Transition metal oxides under X-ray vision

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Transition Metal Oxides under X-ray vision

Georgios Araizi Kanoutas
Transition Metal Oxides
Under
X-ray Vision

ACADEMISCH PROEFSCHRIFT
ter verkrijging van de graad van doctor
aan de Universiteit van Amsterdam
op gezag van de Rector Magnificus
prof. dr. ir. K.I.J. Maex
ten overstaan van een door het College voor Promoties ingestelde commissie,
op vrijdag 16 oktober 2020, te 10:00 uur

doord

Georgios Araizi Kanoutas
geboren te Thessaloniki
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Summary

In this thesis, thin films of transition metal oxides are studied using a variety of X-ray spectroscopy techniques. Complex oxide heterostructures consist of interlocking perovskite building blocks that are combined at the unit cell level. In this way, an unprecedented control over the physical properties of the material is realised. Specifically, through appropriate choice of material combinations and layer thicknesses, an individual tuning of the electronic, orbital and spin degrees of freedom is achieved. This ability, combined with the reduced dimensionality of the systems, promotes the role of the interface which often facilitates emergent physical properties. In a number of material combinations, these properties are completely absent in the parent compounds. In this research, novel, emergent electronic and magnetic states of matter are investigated. The main experimental findings concern three different material systems, each of which is discussed in its own thesis chapter.

The first part examines the effect of interfacial band offset in a material combination in which a large electronegativity mismatch is realised, namely the isopolar LaCoO$_3$ | LaTiO$_3$ interface. This is found to result in an interfacial electron transfer from Ti to Co, an effect which can be exploited to achieve nanoscale control over the number of d electrons in Co via interfacial engineering. By varying the LaCoO$_3$ layer thickness, the number of interfaces and the presence and thickness of a break-layer, the conversion of the valence of Co ions in LaCoO$_3$ through charge transfer can be finely controlled, leading to average valencies that range from d$^6$ to d$^7$ while preserving the perovskite structure throughout. The valence transformation goes hand in hand with increased spin polarisation of the d$^7$ Co state, leading to a significant enhancement of the paramagnetic moments which can reach 1.2 $\mu_{\text{Bohr}}$ per Co atom, as inferred from element specific magnetometry. These results on the LaCoO$_3$ | LaTiO$_3$ interface illustrate nicely the efficacy of O2p-band alignment as a guiding principle for property design in complex oxide heterointerfaces and the ability of soft and hard X-ray spectroscopies to track the transition metal valence, orbital occupancy and magnetism in a site-specific and highly sensitive manner.

The second part discusses interfacial charge transfer driven ultimately by a different phenomenon: that of avoiding a polar catastrophe. In ultrathin (polar) LaMnO$_3$ films, grown on (non-polar) SrTiO$_3$ substrates, the polarity mismatch between the
two perovskites felt most strongly at the interface and leads to strong electron doping of the LaMnO$_3$. This is accompanied by the emergence of thickness-dependent Mn ferromagnetism. Using a combination of valence-sensitive X-ray techniques, a systematic reduction of the Mn valence was observed in thinner LaMnO$_3$ films, ranging from 2.9+ for 10 unit cells to 2.35+ for 2 unit cells. This result along with complimentary electron energy loss measurements, argue for the accumulation of electron-rich Mn$^{2+}$ ions at the abutting interface with the SrTiO$_3$ substrate. Although, ultra-sensitive, element-specific, soft X-ray magnetometry reveals ferromagnetic Mn moments for all thicknesses measured, there is a significant enhancement of the remanent Mn magnetic moments above a “critical” thickness of 6 unit cells. The experimental data do not support a straightforward self-doping mechanism in the LaMnO$_3$ as a response to the incipient polar catastrophe. A combination of oxygen vacancy formation, substrate-imposed strain and heavily overdoped interfacial LaMnO$_3$ magnetically dead layers looks to lie behind the relative lack of remanent magnetisation in thinner LaMnO$_3$ films on SrTiO$_3$.

