimal interfacial doping of $x = 1/3$ ¹³ and $x = 0$ ¹⁴. These are nearly opposite conclusions and similar disagreement is seen in studies on other parameters (for example, interdiffusion is not always present^{9,16}). Therefore, there is a need to thoroughly survey the parameter space surrounding this material (as has been highlighted in¹²) by accounting for *all relevant factors* in the fabrication of these thin films.

LSMO is a popular choice for magnetic thin film devices

One material in particular, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) is often studied for these applications. The work in this dissertation focuses on $x = 0.3$. This alloying ratio leads to ferromagnetic behavior via the double exchange interaction (to be explained shortly) as well as a large spin polarization and above room temperature Curie temperature¹⁵ (in fact, the largest in the phase diagram, as seen in Figure 2). In this work, LSMO will be taken to refer to $x = 0.3$ unless otherwise specified. LSMO (for not only $x = 0.3$ but other ratios as well) too suffers from the dead layer problem – while the exact thickness at which magnetism disappears has been shown to depend on a variety of factors⁸, reduction in magnetic moment can typically be seen below a thickness of 25u.c., with ferromagnetism disappearing almost entirely below 6 u.c.^{8,16} We have chosen LSMO not only because it is an appealing candidate for device applications but also because of its large research base. As we survey the parameter space influencing this material's magnetism, we can take advantage of the work already done to compare against.

As can be seen from the phase diagram in Figure 2, the magnetic behavior depends strongly on the Sr alloying fraction x . The endparents LaMnO_3 and SrMnO_3 (LMO and SMO) are both antiferromagnetic via the superexchange interaction, but ferromagnetism is realized for $0.1 < x < 0.5$ (described below). The oxidation state of the transition metal Mn (responsible for the magnetism) varies based on the La/Sr ratio. The charge state of La and Sr in these materials is 3+ and 2+ respectively. This is due to the fact that the valence electrons (two 5s electrons for Sr and two 6s and 1 5d electron for La) are readily removed in a compound due to chemical bonding. Therefore the Mn charge state will vary due to charge neutrality.

Figure 2. Phase diagram of LSMO. Ferromagnetism is realized for $0.1 < x < 0.5$. The work in this dissertation focuses on $x = 0.3$, corresponding to the highest Curie temperature. Reproduced with permission from ¹⁷.

For the endparents LMO and SMO, the valence of the atomic species will read $\text{La}^{3+}\text{Mn}^{3+}\text{O}_{3^{2-}}$ and $\text{Sr}^{2+}\text{Mn}^{4+}\text{O}_{3^{2-}}$. For an alloying fraction of $x = 0.3$, the Mn valence will be the weighted average 3.3. It is this introduction of mixed 3+ and 4+ valence states that leads to carrier hopping from 3+ sites to 4+ sites and thus to ferromagnetism through the double exchange interaction. Thus the Mn valence is an indicator of the magnetism of the system and deviations from this expected value could elucidate the mechanisms responsible for the magnetic dead layer. The Mn valence of 3.3 for LSMO will be frequently referred to throughout this text.

Magnetism in manganite systems

The effect of the crystal field

Before delving into the origin of magnetism in this system, it is necessary to say a few words about the electronic structure of the atoms in these systems. The Mn atom in its isolated form has a $4s^23d^5$ configuration. The five d orbital energy states (ten, including spin) are degenerate. However, the situation changes when the atom is incorporated into a crystal. In this case, the atom experiences a strongly inhomogeneous electric field due to the neighboring atoms, known as the crystal field. In LSMO, Mn is surrounded by an octahedron of oxygen nearest neighbors (six atoms) – thus it is common to refer to Mn as octahedrally coordinated, as shown in Figure 3 (a).

Figure 3. a) Cartoon of the perovskite unit cell, showing the oxygen octahedron surrounding the B site. b) The t_{2g} (bottom three) and e_g (top two) orbitals, taken from <http://wwwchem.uwimona.edu.jm/gifs/dOrbs.jpg> c) splitting of the d orbital energy levels in octahedral symmetry. The energy levels are degenerate in spherical symmetry.

Figure 3 (b) shows the five possible d orbitals. The overlap of the orbitals with those of the neighboring atoms will modify the energy levels. Due to coulomb repulsion between the Mn d electrons and O p electrons, it is more energetically favorable for the Mn electrons to lie in between the O p orbitals (these are the d_{xy} , d_{xz} , and d_{yz} orbitals) than to overlap with them (the d_{z^2} and $d_{x^2-y^2}$ orbitals). Thus the d energy levels are split into the three lower lying states that do not directly overlap with the neighboring atoms and two higher energy states that do. As this result can also be derived using group theory, these levels are termed the t_{2g} and e_g orbitals respectively, with the names referring to the irreducible representations of the O_h point group that describes the symmetry of these states for a cubic perovskite¹⁸. These energy levels are shown in Figure 3 (c). Additional splittings will occur if the structure is distorted from ideal cubic to a lower symmetry¹⁸.

Superexchange

The exchange interaction between magnetic atoms is typically too short-ranged of an effect to explain magnetism in oxides as the spacing between the magnetic atoms is usually larger than the characteristic length over which the majority of the wavefunction extends (i.e. on the order of the Bohr radius)¹⁹. Magnetic ordering can instead arise indirectly from the magnetic atoms coupling through a nearest neighbor such as shown in Figure 4 (a). As a simple example, we can use MnO (figure 4a). Here, the Mn atom has a valence of 2+ (i.e. a $3d^5$ configuration with the two 4s electrons removed), with two electrons occupying the e_g orbital. The total spin moment of the Mn atom can couple with the spin of one of the electrons on the neighboring O orbital. The alignment of the spins has been shown to depend greatly on the bond angle between the three atoms and has been summarized in a set of empirical rules known as the Goodenough-Kanamori rules^{20,21,22}. For 180° bond angles, the system prefers antiferromagnetic alignment. Since the two electrons in the O p orbital will have oppositely aligned spins (due to Pauli exclusion), this results in the Mn atom on the other side aligning oppositely to the other O p electron and thus opposite to the next-nearest neighboring Mn atom. Superexchange is responsible for the antiferromagnetism observed in LMO and SMO.

Figure. 4. a) Cartoon showing the superexchange interaction for a Mn-O-Mn bond. The antiparallel alignment between the Mn and O spins leads to an overall antiferromagnetic ordering of the Mn magnetic moments. From <https://www.quora.com/What-is-superexchange-coupling> b) Cartoon of the double exchange interaction in LSMO. The spin dependent hopping between the e_g Mn orbitals leads to ferromagnetism in the system. Taken from <https://upload.wikimedia.org/wikipedia/commons/d/da/Double-exchange.PNG>

Double exchange

While LMO and SMO are both antiferromagnetic, something interesting happens when the two systems are alloyed. Due to the different Mn valences in the two materials, there is now a mixture of Mn^{3+} and Mn^{4+} ions in the crystal. The system can delocalize the valence electrons to reduce its overall energy (since the kinetic energy operator is proportional to the curvature of the wavefunction, which is reduced for delocalized states) and this leads to hopping of electrons between Mn sites. This proceeds as a two-step process. First, one of the p electrons from the O atom can hop to one of the Mn^{4+} sites (with empty e_g orbitals). Then, one of the Mn atoms from a Mn^{3+} site (with the e_g orbital occupied by one electron) can hop into the O site to fill the empty state. Due to Hund's rules, in which the system's energy is minimized for spins of maximum multiplicity, hopping is favored only if the spin of the electrons are aligned with those of the Mn t_{2g} orbitals. This leads to ferromagnetism and is also responsible for the spin dependent transport in LSMO, also known as half-metallicity. The double exchange process is shown in Figure 4 (b) (note that figure 4a refers to MnO whereas figure 4b refers to LSMO – MnO does not exhibit double exchange). In LSMO and many other mixed valence magnetic oxides, there is competition between superexchange and double exchange. For bulk LSMO, the double exchange interaction dominates.

Why valence is important to study

The work in this dissertation focuses heavily on atomic valence. Here, valence is used to denote the net positive charge per atom. As mentioned before, a neutral Mn atom has a $4s^23d^5$ configuration. Bonding in solids (such as to oxygen in LSMO) can lead to the electrons being attracted to other atoms, thus creating an overall positive charge on the Mn site. The valence corresponds to the number of electrons removed – the two 4s electrons are removed first, followed by the 3d electrons. Mn^{2+} has an electron configuration of $3d^5$, while Mn^{3+} has a configuration of $3d^4$, and so on. Only the valence states of 2+, 3+, and 4+ are observed in LSMO.

But why is valence of importance to study? Valence in general plays a strong role in material properties, influencing phenomena such as magnetism²³, conductivity²⁴ and superconductivity²⁵. As shown in the phase diagram of LSMO in Figure 2, the magnetic (as well as the transport) properties depend strongly on the Sr concentration x , which alters the Mn valence as a necessary requirement of charge balance. In fact, as discussed above *mixed valence* is necessary for ferromagnetism in LSMO. Valence is often perturbed near surfaces and interfaces, and due to the strong role valence plays in the magnetism in this system, any observed changes may give further insight into the mechanism behind the formation of dead layers.

The thickness dependence of the Mn valence in these materials has been studied previously via X-ray absorption spectroscopy by Shibata *et al.* who observed a shift of the Mn L_3 peak position to lower energies below film thicknesses of 6 u.c.²⁶ which indicates a shift of the Mn valence towards 3. However, the study pointed out the need to more thoroughly determine how the valence and magnetism change layer by layer within the films.

In this work, we study the Mn valence in LSMO thin films over a range of thicknesses. In particular, a combination of two X-ray absorption spectroscopy (XAS) detection modes are employed in order to *non-destructively* resolve the layer by layer Mn valence as a function of thickness. It will be shown that while the Mn valence on average stays at its expected value of 3.3 for the majority of thicknesses surveyed, a substantial deviation from its expected value occurs near surfaces and interfaces. This is supported by theoretical calculations. Early efforts to study depth-dependent magnetization will also be explored.

This work is organized as follows: in section 2, a discussion of the thin film fabrication and characterization methods will be given as well as results demonstrating our ability to realize high quality LSMO films. In section 3, XAS will be discussed in more detail as well as our methods of determining Mn valence with low uncertainty. In section 4, the theoretical models and the layer-dependent model based on theory will be developed as well as the results of this model and physical mechanisms responsible for the observed change. Finally in section 5, concluding remarks and future avenues for research will be given.

2. Material Growth and Characterization

Due to the sensitivity of the material properties of LSMO to a variety of factors, the importance of growing high-quality films cannot be understated. Various methods are used to fabricate LSMO and other oxide films including molecular beam epitaxy²⁷, chemical solution deposition²⁸, and sputter deposition²⁹. Another widely used technique is pulsed laser deposition (PLD). A schematic of the process is shown in Figure 5 (a).

Figure 5. a) Diagram of the PLD process. b) Cartoon showing the variation in RHEED intensity as layers are formed during deposition. A maximum in intensity is observed for completely formed (smooth) layers while a minimum occurs for half-formed (rough) layers. Source: <http://www.emg.ing.tu-bs.de/bilder/forschung/analytik/rheed4.jpg>

In the PLD technique, a target of the source material of the desired phase and stoichiometry is synthesized by one of a variety of solid-state methods³⁰. A laser pulse with sufficiently high energy to vaporize the target (typically in the ultraviolet regime) is focused onto the target, causing a plume of material to eject. A heated substrate that the film is to be deposited on is placed in the plume, causing nucleation of the ejected atoms and crystallization depending on the sample conditions (substrate temperature, pressure, etc.). Additionally, a background of oxygen (and sometimes other gases such as argon or ozone) may be used to both impede the kinetic energy of the adatoms and provide a reactive species for the atoms if one is growing oxide materials³⁰.

The quality of films grown can be greatly improved if one supplements PLD with reflection high energy electron diffraction (RHEED). Various growth modes in PLD can be realized, although layer-by-layer growth is often sought after due to low surface roughness in the resulting films. RHEED can be used to analyze the growth mode (except for step flow³¹) and control the film thickness in layer-by-layer growth. This happens as follows: if the intensity of the specular (i.e. reflected) electron beam is monitored, changes in intensity will be observed as shown by the cartoon in Figure 5 (b).

At the beginning of growth, the bare substrate is smooth and so the reflected intensity will be large. As a layer starts to form, unit cells will begin to crystallize at nucleation sites on the film. This will cause a slight roughening of the film surface which will decrease the RHEED beam intensity due to increased scattering of the electrons. However as the layer completes, the surface will become smoother which leads to an increase in the beam intensity. As new layers begin and complete, the intensity will undergo damped oscillations (because there is almost always some 3D growth – pure 2D growth is difficult to achieve). In addition to indicating the growth mode, these oscillations can be used to control the film thickness by stopping the growth at an intensity maximum after a certain number of complete layers. Note that layer-by-layer growth is only obtained for well-optimized recipes. Pure 3D growth will simply lead to an increased roughening of the surface, and thus a decrease in RHEED intensity. In addition, the growth is not always even necessarily epitaxial. Poorly optimized recipes can result in polycrystalline or amorphous films.

Layer by layer growth is considered ideal, but it remains somewhat of an open question whether or not it results in the highest quality film. For example, LSMO can be grown at lower oxygen pressures than those typically used in the literature which results in a more ideal layer-by-layer growth, but the oxygen deficient conditions lead to oxygen vacancies which degrade the magnetism and transport properties of the film¹⁶. The growth parameters here have been optimized for the magnetic properties of the film. Layer-by-layer growth is observed for about 12 unit cells, after which the growth mode transitions to 3D growth. The recipe here was optimized for LaAlO₃ (LAO) substrates, which impart a compressive strain as opposed to the tensile strain of SrTiO₃ (STO). A more thorough optimization of this recipe for STO is currently underway, but currently, the conditions described in the section “Film Growth” below have resulted in the highest quality magnetic properties.

Substrate preparation

LSMO films were grown on single-crystal STO (100) substrates purchased from CrysTech GmbH. STO is a popular choice of substrate due to its low cost and close lattice match to LSMO which allows for the deposition of high quality epitaxial films. The lattice mismatch f , calculated by³¹

$$f = \frac{a_{STO} - a_{LSMO}}{a_{STO}} \quad (2.1)$$

with $a_{STO} = 3.905$ and $a_{LSMO} = 3.873$ (referred to the pseudocubic lattice, discussed further below in the structural characterization section) imparts a small tensile strain of 0.8%³². Another factor to consider for high quality growth is the quality of the starting substrate. Step-terrace morphology is often preferred for fabrication of these types of films as it allows for greater control over the growth mode and reproducibility, as well as sharper interfaces and smoother surfaces.

Perovskite crystals (like LSMO and STO) will naturally exhibit mixed AO and BO₂ terminations (Figure 6). In addition to adding to surface roughness, these terminations can have an effect on the material properties as well³³; thus there is an interest in fixing the termination of the substrate. TiO₂-terminated STO is often prepared using a buffered HF solution³⁴ with a final annealing step. A much safer alternative using DI water and two annealing steps was developed in³⁵ and is employed here. DI water can be substituted for HF since SrO is a basic oxide that is soluble in water; therefore the SrO terminations can be dissolved while the TiO₂ terminations are unaffected. Note that termination control is not always practiced in studies involving these substrates (particularly those outside of STO³⁶) and the substrate termination may have an impact on the material properties³³.

Figure 6. Diagram of the perovskite ABO₃ structure. AO planes are shaded blue and BO₂ planes are shaded green.

Substrate surface morphology and roughness was characterized by atomic force microscopy (AFM). Figure 7 shows the surface morphology at various stages of the treatment process. The as-received

substrates exhibit a flat surface with mixed SrO and TiO₂ terminations. Prior to annealing, substrates were sonicated for 5 minutes in acetone followed by 5 minutes in isopropanol in order to remove organic contaminants from the surface. It is worth noting that this cleaning step is not always practiced in the literature and that contamination could have an effect on the material properties. After the first annealing, the surface is smoothed into flat terraces (determined by the crystal miscut angle) of about 50-200nm width. Miscuts of 0.1-0.2° are usually chosen to produce these terraces. It is entirely possible that the miscut angle itself plays a role in the film properties³⁷; however, to date, no such dependence has been examined for LSMO. A step height of 0.2 nm is typically observed, indicative of mixed termination. Next, a 5 minute ultrasonic bath in DI water dissolves the SrO terminations, leaving only TiO₂. A final annealing step smooths out the terraces again, leaving flat singly-terminated steps with a unit cell step height of 0.4nm.

Figure 7. AFM images of height and phase-lag for mixed termination (panels a) and c) respectively) and single termination (b) and d) respectively) for an STO substrate at various stages of the treatment process. The SrO terminations appear as the bright contrast bubble-like areas in c). The absence of any contrast (besides the step edges) in d) confirms the single termination. This can additionally be verified by RHEED (see below).

Film growth

Figure 8(a) shows a RHEED image of the STO (100) direction prior to growth. The single bright spot is indicative of TiO₂-termination³⁸ and its sharpness indicates the smoothness of the surface. Conversely, the RHEED pattern of a substrate with mixed terminations will exhibit three spots as opposed to one (Figure 8(b)). A splitting in the specular spot in Figure 8(a) is observed due to the superimposed diffraction patterns from both the surface lattice and the periodic array of terraces resulting from the annealing³⁹.

Figure 8. a) RHEED pattern of bare TiO_2 -terminated STO substrate and b) pattern for a substrate exhibiting mixed terminations. c) LSMO film after deposition was completed. d) Oscillations in RHEED intensity corresponding to layer-by-layer growth. Note that for the RHEED pattern in a), oxygen was briefly removed from the chamber to enhance detail as scattering of the electron beam from the oxygen environment will typically decrease the contrast and slightly blur the features.

Films were grown using a Neocera PLD chamber equipped with a Staib Instruments KSA RHEED system. Substrate temperature was set to 750°C ; however, the temperature at the sample was 700°C due to a temperature difference between the heater coil and the stage. Laser energy was set to 300 mJ/pulse which works out to $\sim 150\text{ mJ/pulse}$ at the target after accounting for the loss due to the optics. Films were grown in a 100% oxygen atmosphere at 100mTorr pressure. After growth, the pressure was increased to 450 mTorr to avoid oxygen loss during cooldown. Films were cooled to room temperature immediately following growth, at 15°C/s . A typical RHEED pattern of the completed LSMO film is shown in Figure 8 (c). Three spots can be seen now which likely indicates some mixed termination at the film surface (in contrast to the substrate). In addition, the increase in surface disorder during growth leads to the broadening of the sharp spots into streaks. Since the electrons are scattering from comparatively smaller domains as opposed to the “infinite” lateral size of the single crystal, the delta-function like spots broaden into a Laue function³⁹. Because in the literature films are frequently grown on substrates with a somewhat larger mismatch than LSMO/STO, streaks are usually considered to be a good thing, corresponding to optimal growth. In our case, due to the small lattice mismatch between LSMO/STO, the broadening is fairly small so the diffraction peaks remain as sharp spots rather than streaks.

Figure 8(d) shows the in-situ monitored RHEED intensity. Layer by layer oscillations can be seen up until about twelve completed layers, after which the laser was switched off for this growth. The high frequency oscillation is an artifact that is related to electrical noise in the RHEED system itself and does not have any physical meaning. Care is taken to ensure that these oscillations are not mistaken for true layer by layer growth.

AFM images taken of the films after deposition (Figure 9) indicate that the films have a step-terrace surface morphology, consistent with that of the substrate. For thicker films, this morphology is eventually lost. An image of a 10 nm thick film is shown. Images taken show that the RMS roughness of this film is approximately 0.33nm, or a little more than half a unit cell.

Figure 9. AFM scans of (a), 9 u.c. LSMO film showing step-terrace morphology (b), and 10 nm film, with RMS roughness = 0.33nm.

Structural characterization

X-ray diffraction (XRD) was performed to determine the crystallinity of the grown films using a Rigaku rotating Cu anode XRD system. A very good introduction to the physics of XRD and application to thin films can be found in⁴⁰.

While LSMO exhibits a distorted orthorhombic structure, it is common to refer to a transformed unit cell, called the pseudocubic structure (this is true of other perovskites as well). The lattice constant a_c of the pseudocubic unit cell are related approximately by⁴¹

$$a_c \approx \frac{a_0}{\sqrt{2}} \approx \frac{b_0}{\sqrt{2}} \approx \frac{c_0}{2} \quad (2.2)$$

where a_0 , b_0 , and c_0 refer to the distorted orthorhombic cell parameters. The exact transformation can be found in ⁴¹. The relation between the two unit cells is shown in Figure 10.

Figure 10. Conversion between the distorted orthorhombic (red, dashed) and pseudocubic unit cell (black, solid). The pseudocubic a and c axes are shown to the left of the structure.

A typical 2θ - ω scan of an LSMO film is shown in Figure 11. LSMO peaks are indexed using the pseudocubic structure. The scans indicate a single (001) orientation with no secondary phases. Due to the close lattice match between LSMO and STO, the LSMO peak appears as a shoulder on the STO peak. Due to the tensile strain, the peak appears to the right of the substrate peak.

Figure 11. XRD scan of LSMO films showing a single out of plane orientation. Inset: zoomed view of the STO/LSMO (002) peaks. The LSMO peak sits as a shoulder on the right of the stronger STO peak.

Thickness characterization

As stated above, the growth mode often transitions to island growth after about 12 completed layers. While an approximate deposition rate can be obtained based on the layer-by-layer growth, a more precise determination is needed for films above 12 u.c. X-ray reflectivity (XRR) was

performed to determine the film thickness for thicker films. The experimental setup for XRR is the same for that of XRD, except that it is performed at grazing angles. At these angles, no diffraction is typically observed.

A cartoon for a typical XRR curve for a thick crystal (taken to be infinite here) is shown in Figure 12. At angles close to zero, the reflected intensity is nearly constant as the x-rays are totally externally reflected. At some critical angle that depends on the material's density, the intensity begins to decrease as x-rays penetrate into the material⁴². This decay rate will be influenced by the surface roughness.

Figure 12. Cartoon of a reflectivity curve of a bare substrate (a) and bilayer film (b). Taken from ⁴².

Something different happens when a thin film is added onto a material, however. Due to the finite thickness of the film, fringes are seen in the reflected intensity due to interference between reflections from the top and bottom surface (referred to as Kiessig fringes). This is shown in Figure 12 (b).

As shown in Figure 12 (b), several material parameters determine the features of the curve. The film thickness (which XRR is typically used to determine) is determined exclusively by the oscillation period, while the surface and interface roughness determine the signal envelope, i.e. rougher films will damp the oscillations more quickly and possibly lead to greater uncertainty in the fit parameters. The material density determines the critical thickness and the oscillation amplitude is determined by the density contrast.

The data was fit using the GenX⁴³ software which uses the Parrat formalism⁴⁴. The software uses a differential evolution algorithm, which is a global fit method. Fits for various sample thicknesses are shown in Figure 13.

Figure 13. Examples of XRR curves (open points) and fits to theory (solid lines).

Interface characterization

Transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS) measurements were performed in order to determine the interface quality and film stoichiometry, as well as to explore other potential factors that might affect the magnetic dead layer.

Measurements were performed by James LeBeau and James Fitch from North Carolina State University as part of a collaboration for a grant. Cross sectioned samples were produced by stacking and wedge polishing 1mm square sections of the as received material. The polishing was done using progressively finer grit diamond lapping film with particle sizes ranging from 9 microns to 0.1 micron, and then wedge polishing to an angle of 2 degrees using 1 and 0.1 micron films. After wedging, the mechanical polishing was finished with a final polish of colloidal silica. All samples were ion milled using a Fischione 1050 Argon ion mill using the following recipe:

- 2kV for 15 mins at beam angles of 6 degrees
- 1kV for 10 mins at beam angles of 7 degrees
- 0.7kV for 10 mins at beam angles of 8 degrees

All steps were done at liquid nitrogen temperature. Both images and EDS maps were collected using a probe corrected FEI Titan G2 60-300 kV S/TEM equipped with an X-FEG source operating at 200kV. The convergence semi-angle for both high-angle annular dark field (HAADF) images and EDS maps was 19.6 mrad. The probe intensity for the EDS maps was 60 pA. The HAADF images were corrected for drift using the RevSTEM method developed by the LeBeau group at NCSU⁴⁵. The RevSTEM data sets were composed of a series of 40 1024x1024 frames acquired using a dwell time of 1s.