The third and final part of this thesis investigates the metal-insulator transition in VO$_2$, which occurs close to room temperature, making this system a promising candidate for future applications. Recent advances in the growth of the VO$_2$ thin films on nanosheets, enable X-ray spectroscopy experiments to be carried out in transmission. Specifically, this chapter relates how - by using a combination of X-ray absorption, linear dichroism and lensless coherent imaging techniques - the electronic, structural as well as the real-space texture of phase segregation across the transition can be tracked as a function of temperature. Firstly, the high-quality of the growth that enables control over the in-plane orientation and orbital occupancy in VO$_2$ was systematically shown to be evident in temperature-, polarisation- and angle-of-incidence-dependent X-ray absorption measurements. This argues for the suitability of these samples for imaging experiments via lensless imaging techniques using coherent soft X-rays, such as holography using extended reference auto-correlation by linear differential operator (HERALDO). This experiment was carried out through a sample mask and revealed the real-space relationship between the metallic and insulating phases during warming up through the temperature driven insulator-metal transition. The main findings point to the initial nucleation of the metallic phase along directions perpendicular to the rutile c-axis of the VO$_2$, followed by growth of these stripe-like metallic domains along the VO$_2$ dimer direc-
Summary

tian. These experiments constitute a first and successful feasibility-test as regards
our ambition to conduct the experiment in ultra-fast (pump-probe) mode and thus
track a Mott-insulator-metal insulator transition in a complex oxide in both space
(nm) and time (fs): the Mott-MIT movie.
Samenvatting

Transitie Metaal Oxides Onder X-ray Visie


Het eerste deel bestudeert het effect van bandverschuivingen in materiaal combinaties waar grote elektronegativiteits verschillen zijn gerealiseerd, namelijk het isopolaire LaCoO$_3$ $|$ LaTiO$_3$ grensvlak. Dit blijkt te leiden tot elektron verplaatsing van Ti naar Co aan het grensvlak, een effect dat kan worden gebruikt om op nanoschaal controle over het aantal d-elektronen in Co te realiseren. Door de LaCoO$_3$ dikte te variëren, samen met het aantal grensvlakken en de aanwezigheid en dikte van een scheidingslaag, kan de valentie conversie van de Co ionen door ladingsverplaatsing precies gecontroleerd worden. Dit leidt tot een gemiddelde valentie van Co ionen in LaCoO$_3$ die varieert van d$^6$ tot d$^7$, terwijl de perovskiet structuur behouden blijft. De valentie transformatie gaat hand in hand met vergrote spin polarisatie van de d$^7$ Co toestand, wat leidt tot een significante vergroting van het paramagnetische moment die 1.2 $\mu_{Bohr}$ per Co atom kan bereiken, zoals gezien wordt in element-specifieke magnetometrie experimenten. Deze resultaten op het LaCoO$_3$ $|$ LaTiO$_3$ grensvlak illustreer een mooi de doeltreffendheid van de O2p-band uitlijning als leidend principe voor het ontwerpen van eigenschappen in complexe zuurstof heterostructuren, en de mogelijkheid van zachte en harde X-ray spectro-
Samenvatting

Scopie om de transitie-metaal valentie, orbitaal bezetting en het magnetisme in een plaats-specifieke en zeer gevoelige manier te volgen.

Het tweede deel bespreekt de ladingsverplaatsing over een grensvlak door een ander fenomeen: Het voorkomen van een polaire catastrofe. In ultra-dun (polair) LaMnO₃, gegroeid op (niet-polair) SrTiO₃ substraten, wordt de polariteits wanverhouding tussen de twee perovskieten het sterkst gevoeld aan het grensvlak, en leidt tot sterke elektron-doping van het LaMnO₃. Dit wordt begeleid door de emergentie van dikte-afhankelijke Mn ferromagnetisme. Door een combinatie van valentie-gevoelige X-ray technieken, is een systematische reductie van Mn valentie gezien in dunne LaMnO₃ filmen, variërend van 2.9+ voor 10 eenheidscellen, tot 2.35+ voor 2 eenheidscellen. Dit resultaat, samen met complementaire elektron energieverlies metingen, spreekt voor de verzameling van elektron-rijke Mn²⁺ ionen bij het aanliggende SrTiO₃ substraat. Alhoewel ultra-gevoelige, element-specifieke X-ray magnetometrie ferromagnetische Mn momenten onthult voor alle diktes die gemeten zijn, is er een significante vergroting van de overgebleven Mn magnetische momenten boven een “kritische” dikte van 6 eenheidscellen. De experimentele data ondersteund geen rechtstreekse zelf-doping in het LaMnO₃ als antwoord op de polaire catastrofe. Een combinatie van lege zuurstof-plekken, spanning veroorzaakt door het substraat, en zwaar overdoopte magnetisch “dode” LaMnO₃ lagen aan het grensvlak, lijken te leiden tot het relatiege gebrek aan overgebleven magnetisatie in dunne LaMnO₃ filmen op SrTiO₃ substraten.