The TEM scans across the LSMO/STO interface shown in Figure 14 (a) indicate a sharp interface with no interdiffusion. EDS scans shown in Figure 14 (b) indicate an approximately constant element profile across the sample. The average and standard deviation of the La and Sr percentages in the film region are

$$\%La = 36.4 \pm 1.91$$

$$\%Sr = 15.3 \pm 1.31$$

Using the propagation of error formula, this works out to a ratio $La/Sr = 2.37 \pm 0.1$ which is within error of the expected value of $La/Sr = 7/3 = 2.33$. Thus the EDS confirms that the films have the expected stoichiometry. Because the Sr percentage is approximately constant over the film, this indicates that there is no significant amount of cation segregation (which can sometimes occur in these systems. See for example, ⁴⁶).

Figure 14. a) TEM scan of LSMO/STO showing a sharp interface. b) EDS scan across the LSMO film showing a constant cation profile and confirming the expected La/Sr ratio. If you consider only the cations in LSMO, then 50% should be Mn, $70\% \times 50\% = 35\%$ La and 15% Sr.

Having confirmed the quality of the films, the next step is to examine the change in valence across the material using XAS methods. This will be discussed in the next chapter.

3. X-ray absorption spectroscopy measurements

In this chapter, the methods used to determine valence will be discussed. First, a description of the essential physics of XAS and the features of the spectra will be reviewed and then the linear combination methods used to determine the valence from the spectra will be developed.

Basic physics of XAS

X-ray absorption occurs when a core level electron in an atom absorbs an x-ray and is excited to an unoccupied valence state. This process creates a hole in the core level. Some time later (the core hole lifetime is ~ 1 fs), an outer shell electron recombines with the hole either through emission of a photon (x-ray fluorescence) or by imparting kinetic energy to another electron (Auger emission). This is shown schematically in Figure 15.

Figure 15. a) The X-ray absorption process – an X-ray comes in and excites a core level electron to an unoccupied valence level. b) The two types of core hole recombination processes. The recombination either leads to the emission of an X-ray (fluorescence) or an Auger electron (Auger emission). Adapted from <http://www.theochem.kth.se/research/xspectra/>

The transitions are labeled as edges depending on the initial state being excited. If the excitation is from the 1s state, it is known as the K-edge; the 2s and 2p states are labeled as the L_1 , L_2 , and L_3 edges, etc. as shown in Figure 16.

Figure 16. a) Diagram showing the transitions between various core levels and their names. From: https://en.wikipedia.org/wiki/X-ray_absorption_spectroscopy

The XAS work in this dissertation deals with the K and L absorption edges of Mn. Examples of both are shown in Figure 17. Different terms are used to describe the regions of the spectrum. While the exact energy ranges that define each region can vary between cases, the features of each region are qualitatively the same. The region before the onset of absorption is known as the pre-edge. Here it is sometimes possible to see weak dipole-forbidden transitions. For the K-edge, these are 1s to nd level where n is the lowest unoccupied orbital. The pre-edge need not be flat as it can contain contributions from other lower energy edges. A standard method exists for removal of the background and will be discussed later.

Figure 17. Examples of the Mn a) K-edge and b) L-edge for LSMO. Both spectra exhibit similar features except that the L edge will have multiple peaks whereas the K-edge has one. The beginning of EXAFS can be seen for the L-edge, although it will be cut off by the La M_5 and M_4 transitions occurring at around ~ 840 eV.

The next region lies near the absorption edge. The absorption edge is typically defined by the location of the maximum in the first derivative of the spectrum. This region is known as X-ray absorption near edge structure, or XANES and extends about 20-30 eV from the absorption edge. Accurate theoretical modeling of the XANES region for the K-edge is quite difficult and relies on Green's function or DFT methods^{47,48}, although as will be discussed later, the L-edge can be modeled by comparatively simpler multiplet calculations.

The third region extends several hundred eV from the XANES region, and is known as the post edge. This part of the spectrum exhibits oscillatory features, referred to as extended X-ray absorption fine structure, or EXAFS. At these energies, the absorbing atom will be ionized, leading to the emission of a photoelectron. This photoelectron scatters from the atoms near the absorbing atom in the solid. Depending on the energy and the structure, the photoelectron scattering paths will either interfere constructively or destructively, leading to the oscillation in the absorption. As compared to the XANES region, theoretical modeling of the EXAFS region is (arguably) simpler and is often used for structural characterization of materials⁴⁹. This can be difficult, however, on the lower energy edges (e.g. the L-edge of first row transition metals) due to closer overlap of different elemental absorption edges with one another⁵⁰. Also, the fact that the L edge contains more than one peak further complicates the EXAFS analysis.

Theoretical description of the spectrum.

The absorption spectra shall now be described in more detail. In general, the transition probability from the initial state to the final state (with a core hole left behind) is given by Fermi's Golden Rule:

$$W_{fi} = \frac{2\pi}{\hbar} |\langle \Phi_f | H' | \Phi_i \rangle|^2 \delta(E_f - E_i - \hbar\Omega) \quad (3.1)$$

Where H' is the operator for the electromagnetic field in the Coulomb gauge, given by

$$H' = \frac{1}{2m} (\vec{p} - q\vec{A})^2 \quad (3.2)$$

Neglecting terms of order A^2 and treating the vector potential as a perturbation gives

$$H' = \frac{q}{m} \vec{p} \cdot \vec{A} \quad (3.3)$$

The next step is to quantize the electromagnetic field and turn it into operator form.

$$\vec{A} = \sum_{q,\lambda} A_0 \vec{\epsilon}_q (b_{q\lambda} e^{i\vec{q}\cdot\vec{r}} + b_{q\lambda}^\dagger e^{-i\vec{q}\cdot\vec{r}}) \quad (3.4)$$

Where A_0 is an amplitude, b and $b^\dagger$ are creation and annihilation operators, q is a wavevector, and λ is a polarization index. In the dipole approximation, one expands the exponential $e^{i\vec{q}\cdot\vec{r}}$ and keeps only terms of 1st order⁵¹. Substituting the expression for the vector potential into (3.3) and then substituting the expression for H' into the Golden rule gives the result

$$W_{fi} \propto \sum_q \frac{2\pi}{\hbar} |\langle \Phi_f | \vec{\epsilon}_q \cdot \vec{r} | \Phi_i \rangle|^2 \delta(E_f - E_i - \hbar\Omega) \quad (3.5)$$

This result gives the probability, or line strength, of the transition of interest. The energy positions E_i and E_f are obtained by computing the expectation value of the Hamiltonian $\langle H \rangle$. Methods of obtaining these spectra theoretically, utilizing perturbation theory and Hartree-Fock codes exist and are discussed extensively in⁵².

The initial and final states Φ are given by the one electron states. This picture works well for the K-edge but some discrepancies arise when trying to apply this to the other absorption edges. The reason for this is because the overlap of the core hole wavefunction with the promoted electron is

not small, and the core hole can couple its angular momentum to the valence electrons. This results in considerable fine structure, known as multiplet structure, as we will discuss further.

What is a multiplet and where do they come from?

When one thinks of the processes involved in XAS, they usually think of a picture of one electron in an occupied orbital being promoted to an unoccupied orbital. If one knows the wavefunction for the electron in its initial and final states, the transition probability (and thus the spectrum) could be calculated by Fermi's Golden Rule. However, calculations that try to reproduce the L-edge spectrum using this picture fail. Why is this?

To illustrate the essential concepts, let us use the Ti L-edge of STO as an example as it is a very simple but relevant system. The Ti atom has a d^0 (Ti^{4+}) configuration. The crystal structure of STO is cubic, so the d energy levels will be split into e_g and t_{2g} states due to the octahedral coordination of the Ti atom. Therefore, there are four states to which an electron can be promoted, so if we were to take a Ti absorption spectrum, we would expect two peaks on the L_3 edge and two on the L_2 edge (for a total of four).

That's not actually what happens. An experiment will show that there are more peaks than this, 6 or 7 will be visible (it is actually seven, as will be shown, but depending on the energy resolution of the instrument it can sometimes be difficult to see all of them). An example of a scan of the Ti L edge from one of our STO substrates is shown in figure 18. So what's actually happening?

Figure 18. The Ti L-edge for STO. The data (black line) was taken at beamline 6.3.1 of the Advanced Light Source. As STO is a common substrate, we took this data as a reference for other measurements. The data has been offset vertically for clarity. Calculations (red dashed curve) were performed using the CTM4XAS software using parameters from the literature⁵³ and Lorentzian and Gaussian

broadenings of 0.2eV. The blue sticks show the position of the seven individual multiplet peaks. Charge transfer effects were not considered which would affect the peak broadenings and number of transitions.

The absorbing atom is a multi electron system. For L-edge absorption, radiation is absorbed and a 2p electron is promoted to one of the unoccupied d orbitals. There are several consequences to this:

- A hole now exists in the 2p level.
- The overlap between the core hole and 3d wavefunctions is not small. Therefore the angular momentum and spin of the hole can couple to the 3d electrons.
- The excited state configuration is $2p^5 3d^{n+1}$. Thus the energy levels of the final state differ from the initial.
- There are multiple accessible final states to the promoted electron, so long as they satisfy selection rules.

These effects give rise to a large amount of splitting in the energy levels. These splittings are known as multiplets and considering them is essential for an accurate description of L-edge absorption spectra. Note that these are an *atomic* phenomenon and not a many-body effect due to the absorbing atom being in a solid (such as the crystal field potential and charge transfer effects, to be described later).

So how does one treat these spectra? By considering the *multi-electron* states of the absorbing atom rather than the one electron states. This discussion uses the L-S coupling scheme. For heavier atoms, different schemes may be required to be used, such as j-j coupling.

Let's again look at STO. The Ti atom has a valence of 4+ meaning a d^0 configuration. In spectroscopic notation, $s = 0$ and $l = 0$ give a ground state of $^1S_0$. The excited state will be $2p^5 3d^1$. This gives J values of 0 through 4 and possible states of (sorted by increasing J): $^3P_0$, $^1P_1$, $^3P_1$, $^3D_1$, $^1D_2$, $^3P_2$, $^3D_2$, $^3F_2$, $^1F_3$, $^3D_3$, $^3F_3$, and $^3F_4$ (twelve in total). The only allowed (dipole) transitions must satisfy the selection rule $\Delta J = 0$ (unless $J=J'=0$), ± 1 . The term symbols satisfying this are $^1P_1$, $^3P_1$, and $^3D_1$. This leaves 3 transitions. However, look at experimental results, and you will see not three but *seven* peaks. What have we left out?

The above would be correct for an isolated Ti atom; however, the Ti^{4+} atom is in a cubic crystal system which has some degree of anisotropy. Thus the symmetry of the system must be accounted for. As discussed before, the d-orbitals will split in energy depending on their orientation with respect to the crystal axes. Orbitals which lie along the diagonals form the t_{2g} orbitals, which are lower in energy than the e_g orbitals which lie along the crystal axes (and thus experience repulsion due to the neighboring oxygen orbitals, raising their total energy). The p orbitals will not split in cubic symmetry as they all lie along the crystal axes.

Now, we need to reconsider the term symbols we derived earlier, as all of these will branch when placed into a cubic environment, and some of the transitions will no longer be zero. However, our system has a non-negligible contribution from spin-orbit coupling, so it is not sufficient to consider how the different orbitals (that is, orbital angular momenta) are branched. Instead, the branching occurs by J values instead of L. Table 1 shows the branching in cubic (O_h) symmetry.

O_3	O_h
J = 0	A ₁
J = 1	T ₁
J = 2	E + T ₂
J = 3	T ₁ + T ₂ + A ₂
J = 4	A ₁ + T ₁ + E + T ₂

Table 1. Branching rules for different values of total angular momentum J⁵².

The selection rules one is familiar with become relaxed in a crystal. The full details of this require some group theory to explain, but the main point is that the final state must have the same symmetry as the dipole operator, namely T₁ (the dipole operator is proportional to the L=1 spherical harmonic and branches the same way). Based on the table, the same J=1 transition branches to T₁ symmetry, so those transitions from the atomic case will still be observed. But one can also see that the J=3 and J=4 terms branch and now will contain some T₁ symmetry component and can be allowed now. From our earlier results, there are 3 J = 3 terms and 1 J = 4 term. This will make a total of seven terms with T₁ symmetry and this leads to 7 peaks. The calculated position of these peaks for STO are shown in Figure 18 as a dashed red curve with blue sticks to indicate the transition energy positions.

At this point, one may try to connect each peak observed in an experiment to one of these J term symbols, but the peaks observed in an experiment do not correspond to transitions to each of the individual terms – rather, due to spin-orbit coupling, the states are mixed. Thus the seven states are superpositions of the individual J terms. Determining which states contribute to which peaks requires solving for the eigenvectors of the Hamiltonian.

Despite this complex picture, it is nevertheless common in the literature to refer to the one-electron picture. Indeed, for STO, there are only 4 strong transitions, which can be roughly associated with one-electron transitions to the crystal-field split e_g and t_{2g} orbitals as well as three small “spin-forbidden” transitions (note that as shown by the calculations above, the two large peaks at 457 and 460 eV comprising the L₃ transition actually consist of three transitions). How can we connect these two pictures?

This type of picture is approximately correct for this example, but will fail for elements like Mn, which can have a very complex spectrum. For a compound like pyrolusite (MnO₂ – see Figure 19 below) the symmetry is tetragonal, but only 3 obvious transitions are observed as opposed to the expected 8. While the core hole can be viewed as a potential that splits the one-electron states, the full details require the multi-electron theory to adequately describe. Some caution should be taken when ascribing transitions to those from the one-electron picture, particularly if one is trying to assign some physical meaning to the features.

The approach outlined here, which has been worked out for an empty valence level, holds for higher numbers of electrons, but becomes a bit harder to work out. Some differences are:

- If the ground state contains 1 or more electrons in the d orbital, there are multiple *initial* states accessible and this will lead to more transitions (so-called “ground state effects”)
- The actual electron configuration of the atom can be a superposition of different possibilities (“configuration-interaction picture” or “configuration mixing”). Some of these configurations may be equivalent to each other while others may not.

In practice, no experimentalist typically tries to keep track of all the term symbols and individual transitions. Why? Because there are often too many to even spectrally resolve. Let’s consider Mn₂O₃

(a d^4 system). The excited state $2p^53d^5$ can be described by 205 symbols, implying 205 possible transitions! Not all of these will be allowed due to selection rules, but this is still a large number of transitions and due to effects such as lifetime broadening, it can become impossible to resolve individual transitions (although multiplet simulations can give an indication of where they are). In addition, charge transfer effects, in which the electronegativity of the transition metal ion makes it possible to pull electrons from the oxygen ligands, can further complicate the picture. (Simply put, this is a model of the effects of covalent bonding.) This leads to the creation of many additional states and manifests itself as the broadening of peaks and creation of satellites. For STO, this leads to features on the post edge as well as broadening of the main features of the spectrum. These effects are discussed in detail in ⁵².

Multiplet theory is a dense subject and the discussion here only touches on the essential physics. The details of computation of these spectra are described in detail in ⁵² and ⁵⁴. The CTM4XAS software⁵⁵ is freely available for the computation of these spectra and can be used to determine, for example, valence and crystal field splittings in materials. The calculation of charge transfer effects is a complicated subject and while CTM4XAS allows for the calculation of some qualitative effects, dedicated programs may be required if the effects are large (as is the case for accurate modeling of SrTiO_3 ⁵⁶).

Putting the Ti L-edge aside, we shall now discuss the features of the Mn absorption spectrum which is extensively discussed in this dissertation. Some examples of the Mn L-edge are shown in Figure 19 (in fact, these are references for the linear combination fitting method which is used to determine valence, discussed later).

Figure 19. Examples of the Mn L-edge absorption spectra for various electron configurations. As the number of possible initial and final states increases, the multiplet structure becomes more complex.

Several spectra are shown. The specific features will depend on the Mn valence state (this will be important later), but some trends can be seen. The Mn L-edge absorption spectrum will consist of two broad peaks which can be described as the L_3 and L_2 transitions in the one-electron picture with some fine structure that reflects the multiplet and crystal field splitting. As the number of electrons in the initial and final states increases, the multiplet structure will become very dense and broaden into a continuum (e.g. compare the relatively well resolved peak structure of MnO due to fewer transitions to the smeared out features of Mn_2O_3). Typically, very good energy resolution is needed to resolve the fine structure.

Having discussed the features of the K and L edges, we shall now discuss the experimental methods used to obtain them and the analysis of the spectra to determine the Mn valence.

Experimental

Different detection modes can be utilized to measure the absorption edges. The incident X-rays are absorbed by exciting core electrons to empty states above the Fermi energy, leaving a hole. Recombination of the hole leads to either the creation of an X-ray--measured by fluorescence yield (FY)--and creation of an Auger electron⁵⁷. As the Auger electron scatters through the material, it creates many secondary electrons. Both types of electrons are collected in total electron yield (TEY) mode. These detection modes are illustrated in Figure 20. In electron yield, typically one collects only the electrons that escape from the sample, making it a very surface-sensitive technique.

Figure 20. Cartoon showing the TEY and FY processes⁵⁸. Violet arrows indicate scattered secondary electrons. The brightly shaded areas show the relative probing depths of the two techniques. Electrons created deeper in the samples are less likely to escape the sample and reach the detector while photons have longer scattering paths.

As X-rays are much less easily scattered than electrons, the two techniques have very different probing depths, which will also depend on the incident X-ray energy. As it requires more energy to excite an electron from the $n=1$ states (K edge) than the $n=2$ states (L edge), K -edge absorption requires higher energies and probes deeper into the sample. The energies of the K and L edge⁵⁰ (and probing depths for Mn) are listed in Table 1. It should be noted that these values are estimates, with the exception of the probing depth for L edge TEY, which was determined specifically for LSMO by Ruosi *et al.*, although the probing depth can be significantly influenced by the material density which varies from sample to sample. We tried various values of the TEY probing depth in order to assess the affect that any variation in its value would have on our modeling and found that it does not significantly affect the results. This is elaborated on further in the appendix.

The contribution from a specific layer of depth z within the material can be determined by the exponential formula^{59,60} $e^{-z/\lambda}$, where λ is the probing depth of the measurement technique. Note that

this factor needs to be normalized by integrating over the thickness of the sample in order to give the relative contribution to the signal. The details of this procedure are discussed in Chapter 4.

Edge	Energy (eV)	λ_{TEY} (nm)	λ_{FY} (nm)
K-edge	6539 ⁵⁰	14.8 ⁶¹	4000 ⁶²
L-edge	638.7 ⁶³	2.6 ⁶⁴	14062

TABLE II. Edge energies and probing depths for TEY and FY on the Mn K and L-edges.

In this study, we have used K-edge FY and L-edge TEY. Given the probing depths listed in Table II, the exponential curves for the TEY and FY are illustrated in Figure 21. Due to the small probing depth, the TEY mode at the *L*-edge is the most surface sensitive of these techniques. Thus, while *L*-edge TEY would be excellent at determining the Mn valence at the surface, little contribution would come from deep within the sample. On the other hand, FY of the *K*-edge probes many microns into the sample; thus, for the measurements of thin films, this technique nearly produces a straight average of the valence of all layers. Utilizing two techniques that measure the same property (valence here) with different probing depths can allow one to back out the depth-dependence of that property if combined with samples of varying thickness.

Figure 21. XAS intensity as a function of depth for TEY (black, $\lambda \sim 1\text{nm}$) and FY (red, $\lambda \sim 1\mu\text{m}$). The contribution to the TEY signal for the first two layers is shown in shaded green areas⁵⁸.

To study the depth dependent valence, XAS measurements were performed at the Advanced Light Source (ALS). FY and TEY measurements were taken at ALS beamlines 10.3.2 and 6.3.1, respectively. Spectra were measured at 300K. TEY measurements were taken at normal incidence while FY measurements were taken at grazing incidence. The choice of angle is important for TEY as the depth sensitivity depends strongly on angle, and experiments are typically only well-optimized for angles above 60 degrees from the sample surface⁶⁵. The choice of angle is less critical for FY as the entire sample thickness will be probed for thin films. To maximize the beam path travelling through LSMO and thus the resulting intensity, spectra were recorded at grazing incidence for FY mode.

Several steps are taken to normalize XAS spectra. First, the spectra are normalized to the incident X-ray intensity. Second, the pre-edge, due to absorption tails from other elements and lower energy states, must be subtracted. This is done by fitting the pre-edge region to a polynomial or power law (this is a standard method but see ^{66,67} for examples). Finally, the spectrum is multiplied by a constant factor so that the post edge is equal to one. The edge subtraction is shown in Figure 22. For the L-edge, a linear background is typically sufficient.

Figure 22. Subtraction of the pre-edge needed for the normalization of XAS data.

Determination of valence

Once the spectrum is properly normalized, several ways exist to determine the valence state of an element in a material. One method, commonly used in electron energy loss spectroscopy (EELS) is to take the integrated intensity ratio of the L_3 and L_2 peaks and compare with references. However, this can be difficult to apply due to a significant amount of scatter in the observed trend⁶⁸. One complicating factor is the multiplet structure of the spectra, which can cause errors in the estimate. A second problem is the presence of charging effects in electron yield spectra obtained from insulating samples, which causes a time-dependent decrease in measured intensity which is not reflective of the electronic structure of the material⁶⁹. This effect results in a systematic bias of valences obtained through this method towards lower values by modifying the peak height ratio between the L_3 and L_2 transitions. Fluorescence yield on the L-edge also suffers from artifacts due to a strong energy dependence of the probing depth (known as overabsorption or self-absorption effects) which can be difficult to correct for⁷⁰.

Another method involves fitting the spectra to a linear combination of references that one would expect to describe the system. For LSMO, this would involve fits using LMO and SMO spectra and also with Mn^{2+} if oxygen vacancies are present⁹¹. However, fits using this method are often poor for mixed valent compounds⁷¹. This arises from several factors: one is that in mixed valent systems, there are interactions between the different valence species (i.e. double exchange) which can modify the energy levels. Other problems arise from subtle differences in chemical and crystallographic environments surrounding the element which may affect the spectral features.

While it could be possible to determine the valence by theoretically modeling the spectra⁷², an empirical method was developed by Manceau *et al.* known as the combinatorial approach⁷³. The

assertion is that while some aspects of the spectra features may vary between materials, there should be features of the different valences that are more or less consistent between references of the same valence. This is illustrated in Figure 23. Here, Mn^{2+} is seen to exhibit a strong peak near 6550 eV with a rapid decay following, while for example, Mn^{3+} is shifted towards higher energy values and does not show such a sharp peak.

Figure 23. References used for linear combination fits for the Mn L-edge (right) and K-edge (left). The spectra shown correspond to the references that produced the best fit to our data.

To use the method, a database of references must be assembled using either existing data from the literature or references measured by oneself. It is ideal that the references resemble the material of interest as closely as possible. The more references that are used, the better the resulting fit will be. The spectrum is then fit to every possible combination of references in the database. At most five have been used here as the improvement in fit quality by including more references is usually not significant and the program run time increases exponentially. It is important to note that to avoid overfitting, the references are constrained to contribute *positive* amplitudes, i.e., you cannot subtract a contribution. This is physically justified by the assertion that one of the features of the references actually comprises part of the experimental data, rather than allowing the program to subtract off certain features to improve the fit quality. Furthermore, one should only select references of valence species that one actually expects to exist in the material. For example, including a reference taken from KMnO_4 (in which Mn has a valence of 7+) to fit an LSMO spectrum may improve the fit, but the valence obtained from the fit will not have any physical meaning since Mn^{7+} is not known to exist in that system.

References were selected using Mn^{2+} , Mn^{3+} , and Mn^{4+} species as well as several bulk LSMO references. Including the mixed valent references resulted in much greater quality of fit; as

mentioned above, interaction between different valence species can introduce additional features. The spectra used for fitting the K-edge are available online at ⁷⁴. No such database exists for the Mn L-edge and this method has not to our knowledge previously been applied to this absorption edge, so a set of references was assembled by digitalizing data from refs [^{75,76,77,78,79,80}]. These are shown in Figure 23.

The model used to fit the data is

$$\text{model} = \sum_{i=1}^{n_{\text{comp}}} a_i r_i(E - E_0) + BG(E) \quad (3.7)$$

where r_i represents the i^{th} reference spectrum with weight a_i and energy offset E_0 . An energy offset is included if needed to account for differences in energy calibration. For radiation produced by bending magnets, the offset can be as large as several eV (typically one takes care to properly calibrate the energy using a known reference). The offset is much smaller in more modern undulator beamlines, as long as they have been calibrated for the measurement energy (which is typical). n_{comp} refers to the number of references to be used. Here, at most five references were used.

$BG(E)$ is the background function given by

$$BG(E) = c_0 E \quad (3.8)$$

for the Mn K-edge and

$$BG(E) = c_0 E + H_0 \left(1 - \frac{2}{3} \frac{1}{1 + e^{(E - E_{L3})/d}} - \frac{1}{3} \frac{1}{1 + e^{(E - E_{L2})/d}} \right) \quad (3.9)$$

for the L edge. The term $c_0 E$ represents a linear background that accounts for small differences in edge removal between references as well as possible charging effects (for XAS taken in TEY mode). The second term represents the two-step function continuum⁸¹. H_0 is the height of the steps and d is the rounding of the step edges. It can also be modeled as an arctangent, which gives very similar results. E_{L3} and E_{L2} correspond to the start position of the step edges and are set by determining the maximum in the first derivative of the spectra at the L_3 and L_2 peaks. The contribution of the background is typically small.

Fit parameters are the a_i , c_0 , and H_0 . Since this model is linear in the fit parameters, the global minimum can be found in each case, unless one is fitting with an energy offset, in which case the fitting problem is no longer linear.

Some example fits for the K and L-edge are shown in figure 24 (a). Fitting using the combinatorial method produces good fits with near-noise residuals. The spectra that contribute to the fit are shown in dashed lines. The spectra of bulk LSMO is the most significant in each of the fits. The full set of spectra and fits are shown in figure 24 (b).

Figure 24. a) Example fits for the K and L-edges showing the components used and typical residuals and b) all data (black) and fits (red) for the Mn K and L edges⁵⁸.

Results

Figure 25 shows the results of the combinatorial fits for TEY (red points) and FY (black points). The determination of error bars is discussed in the Appendix and involves analyzing the variation in the results from choosing different combinations of references to fit the data. The dashed line corresponds to the expected Mn bulk valence of 3.3.

Figure 25. Valence obtained from the combinatorial fits as a function of thickness. The dashed line indicates the Mn valence in bulk LSMO of 3.3.

While the points for FY (the bulk average technique) hover around this expected value, a drop is seen at low thicknesses. Additionally, the valence obtained from TEY is greater than 3.3. As TEY is a surface sensitive technique, this indicates a raised surface valence. However, as will be discussed in Chapter 4, combining both a surface and bulk sensitive technique can enable us to learn about the interface as well. The modeling of this experimental data shall now be discussed.

4. Modeling the depth dependent Mn valence in LSMO thin films

In this chapter, the development of the layer by layer valence model and its application to the experimental data will be discussed, as well as theoretical calculations that were performed in order to better understand the physics behind the experimental results. To avoid confusion, I note here that there are three different models to be discussed: first, I will discuss tight binding calculations (TB) performed by Shuai Dong at Southeast University of China which motivated our experimental modeling. Second, I will discuss the experimental model based on the TB calculations with which we fit the data in Figure 25 in order to determine the layer by layer valence change in our own system. Third, I will discuss the DFT modeling done by Aldo Romero and his students at WVU which reveal the physical mechanisms responsible for the observed change in valence.

Tight binding model

In order to better understand the change in valence seen in our experimental data, a simulation of thin film LSMO was performed using a model Hamiltonian (Shuai Dong, SEU China). The Hamiltonian is based on the two orbital double exchange model^{82,83} and is given by

$$H = - \sum_{(ij)\gamma\gamma'} t_{\gamma\gamma'}^{\vec{r}} (\Omega_{ij} c_{i\gamma}^{\dagger} c_{j\gamma'} + H.c) + \sum_i V_i n_i + \sum_{(ij)} J_{AF} \vec{S}_i \cdot \vec{S}_j \quad (4.1)$$

A large amount of physics is contained in this equation. The first term describes the double exchange interaction. Here, γ and γ' are summed over the two e_g and t_{2g} orbitals (after which the model is named). The t term describes hopping probabilities (typically taken from first principles calculations) between neighboring sites. Note that this term contains three components, describing hopping in the x, y, and z directions. The Ω_{ij} term is a phase factor describing the alignment between spins. It can have a complicated angular dependence, but for a ferromagnetic system (which is assumed here in the calculations) it is equal to unity as the spins are aligned in the same direction.

The second term describes the electric potential of the system. The determination of the potential V_i will be discussed shortly.

The third term describes the superexchange interaction. The coupling constant J_{AF} is equal to 50 meV and is roughly one tenth the contribution to the system's energy of double exchange; hence, ferromagnetism is favored. Note that the superexchange term favors anti-aligned spins, i.e. the energy is minimized when the dot product of the two spins is negative. In our work, the contribution from the superexchange interaction was not considered as we were concerned about the electrostatic rather than magnetic properties of the system.

To obtain the Mn valence, the model is solved self consistently with the Poisson equation. Diagonalizing the Hamiltonian gives the charge density, which is then fed into the Poisson equation to determine the electric potential. This process is repeated iteratively until convergence is reached. The charge density ρ_{eg} gives the e_g orbital occupancy, which is related to the Mn valence by $V_{Mn} = 4 - \rho_{eg}$.

In this model, the dielectric constant and interfacial charge are adjustable parameters. For best agreement with the experimental data (to be discussed), the dielectric constant was set as $\epsilon_r = 30$ and the polar termination charge is set to 1.45e. The hopping amplitudes can be all related to a single value t_0 which was then factored out, i.e. all of the material constants and energies are given in terms of multiples of t_0 .

Calculation results

The layer by layer Mn valence as determined from the simulation are shown in Figure 26. The single square point corresponds to the Mn valence for a thickness of 1 u.c. Here, the valence is near its expected bulk value. However, when the sample is 2 u.c. thick (circular points), the situation is different. Here, the surface layer is raised above its bulk value, while the interfacial layer drops below the expected bulk valence, although they still average out to close to 3.3. The trend is similar for the other thicknesses: the valence in the layers towards the surface is raised above the expected value of 3.3, approaching 3.8, while the interface valence is lowered and approaches 2.5 at larger thicknesses.

Figure 26. Layer dependent Mn valence as determined by the TB calculations, shown for a variety of thicknesses.

Development of the model

The TB results shown here indicate the expected layer by layer valence for an ideal LSMO film. However, direct comparison to experiment is not possible since as discussed before the valence measured by XAS probes multiple layers into the sample, so there are weighted contributions for each layer. Therefore, the calculation results do not look like the points shown in Figure 25, nor should they. What is desired here is to develop a model based on these calculations that can extract the layer by layer valence from the *experimental* data in order to compare to theory.

The TB results for the case of 8 u.c. thickness is presented in figure 27a. By analyzing the data, we found that it is very well described by a two-term exponential trend of the form

$$V(z) = \frac{V_{bulk}}{2} \left[1 - \alpha e^{-(z-1)/L_{surf}} \right] + \frac{V_{bulk}}{2} \left[1 - \beta e^{(z-z_{int})/L_{int}} \right] \quad (4.2)$$

where the two coefficients

$$\alpha = \frac{2e^{(z_{int}-1)/L_{surf}} (V_{bulk}(e^{(z_{int}-1)/L_{int}} - 1) + V_{int} - V_{surf}e^{(z_{int}-1)/L_{int}})}{V_{bulk} \left(e^{\frac{(z_{int}-1)}{L_{surf}} + \frac{(z_{int}-1)}{L_{int}}} - 1 \right)} \quad (4.3.1)$$

$$\beta = \frac{2e^{(z_{int}-1)/L_{surf}} (V_{bulk}(e^{(z_{int}-1)/L_{surf}} - 1) + V_{surf} - V_{int}e^{(z_{int}-1)/L_{surf}})}{V_{bulk} \left(e^{\frac{(z_{int}-1)}{L_{surf}} + \frac{(z_{int}-1)}{L_{int}}} - 1 \right)} \quad (4.3.2)$$

have been obtained by requiring that $V(1) = V_{surf}$ and $V(z_{int}) = V_{int}$. These are simply boundary conditions that fix the value of the valence at the surface or interface, which are then used as fit parameters. L_{surf} and L_{int} are characteristic length scales that describe the distance over which the valence changes from its bulk value V_{bulk} to e.g. $(V_{bulk} - V_{surf})/e$. The blue curve in Figure 27a shows a fit of the TB calculations to this formula. A cartoon of this variation is shown in figure 27b. Here, $z = 1$ is taken to be the surface. Note that when $z_{int} = 1$ (a monolayer thick material), the denominator of the coefficients α and β are zero, and $V(z)$ diverges, because it is impossible for the valence at this thickness to simultaneously be equal to the values of the surface valence and interface valence. Because of this divergence, $V(1)$ was set to a value V_{mono} which was included as a fit parameter. Also considered was a power law variation; however, this approach led to overfitting of the data due to highly coupled fit parameters – details of this model are discussed in the appendix.

Figure 27. a) Fit of the TB model results for 8 u.c. to an exponential and power law variation. b) Cartoon of equations_ showing the essential features and the effect of the different parameters.

As mentioned before, the valence measured by experiment does not solely measure the valence of one layer (unless the sample is a monolayer thick), so in order to compare to the modeled results to experiment, the valence in each layer has to be summed, weighted by the appropriate signal contribution $e^{-z/\lambda}$ (where λ is the probing depth) from each layer. Additionally, a factor e^{-z/λ_0} must be included to account for the attenuation of the incoming X-rays (on the order of 100 nm). The experimentally obtained weighted average is then given by the expression

$$V_{exp}(N) = \frac{\sum_{i=1}^N V(i) \int_{i-1}^i e^{-z/\lambda} e^{-z/\lambda_0} dz}{\int_0^N e^{-z/\lambda} e^{-z/\lambda_0} dz} \quad (4.4)$$

Here the integration in the numerator is carried out over the i th unit cell while the term in the denominator normalizes to the whole sample thickness. For FY mode, $\lambda \sim \lambda_0 \sim 1 \mu\text{m}$ which is much larger than the thickness of the sample, so $V_{exp}(N)$ is essentially a straight average and the

exponential factors are approximately equal to 1. For TEY mode, the escape depth of the electrons is on the order of nanometers, so this detection mode is more surface-sensitive. The term $V(i)$ is the layer by layer model for valence, equation 4.2, evaluated at a given depth.

The experimental data for both TEY and FY was simultaneously globally fit to equation 4.4 using a differential evolution algorithm. In our fitting, the probing depths λ were set to 2.6 nm for TEY⁶⁴ and 4 μm for FY⁶². The attenuation lengths λ_0 of the incoming X-rays were set to 4 μm for the Mn K-edge and 140 nm for the Mn L-edge⁶². As mentioned in Chapter 3, there can be a considerable amount of variation in the TEY probing depth due to different material densities – to examine the effect of this, we varied the value of the TEY probing depth λ between 1.5 and 4.0 nm, which is expected to account for any variation in the probing depth due to sample dependent effects, and found that this resulted in only small changes in the fitted results. This is further discussed in the Appendix.

Fit results are shown in Figure 28 a) as dashed curves and indicate that the model provides a reasonable fit to the data (the solid lines are fits to a more sophisticated model, which will be discussed later). The extracted layer by layer valence is shown in Figure 28b as red markers (the model producing the purple markers will be discussed below). The fitted layer by layer valence shown in Figure 28b indicates that the surface and interface Mn valence are quite different than their expected bulk value, with the valence approaching 4.0 at the surface and 2.5 at the interface. As will be discussed later, the primary physical mechanism behind this charge separation lies in the polar discontinuity at the LSMO/STO interface, and the Mn carriers are redistributed in order to make the material electrostatically stable.

Figure 28. a) Experimental data (solid points) and fits to the data with models where the surface and interface valence are constant (allowed to vary with thickness) shown as dashed (solid) lines. b) Comparison of the depth dependent valence profiles obtained from the model where the surface valence does not vary (varies) with thickness shown as open (solid) markers with dashed (solid) lines.

While the above experimental model provides a good fit to the data, careful inspection of the TB calculations shown in Figure 26 shows that there is actually a small thickness dependence to the values of the surface/interface valence over the first few unit cells (as will be discussed later, the DFT results also indicate this). In order to account for this predicted variation in our own system, an extension to the experimental model incorporating a thickness dependence to the surface and interface valence values was considered.

The valence of each layer as a function of thickness predicted by the TB model was analyzed and found to be well described by a saturating exponential variation given by

$$V_{s,i}(t) = \gamma \left(1 - e^{-\frac{t}{L_{V_{s,i}}}} \right) + \delta \quad (4.5)$$

It should be noted that this formula represents two equations, one for the surface valence V_s and one for the interface valence V_i . These formulas represent the thickness dependence of the parameters V_{surf} and V_{int} in equation 4.2. The coefficients γ and δ are solved in a similar manner to the α and β coefficients; that is, by fixing the behavior at small and large thicknesses. These boundary conditions are $V_s(1) = V_i(1) = V_{mono}$, $V_s(\infty) = V_{surf}$ and $V_i(\infty) = V_{int}$ and the coefficients have the form

$$\gamma = e^{\frac{1}{L_{Vs}}} (V_{mono} - V_{surf}) + V_{surf} \quad (4.6.1)$$

$$\delta = e^{\frac{1}{L_{Vi}}} (V_{surf} - V_{mono}) \quad (4.6.2)$$

The first condition reflects the fact that at 1 u.c., the surface *is* the interface, while the conditions at $t \rightarrow \infty$ indicate that the values of the surface and interface valence should saturate after some characteristic variation L_{Vs} or L_{Vi} . The values of L_{Vs} and L_{Vi} in the theoretical data were determined to be 1.1 u.c. for both the surface and interface valence, though we allowed these values to be parameters in our fitting of the experimental data. Other layers within the material were analyzed and found to follow a similar variation as shown in Figure 29a. The length scales L_s and L_{int} appear to increase with sample thickness and potentially saturate. (Figure 29b).

Figure 29. a) Variation of the surface and interface layer valence with thickness as predicted by theory. As each layer follows similar thickness dependent trends, Equation (4.5) was employed and the resulting dashed lines are shown. Here V_{s-n} (V_{int-n}) refers to the valence of the n -th layer from the surface (interface). b) Thickness dependence of the surface and interface length scales L_s and L_{int} as determined by fitting the theoretical data in Figure 26 to Equation (4.2). Points below 5 u.c. have been omitted as there are a sufficient number of parameters to fit equation (4.2) exactly to the data, i.e. the error is zero.

Results of the fit using the thickness-varying surface and interface valence are shown in Figure 28 a) (solid lines). As can be seen, both solid and dotted fits provide nearly the same quality. However,

the error on the parameters is much lower using the thickness varying model. Figure 28 b shows a comparison between the layer dependent valence obtained from the two models, where the thickness dependent surface and interface layers are either constant (dashed lines and open points) or not (solid lines and filled points). Besides the surface and interface valence values, the profiles are quite similar. In fact, the agreement is within error for the larger sample thicknesses. The best fit values for the surface and interface valence are different by approximately 0.1 for both models.

The plane resolved valence obtained from the fit is compared to theory in Figure 30. The trend indicated by the experimental fit generally follows the theoretical predictions, with a difference of 0.1-0.2 between the predicted and fitted surface and interface values. The length scales L_s and L_{int} vary from theory by about 1 u.c. and may be related to the presence of charge transfer effects and oxygen vacancies not considered by the TB model. The thickness variations L_{Vs} and L_{Vi} are quite similar to the trends predicted by the TB model, with the surface and interface valence saturating after 2-3 u.c. Additionally, as we will show later, incorporating this thickness variation provides good agreement with DFT calculations.

Figure 30. Comparison of the experimentally determined layer by layer valence (solid points) with TB calculations (open points).

While some small differences from the theoretical calculations are apparent, we find reasonable agreement between the model and theory and that the trends indicated by theory can be used to model the change in valence in this system. Having discussed the results of the model, we will now examine the physical mechanisms responsible for the observed trends in more detail.

Charge reconstruction and the polarization catastrophe

One reason for this observed charge separation lies in an inherent electrostatic instability of the material in its unaltered state. The basis of the perovskite unit cell ABO_3 is comprised of alternating layers of AO and BO_2 atoms (Figure 6, Chapter 2). If one sums the net charge within each plane, the result is not necessarily zero (although the total charge in the *unit cell* is zero as required by charge neutrality). In what follows, we make the approximation that the bonding is fully ionic. Then the charge of each atom is given by their formal valence states.

Summing the charges of the atoms within each plane of LSMO gives $0.7La^{3+} + 0.3Sr^{2+} + O^{2-} = +0.7$ for the (La,Sr)O planes and $Mn^{3.3+} + 2O^{2-} = -0.7$ for the MnO_2 planes. A similar calculation for STO yields $Sr^{2+} + O^{2-} = 0$ for the SrO planes and $Ti^{4+} + O^{2-}$ for the TiO_2 planes.

Considering the LSMO/STO interface, as shown in Figure 31 below: the LSMO crystal is composed of layers of alternating positive and negative charge density which abruptly changes to charge neutral planes in the STO planes. This is known as polar discontinuity. In what follows, I present a simple toy model in order to emphasize the essential physics of this phenomenon.

The electric field between two atomic planes can, as a simple approximation, be thought of as the same as the electric field between two infinite and continuous sheets of charge. Using Gauss's law, the electric field is found to be constant between the charge sheets and zero outside. The electric field of a single charge sheet i at a distance d_i from the origin is given by⁸⁴.

$$\vec{E}_i = \frac{\sigma_i}{2\epsilon} \text{sign}(z - d_i) \hat{z} \quad (4.7)$$

where ϵ is the static dielectric constant of the material and σ_i is the charge density. Here, the sign function is simply used to indicate that the electric field (assuming a positive charge density) always points outward from the sheet of charge. The total electric field inside the material is then given by the sum of the contributions from each plane

$$\vec{E} = \sum_{i=1}^{2N} \vec{E}_i \quad (4.8)$$

To determine the electric potential across the material, we set the film/substrate interface ($z = 0$) as the reference and integrate to some distance z from the interface using a path along the z direction.

$$V = \int_0^z \vec{E} \cdot \hat{z}' dz' = \sum_{i=1}^{2N} \frac{\sigma_i}{2\epsilon} |z' - d_i| \Big|_0^z = \sum_{i=1}^{2N} \frac{\sigma_i}{2\epsilon} (|z - d_i| - |d_i|) \quad (4.9)$$

It can be seen that the potential diverges for increasing thickness since we are adding increasingly many positive terms together. Alternatively, one could consider the alternating planes of charge to be similar to a string of serial capacitors, in which the voltage across the circuit adds linearly with the number of capacitors. Such a situation is clearly electrostatically unstable and the system must respond in some manner to accommodate this.

This instability is called the polar catastrophe and while most closely associated with the LAO/STO interface⁸⁵, can occur in numerous other systems. How the system responds is somewhat of a topic of debate⁸⁶ and will actually vary with the material system. For example, while the LAO/STO interface will be seen to exhibit a 2-dimensional electron gas or accumulation of interfacial oxygen vacancies (depending on the interface termination), materials like MgO (111) can undergo a crystallographic reconstruction. While an electronic reconstruction can always occur, other scenarios can be more energetically favorable⁸⁷.

In the case of LSMO/STO, the results indicate that the energetically favorable solution is to offset the diverging potential by a redistribution of the Mn valence electrons. It is worth noting that in addition to the interface, material *surfaces* can also exhibit the same

Figure 31. Supercell of LSMO/STO used in the DFT calculations showing the polar layers of (La,Sr)O (+0.7e) and MnO₂ (-0.7e). The apical oxygen is indicated at the top of the structure by the arrow.

effect⁸⁷, requiring some compensating charge reconstruction. Qualitatively, this electric potential pulls electrons to the interface in order to neutralize the charge. However, some problems with this toy model are evident in that the charge needed to offset the divergent potential is greater than the result of $1 e^-$ predicted by the polar catastrophe model and that additional mechanisms need to be considered.

Density Functional Theory Calculations

While the above model fits the data well and provides good agreement between experiment and theory, neither experiment nor the TB calculations say much about the origin of the observed valence change. In order to learn more about the physical mechanisms responsible for the effects observed in this system, DFT simulations of LSMO films of varying thickness were performed. The full computational details are discussed in the appendix.

Early on it was realized that performing calculations with an LSMO/STO supercell with MnO_2 termination (i.e. the top Mn oxygen octahedron is not completed and missing its apex, see the oxygen at the top of Figure 31) resulted in a surface valence of 3.0, in complete disagreement with the experimental results. A cell with a completed octahedron (surface oxidation) was needed in order to achieve agreement. This result is not entirely surprising. A Mn atom surrounded by a completed octahedron will tend to have a greater valence because more of its electrons are shared with neighboring oxygen atoms than would be the case if one oxygen was missing. As stated before, our films are cooled down in a high oxygen pressure environment to discourage oxygen desorption, so an oxidized surface seems likely. Our results in what follows refer to the latter scenario.

The overall valence difference between the film surface and interface as a function of thickness is summarized in Figure 32. The grey and blue bars show the DFT predictions and the purple bar shows the experimental results (the blue bar will be discussed shortly). A clear thickness dependent trend is noted here. When the films are very thin (2 u.c.), DFT predicts a net valence difference of $0.5 e^-$ (grey bars), whereas for the case of 8 u.c. the valence difference is close to $1.1 e^-$. A similar trend is seen in the experimental data. Thus the thickness dependence of the layer valence predicted by the TB calculations is also reproduced by DFT.

As mentioned previously, DFT predicts a valence change of more than 1 electron across the film contrary to the results of the polar catastrophe model. To explain this, octahedral rotations (here referred to as antiferrodistortive or AFD due to the particular type of rotation) needed to be taken into account. The blue bar in Figure 32 shows the valence difference across the film when the octahedra are fixed and cannot move. These calculations show a much lower valence difference than the experiment, but with an overall difference of less than $1 e^-$, as expected. This enhancement due to AFD is because the rotations increase the Mn-O orbital overlap, leading to increased charge transfer between sites, similar to earlier results reported for the LAO/STO system^{88,89}. In order to fully explain the experimental results, these rotations have to be considered.

Figure 32. Comparison between the net valence difference between the surface and interface as a function of film thickness for DFT considering and neglecting AFD contributions (gray and blue bars, respectively) and from the experimental model (purple bar).

Given the agreement between experiment and both sets of theoretical calculations, the next question is to ask whether or not the observed change in valence results in an overall electrostatically stable crystal, i.e. cancels the effects of the polar catastrophe. To answer this, the layer dependent electric potential across the films was computed using DFT (Romero group, WVU). In order to obtain the electrostatic potential the 3D local electronic potential is computed including the exchange correlation contribution, then an integration along the z-axis is performed and a moving average, of one unit-cell window, is applied. The results are shown in Figure 33a.

Figure 33. a) Electric potential per layer for several thicknesses of LSMO. b) Average electric field across the sample as a function of LSMO film thickness.

It can be seen that the potential is nonlinear near the film boundaries but approximately linear within the material and that the slope of this linear region decreases as the sample is made thicker, suggesting that the electric potential decreases. To confirm this, the potential across the sample was fitted to a linear function (neglecting the nonlinear surface contribution) and the slope, or the averaged electric field, is shown in Figure 33b. While the 2 u.c. sample has a finite average potential of 500 meV/Å (note that some potential difference across the crystal is allowed but cannot diverge with increasing thickness), the potential drops to nearly zero for larger thicknesses. This trend indicates that as the sample becomes thicker, the potential created by the polar layers becomes

stronger and forces a charge reconstruction, which makes the layers electrically neutral. This effect saturates at larger thicknesses and is responsible for the thickness dependence of the valence change observed from our modeling.

Having confirmed that the charge redistribution cancels the divergent potential, we next examined the effect of this redistribution on the material's electronic properties. Figure 34a shows the layer and orbital resolved DOS for an 8 u.c. film. First, we observe a nonzero DOS at zero energy (the Fermi level) for the e_g spin up bands but not for the spin down case. This difference implies half-metallicity, as expected for this system. Additionally, it is noted that the conduction band minimum shifts to progressively lower energies as we move from the surface to the interface, indicating an accumulation of carriers at the interface, in agreement with experiment and the TB model. Since the conducting spin up states are metallic and as such delocalized across the sample, this accumulation of charge instead comes from the gapped spin down states. This process is schematically illustrated in Figure 34b. The polar LSMO/STO interface creates a band bending at the interface that leads to the accumulation of charge (shaded regions) which increases with sample thickness. We note that the STO layer also contributes to this interfacial 2D electron gas, although the carrier density is much smaller and has a value of $6.0 \times 10^{12} \text{ cm}^{-2}$. This value is at least 2 orders of magnitude smaller as the one found at the LAO/STO and GTO/STO interfaces^{89,90}.

Figure 34. a) Layer and orbital resolved density of states for an 8 u.c. thick LSMO film on STO. b) Cartoon of the charge transfer process in LSMO as a function of thickness. The vertical segmented line represents the Fermi level, the blue filled line represents the first conduction band of STO while the gray filled lines represent states from LSMO layers. Different dashed lines represent the slope of the

electrostatic potential for different LSMO-layers deposited. Finally, blue arrows depict the charge transfer from the surface to the interface.

Oxygen vacancies

The final contributing factor to an alteration of the system's charge state lies in crystallographic point defects, specifically oxygen vacancies (OV). While the Mn d electrons will normally bond with neighboring oxygen atoms, an oxygen vacancy will cause the electrons to remain localized on the Mn site, decreasing the valence. Spectroscopically, this is indicated by the presence of Mn²⁺ species and appears as a peak on the pre-edge of Mn L-edge absorption spectra⁹¹ although seeing that feature requires a significant amount of them. Dilute OV can be incredibly hard to detect and effective methods of doing so are an ongoing area of research. The combinatorial fit results typically had a small contribution of Mn²⁺ of a few percent, so it is likely that OV play some role in the observed results, although less so than the mechanisms discussed above. OV have been observed to accumulate at the interface⁹², and the increased positive charge at the interface will require more carriers to be moved from the surface in order to compensate it.

5. Concluding Remarks

I have presented in this dissertation the development of a model to experimentally determine the layer by layer valence within a material. Here, the model has been applied to LSMO in order to learn about the effect of the polar interface on the electronic properties of the material. The model here can be used to study the depth dependent valence in other systems and in principle can be used to learn a variety of phenomena outside of magnetism such as ferroelectric dead layers⁹³, superconductivity⁹⁴.

The next step from here is to link these results to the material's magnetism. Very few methods exist to determine the magnetic depth profile in a film. One proven method is polarized neutron reflectometry which has had great success at learning about the depth dependent magnetism in many materials^{95,96}. A cartoon of the experimental technique is shown in Figure 35a. Here, the sample angle is scanned and the reflected intensity is measured for both spin up and spin down neutrons (with intensities given by R^{++} and R^{--}). The sample angle is typically converted to the out of plane momentum transfer q_z . Some preliminary results taken at the NG-D reflectometer at the National Institute of Standards and Technology Center for Neutron Research are shown in Figure 35b (symbols) along with the fits to a model (solid lines)⁹⁷.

Figure 35. a) Cartoon of a neutron reflectivity measurement. b) Reflected spin up (R^{++}) and spin down (R^{--}) intensity measured as a function of the out of plane momentum transfer q_z . c) Modeled depth profile of nuclear SLD (black) and magnetic SLD (red) as a function of distance from the LSMO/STO interface.

Figure 35c shows the density and magnetization profiles extracted from fitting the reflectivity curves. These curves are expressed in terms of the nuclear and magnetic scattering length densities (SLD) which are parameters that determine how strongly a nucleus or magnetic moment scatters

and neutron and the density of scatterers. The nuclear SLD is indicative of the material density and the magnetic SLD is proportional to the magnetization. These results show that the magnetization is enhanced at the interface and suppressed at the surface, consistent with the literature. However, the sample measured here is 16 nm (roughly 40 u.c.) which is much larger than the thicknesses discussed in this dissertation. It is difficult to apply PNR to very thin films because neutron sources suffer from a dropoff in intensity at high q_z values which limits the angular range over which the data can reliably be measured; because the intensity scales as approximately q^{-4} and the period of the reflectivity oscillations lengthens as the film thickness decreases⁹⁵, it is difficult to measure a wide enough q range in order to accurately determine the structure of very thin films.

As PNR does not work well for the film thicknesses discussed here, another possibility is to use an extension of the model discussed in this work to include magnetism, using magnetic circular dichroism (MCD). Here, MCD is defined as the difference in XAS taken using left and right circularly polarized light (Figure 36a) and is indicative of the magnetization⁵². Some preliminary measurements taken at the Advanced Photon Source beamline 4-ID-C are shown in Figure 36. Similar to before, dichroism can be obtained in surface sensitive TEY mode (Figure 36a-b) and bulk sensitive FY mode (Figure 36b-c). This beamline also allows the simultaneous acquisition of soft X-ray reflectivity (Figure 36d-e) which can also provide detailed magnetic information on the material and will be discussed further below.

An advantage to this method is that valence and magnetism information can be obtained simultaneously. However there are some difficulties in using L-edge fluorescence due to overabsorption, which distorts the true peak shape and makes valence determination difficult⁹⁸. Additionally, since the probability of fluorescence vs Auger emission increases with increasing nuclear charge Z^{52} , a low Z element like Mn has a relatively weak FY signal, which increases the noise level and makes quantifying the magnetic moment in very thin films difficult.

Figure 36. a) and b) XAS and XMCD for TEY mode. c) and d) XAS and XMCD for FY mode. e) and f) resonant X-ray magnetic scattering (discussed further below). The top panels show the absorption/scattering of the material for left and right circularly polarized light, while the bottom panels show the difference between the two spectra. We note that while the XMCD and XRMS in panels b, d, and f look similar, the XRMS contains different magnetic information than the XMCD.

Another difficulty is that the way the magnetic moment is determined from dichroism is by use of a set of equations called sum rules. These formulas determine the expectation value of the quantum mechanical magnetic moment operator (in Bohr Magnetons) and are given as integrals over the L_3 and L_2 peaks by the following formulas^{99,100}:

$$\langle L \rangle = -\frac{4}{3} h_d \frac{\int_{L_3+L_2} dE (\mu^- - \mu^+)}{\int_{L_3+L_2} dE (\mu^- + \mu^+)} \quad (5.1)$$

$$\langle S + 7T \rangle = -h_d \frac{6 \int_{L_3} (\mu^+ - \mu^-) dE - 4 \int_{L_3+L_2} (\mu^+ - \mu^-) dE}{\int_{L_3+L_2} (\mu^+ + \mu^-) dE} \quad (5.2)$$

Here, L and S are the orbital and spin angular momenta, T is the magnetic dipole operator (which quantifies the asphericity in the magnetic moment), and h_d is the number of holes in the d band, which can be determined from valence measurements. Note that in order to use these formulas, the continuum background (equation 3.9) needs to be subtracted from the spectra. These formulas work for a number of systems but fail for elements Mn and other elements with similar electron configurations. The reason is that the original derivation assumes pure L_3 and L_2 edges, i.e. they do not overlap. However, multiplet effects discussed in chapter 3 create a substantial amount of mixing – transitions from the $2p_{1/2}$ state are mixed with those of the $2p_{3/2}$ state, making separation of the contributions impossible¹⁰¹, although some empirical correction factors have been devised¹⁰². Regardless of this issue, the error is systematic and therefore *qualitative* information can be extracted from sum rules calculations to allow comparison between the relative magnetic moments measured on similar systems.

Figure 37 shows the relative magnetization calculated from XAS as a function of thickness for both TEY and FY mode. Similar to the valence, the magnetization can be seen to decrease with decreasing thickness, but here the magnetization drops to *zero* (or enters noise) for very thin films, in contrast to the trend observed in valence. Surprisingly, the XMCD shows a greater asymmetry for TEY mode than FY, which at first glance would suggest that the film's surface magnetization is larger than that of the bulk, in contrast to our PNR results. However, this may also be a result of overabsorption effects present in FY which can attenuate the peak intensity in a somewhat unpredictable manner, and therefore could reduce the asymmetry of the spectra as well.

Figure 37. Relative magnetization for LSMO films as a function of thickness obtained from XMCD taken in TEY (black) and FY mode (red).

A third way is a technique using reflectivity known as X-ray magnetic scattering (XRMS) (Figure 36 e-f). The technique is similar to XRR and PNR in that the reflectivity of the sample is measured as a function of energy or angle, but differs in that the reflectivity is at a resonance. Analysis of this data is difficult, but can be done using a similar transfer matrix formalism to XRR and PNR to model the polarization dependent reflection coefficients. From this analysis one can determine the layer by layer magnetization in a material as demonstrated by Freeland *et al* for LSMO¹⁰³¹⁰⁴ although the analysis can be significantly more complex than other reflectivity methods like PNR and XRR.

Figure 35d-e shows some preliminary XRMS measurements and efforts to model this data are currently underway.

To conclude, this dissertation details the study of the depth dependent properties of thin film LSMO in order to gain further insight into the physical origins of the dead layer. As I discussed in Chapter 2, our first step was to realize high quality growth of these films. To do so, a substrate preparation and DI water treatment process was developed in order to achieve flat single-termination surfaces which encourage layer-by-layer growth. Then, characterization was undertaken to verify the quality of the films.

Having characterized our films, we then performed XAS measurements in two different detection modes in order to learn about thickness dependent changes in the average and surface material valence. The work presented here adds the novel approach of the error vs. valence scatterplots, which allowed for a much more thorough assessment of uncertainty and increased our confidence that the fit solution we obtained was unique. After developing a way to accurately determine valence, we studied its thickness dependence in our films. While the average valence was relatively unaffected, a raised surface valence was noted for our films indicating an overall positively charged surface.

In order to learn more about the origins of this trend, two different sets of theoretical calculations were performed. These results suggested a charge separation across our films. The TB model calculation motivated the development of an experimental model; by fitting our data to this model, the layer-dependent valence was extracted in order to compare to theory. From DFT calculations, the physical origin of this change in valence was uncovered and found to be at least predominantly related to the polar discontinuity at the LSMO/STO interface. The change in valence was therefore the effort of the system to relieve the inherent electrostatic instability in the crystal. Additionally, we found good quantitative agreement between our results and the predictions of theory.

The experimental model developed in this work shows promise to study depth dependent material properties outside of LSMO or even ferromagnetic materials. Future efforts will be undertaken in order to extend the model to magnetic circular dichroism in order to simultaneously assess the depth dependence of magnetism and valence, which will provide a fuller picture of the physics of the magnetic dead layers.

Finally, some preliminary work has been conducted in depth profiling the magnetism of our films in order to relate to our valence studies. These results in a similar manner show that the magnetism of the film surface and interface are modulated from that of the film bulk – however, the length scales do not precisely correspond with the observed trend in valence. This is explicitly shown in Figure 38. Here it can be seen that the length scales of variation in valence are much smaller than those of the magnetization (although both measurements show changes at the film surface/interface). Therefore, other factors not considered by our valence modeling such as depth dependent strain and oxygen deficiencies may affect this behavior.

Figure 38. Comparison of the variations of the nuclear and magnetic SLD (left axis) determined from PNR and the Mn valence (right axis) determined from fitting the thickness dependent XAS data.

To fully elucidate the connection, the influence of material properties such as strain and stoichiometry on the depth dependent valence and magnetism must be established. Some work has already been undertaken in understanding the role of oxygen vacancies in affecting the magnetism. The simplest study would be to look at the link between a material's saturation magnetization and the oxygen deficiency, as shown in Figure 39. Here, 100 mTorr corresponds to the standard recipe to grow the films as discussed in Chapter 2.

Figure 39. Saturation magnetization of LSMO films at 20K as a function of growth pressure.

The results are somewhat striking. It is seen that for several pressures lower than 100 mTorr, the magnetization decreases as one would expect from removing the oxygen molecules that link the magnetic atoms in the material. However below 10 mTorr, the magnetization *increases*! One possibility, as has been shown in LaMnO_3 ¹⁰⁵ is that while oxygen vacancies decrease the hopping between Mn^{3+} and Mn^{4+} sites, they *also* create a number of Mn^{2+} sites. In a very similar fashion, hopping can occur between Mn^{2+} and Mn^{3+} sites which gives once again rise to spin-polarized hopping and increases the magnetism. Therefore, oxygen vacancies may actually be useful in controlling the magnetism in very thin films. X-ray absorption measurements like those discussed in Chapter 3 will be vital in establishing the relative ratios of different Mn valence species and their relation to changes in film magnetization.

The depth dependent *magnetic* properties in oxygen-poor films become quite interesting as well. Figure 40 shows a fit to PNR data taken on a 10 mTorr grown sample, measured in a low magnetic field after zero-field cooling. After trying various models, the best fit was obtained by considering a scenario where the spins rotate between the material interface and surface much like is seen in exchange spring systems^{106,107} and has been observed in LSMO previously although the mechanism wasn't established¹⁰⁸. The surprise here is that this occurs in a single material rather than the traditional FM bilayer exchange spring system which may point to the clustering of oxygen vacancies in a particular part of the material which divides it into high and low coercivity regions which then couple to each other. This effect is not observed in a 100 mTorr sample (which corresponds to nearly no oxygen deficiency).

Figure 40. PNR fit results for an LSMO film grown in 10 mTorr. The magnetic angle is displayed on the right axis. In order to fit the data, two domain types had to be considered where the magnetization rotated in opposite directions. The rotations are slight, only a few degrees.

Another puzzle is that many of these magnetic films display some sort of exchange bias, defined by a shift of the magnetic hysteresis loop so that it is no longer symmetric about $M=0$ (i.e. it takes more energy to magnetize the material in one direction as opposed to the other). Figure 41 shows both an example of exchange bias as well as the pressure dependence of this effect. The factors that influence exchange bias in these films are not yet clear, although it has been observed by other groups as well¹⁰⁹. As many groups have indicated the possible presence of an antiferromagnetic region in LSMO (usually the surface)^{103,110,111,112}, this may point to exchange coupling between the normal FM phase of LSMO and an emergent AFM phase.

Figure 41. a) Example of exchange bias in a film grown in 100 mTorr oxygen. b) Exchange bias in a series of 16nm LSMO films as a function of growth pressure.

These results indicate that the interplay between the various material parameters in these thin film systems is quite complicated, and that these factors will need to be considered simultaneously. Manipulating these factors may even cause different magnetic phases such as antiferromagnetism to stabilize which further complicates the analysis. The preliminary results discussed in this thesis have given us a window into what is really going on inside the magnetic dead layer. Rather than being truly “dead”, the dead layer appears to be quite alive with competing magnetic order that is influenced by a number of material properties. In order to control or eliminate the magnetic dead layer, careful studies will need to be undertaken in the future in order to thoroughly understand the interplay between various material parameters, atomic valence, and emergent magnetic order – a formidable challenge but one that promises to be rewarding.

Appendix

Determination of error bars

The determination of the error bars on valence estimates contains many details and has been reserved for a separate discussion. There are two types of error that must be quantified – one is on the experimentally obtained valence itself (through the combo fit) and the other is the error in the layer by layer valence from the experimental model, which depends on the parameter error in the fitting. Let us first examine the valence obtained from the combo fit, reported in Figure 25.

The question is what we expect the accuracy of the experimentally determined valence to be. One possible way to derive the error bars for the experimentally obtained valence is from the uncertainty in the fit parameters which would subsequently be fed into the propagation of error formula for the weighted average valence (and this is in fact part of the process). However, error bars derived in this way are only reflective of the uncertainty in the fit, that is, they give no indication on the *accuracy* of the valence estimate.

How do we know what the true value of the valence is? Of course, if the combination of references completely reproduces the spectrum, we would expect the valence estimate to be very accurate. Likewise, if the references do not reproduce the spectral features, the estimate should be very poor. As a possible method of evaluating this accuracy, the mean squared error (MSE) was collected for the fit to each possible combination of references (approximately 15,000), as well as the valence for each fit. In principle, the most accurate fits should have the lowest sum of squares value and be clustered around some value of the valence which could be thought of as the true value and spread out away from this as the fit quality worsens. This cluster need not be symmetric.

A scatter plot of the goodness of fit (here the value of the MSE) vs. valence from the fit for the 8 u.c. thickness (taken in TEY mode) is shown in Figure A1. The dashed line indicates the position of the valence obtained from the best fit. As can be seen, there is a cluster of points around the best fit value of 3.43 that spreads out as the MSE increases. It is noted that the y axis is plotted on a logarithmic scale, showing that the fits quickly worsen as one moves away from the best fits in the set.

Figure A1. Scatterplot of the goodness of fit vs valence obtained for each fit to each combination of references in the database. The red box shows the cluster of best fits that were analyzed to produce the data points in Figure 25. The blue line denotes the cutoff designating the end of the cluster. The vertical orange line denotes the best fit value out of all the set. Note that the y axis is plotted on a log scale.

To evaluate the error bars, we wish to determine the spread of the good quality linear combination fits of the valence around the best value obtained with the references. As a metric for what constitutes a good determination of the measured valence, we designated a cutoff for the cluster, below which all fits will be considered and above which all fits will not (if the fit is poor then it should not be included in the analysis). There is some arbitrariness to this method but testing the resultant valence and error bars for slight adjustments in the cutoff (including or discarding 1-2 more fits) produced little change in the results. The idea here is to assess the variation in the results that we expect to be accurate. Once the cutoff is set, the mean and standard deviation of the cluster are computed. These are the values of the valence and error bars reported in Figure 25.

Additionally, the error from the linear combination fit itself (described above) should be taken into account as this too will affect the accuracy of the valence estimate. The valence is calculated as a weighted average by

$$V_{avg} = \frac{\sum_i a_i V_{ref,i}}{\sum_i a_i} \quad (A.1)$$

where i runs over all of the references used in the fit and the a_i are the coefficients for each of the references. The error in the linear combination fit parameters δa_i are the standard parameter errors reported from the fit. These results were then input into the standard propagation of error formula as

$$\text{error}(\text{fit}) = \sqrt{\sum_i \left(\frac{\partial V_{\text{avg}}}{\partial a_i} \right)^2 \delta a_i^2} \quad (\text{A.2})$$

Combining the results, the error bars reported on the plots in the main text are then calculated as

$$\text{error}(\text{valence}) = \text{error}(\text{scatter plot}) + \text{error}(\text{fit}) \quad (\text{A.3})$$

The error from the scatter plots is usually 1-2 orders of magnitude greater than the error from the fit itself and thus is the dominant contribution to the uncertainty.

Error bars for the layer valence

Upon fitting the data in Figure 25 to the layer dependent model in Chapter 4, the parameter error bars can be obtained from the output of the fit. However, these only relate to the error on the parameters in the equations, and in the case of V_{surf} and V_{int} , the error on the layer valence at the material boundaries. What we would like to do is to compute the error on the valence within each layer as shown in Figure 28b, for example.

Applying the propagation of error formula to layer dependent model equation 4.4 gives the result

$$\begin{aligned} \delta V(z)^2 = & \left(\frac{\partial V(z)}{\partial V_{\text{surf}}} \right)^2 \delta V_{\text{surf}}^2 + \left(\frac{\partial V(z)}{\partial V_{\text{int}}} \right)^2 \delta V_{\text{int}}^2 + \left(\frac{\partial V(z)}{\partial V_{\text{mono}}} \right)^2 \delta V_{\text{mono}}^2 + \left(\frac{\partial V(z)}{\partial L_{\text{surf}}} \right)^2 \delta L_{\text{surf}}^2 \\ & + \left(\frac{\partial V(z)}{\partial L_{\text{int}}} \right)^2 \delta L_{\text{int}}^2 + \left(\frac{\partial V(z)}{\partial L_{V_s}} \right)^2 \delta L_{V_s}^2 + \left(\frac{\partial V(z)}{\partial L_{V_i}} \right)^2 \delta L_{V_i}^2 \end{aligned} \quad (\text{A.4})$$

which is then evaluated for each layer. The above formula is for the case when the surface and interface valence are allowed to vary with thickness. If those parameters are set to be thickness independent, then the result is the same with the final two terms in the square root dropped.

Power law model

It is possible that rather than varying exponentially, the valence changes in a power law fashion from its bulk value. To parameterize this change, we introduce the piecewise power-law function

$$P(z, n) = \begin{cases} z^n & z > 0 \\ 0 & z < 0 \end{cases} \quad (\text{A.5})$$

Considering both surface and interface contributions, a similar form to Equation 4.2 is developed

$$V(z) = \frac{V_{\text{bulk}}}{2} [1 - \alpha P(-(z - L_{\text{surf}}), n_{\text{surf}})] + \frac{V_{\text{bulk}}}{2} [1 - \beta P(z - (z_{\text{int}} - L_{\text{int}}), n_{\text{int}})] \quad (\text{A.6})$$

with the coefficients α and β determined algebraically from the same boundary conditions as before. Figure 6 b) in the main text shows the comparison between the power law variation Equation A.6 and the exponential variation Equation 4.2. In this case, the characteristic length L refers to the distance from the surface/interface where the valence returns to its bulk value, rather than varies by $1/e$ as in the exponential fits.

Fitting was performed similar to those shown in Figure 28 in the main text and are shown in Figure A2. While the fits appears to be reasonable, the obtained fitted values for the parameters L_{int} and n_{int} were 1445.1 ± 198.2 u.c. and 773.8 ± 103.9 respectively. These results with the large error suggest a high degree of coupling between the length scale and power parameters and that the model is likely overfitting the data. Qualitatively, this issue means that adjusting the length scale and the exponent parameters can create many similar, albeit not identical variations between the material

bulk and surface/interface which makes determining the correct variation difficult. For this reason, the exponential variation was chosen instead.

FIG. A2. Valence obtained from the linear combination fits (solid points) and best fit using the layer dependent valence model (dashed lines) with the power law variation. The horizontal dashed line indicates the bulk Mn valence for LSMO of 3.3.

Role of the probing depth in the depth dependent fits

As mentioned in Chapter 4, the density of the material can have a significant impact on the probing depth for TEY and there can be variation in its values between systems. In order to determine the implications this has for our model, we ran the fit for a variety of values for the L-edge probing depth. While in the manuscript this value is fixed at 2.6 nm, the figure below shows the fit results for when the probing depth is fixed at different values between the range of 1.5 – 4.5 nm. We believe this range is sufficient to demonstrate the sensitivity of the model due to possible variation in probing depths due to material dependent parameters.

Figure A3. Fitted layer dependent valence for 8 u.c. with the probing depth λ_0 fixed at different values indicated by the legend.

Shown in Figure A3 are the fitted valence profiles for 8 unit cells for each value of the probing depth selected. It can be seen that there is some variation between the profiles, most pronounced at the surface and interface (less so in the bulk of the film) but the overall trend of a raised surface valence and lowered interface valence with similar characteristic lengths of variation can be seen regardless of the value of the probing depth. The overall variation between the surface/interface layer valences between fits is roughly 0.15. We also note that the fits begin to become poor when the probing depth is raised above 3.5 nm. Therefore, the model is most sensitive to the difference in probing depths between the two detection modes and is relatively insensitive to experimental variations of the probing depth.

DFT Calculation Details

We have performed ab-initio calculations in the framework of Density Functional Theory (DFT) as implemented in the Vienna Ab-Initio Simulation Package (VASP)^{113,114,115,116}, where the pseudo-electron wave functions are described through the Projector-Augmented Wave (PAW) method^{117,118}. We have used a plane-wave energy cutoff of 550 eV to ensure good convergence of values for total energies and ionic forces. The exchange-correlation energy was described using the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof exchange correlation functional revised for solids (PBEsol)¹¹⁹. The electronic configuration of elements pseudopotentials are: 10 electrons for Sr ($4s^2 4p^6 5s^2$), 11 for La ($5s^2 5p^6 5d^1 6s^2$), 12 for Ti ($3s^2 3p^6 3d^2 4s^2$), 13 for Mn ($3p^6 4s^2 3d^5$) and 6 for O ($2s^2 2p^4$). We have used the LDA + U approximation within the Liechtenstein formalism to increase the localization of d-electrons in Mn atoms. The values of U and J that we have imposed are 2.7 and 1.0 eV, respectively. We have discretized the reciprocal space with a Monkhorst-Pack k-point grid of $8 \times 8 \times 1$ for the thin-films and $6 \times 6 \times 4$ for the bulk structures with 20 atoms per unit cell. The thin-film structure consists of 5 cubic layers of SrTiO_3 (STO), where we have fixed the first layer to simulate the bulk while the remaining 4 layers and those of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) were set free to relax. On top of the 5 layers of STO, we have put 2, 4, 6 and 8 layers of LSMO and we have included extra oxygen atoms at the surface to complete the Mn octahedron. To avoid artificial effects caused by the interaction with periodic images, we have imposed a 16 Å vacuum perpendicular to the LSMO surface. We have performed atomic relaxation until the forces were no larger than 1 meV/Å. We have used the virtual crystal approximation (VCA) to model Sr doping¹²⁰.

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