Het derde en laatste deel van deze thesis onderzoekt de metaal-isolator overgang in VO₂, die plaatsvindt vlak bij kamertemperatuur. Dit maakt dit materiaal een veelbelovende kandidaat voor toekomstige toepassingen. Recente vooruitgang in het groeien van de VO₂ films op nano-sheets, geven de gelegenheid om X-ray spectroscopie uit te voeren in transmissie. Specifiek laat dit hoofdstuk zien hoe, door een combinatie van X-ray absorptie, lineair dichroïsme en lensloze coherente afbeeldings technieken de elektronische en structurele fase-segregatie over de transitie kan worden gevolgd als functie van temperatuur. Ten eerste is de hoge kwaliteit van de groei, die verantwoordelijk is voor de controle over de orientatie in het vlak en de orbitale bezetting in VO₂, laten zien in temperatuur-, polarisatie- en invalshoek-afhankelijke X-ray absorptie metingen. Dit pleit voor de geschiktheid van deze monsters voor het uitvoeren van afbeeldingsexperimenten via lensloze technieken die gebruik maken van coherente X-rays, zoals “holography using extended reference auto-correlation
Samenvatting

by linear differential operator” (HERALDO). Dit experiment is uitgevoerd door een masker, en heeft de relatie tussen de metallische en isolerende fases in de ruimte laten zien tijdens opwarmen, door de temperatuur gedreven isolator-metaal transitie. De bevindingen wijzen naar initiële nucleatie van de metallische fase langs richtingen loodrecht op de rutiele c-as van het VO₂. Gevolgd door groei van deze streep-achtige metallische domeinen langs de VO₂-dimer richting. Deze experimenten vormen een eerste en succesvolle haalbaarheidstest betreffende onze ambitie om het experiment in ultrasnelle (pump-probe) modus uit te voeren, en zo de Mott isolator-metaal transitie in een complexe oxide in zowel echte ruimte op het nanometer niveau, als in tijd op het femtoseconde niveau te volgen: de Mott-MIT-Movie.
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Abbreviations

(HAX)PES  (Hard X-ray) Photoemission Electron Spectroscopy

CCD  Charge Coupled Device

DFT  Density Functional Theory

EELS  Electron Energy Loss Spectroscopy

EXAFS  Extended X-ray Absorption Fine Structure

FIB  Focused Ion Beam

FY  Fluorescence Yield

HAADF  High Angle Annular Dark Field

HERALDO  Holography with Extended Reference Auto-correlation by Linear Differential Operator

HS  High Spin

IMFP  Inelastic Mean Free Path

IP  In Plane

IS  Intermediate Spin

LCO  LaCoO₃

LMO  LaMnO₃
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>LNO</td>
<td>LaNiO$_3$</td>
</tr>
<tr>
<td>LS</td>
<td>Low Spin</td>
</tr>
<tr>
<td>LSMO</td>
<td>La$<em>{0.7}$Sr$</em>{0.3}$MnO$_3$</td>
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<tr>
<td>LTO</td>
<td>LaTiO$_3$</td>
</tr>
<tr>
<td>MIT</td>
<td>Metal-Insulator Transition</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near Edge X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>OOP</td>
<td>Out Of Plane</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection High Energy Electron Diffraction</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting Quantum Interference Device</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>STO</td>
<td>SrTiO$_3$</td>
</tr>
<tr>
<td>TEY</td>
<td>Total Electron Yield</td>
</tr>
<tr>
<td>TMO</td>
<td>Transition Metal Oxides</td>
</tr>
<tr>
<td>TO</td>
<td>T$_{0.87}$O$_2$</td>
</tr>
<tr>
<td>uc</td>
<td>unit cell</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>XMCD</td>
<td>X-ray Magnetic Circular Dichroism</td>
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Chapter 1

Introduction

The arduous quest for exotic materials in condensed matter physics is driven by the need for emergent physical properties that inspire novel technological functionalities. Transition Metal Oxides (TMO) are a family of materials that has been put consistently in the forefront of this effort. These are compounds consisting of transition metal elements that are primarily bound to oxygen. The unique properties found in TMO have been known to humans for a long time and their technological applications place them in the centre of research in the field of solid state physics.

Over two and a half millennia ago, Thales of Miletus attributed a divine essence to lodestone, a rock mineral found in the area of Magnesia, due to its ability to attract metals. Lodestone is a naturally occurring magnet whose magnetic properties are ascribed to its magnetite (Fe₃O₄) content that is believed to have been magnetised during lighting strikes [1]. Magnetites constitute an active frontier of research to date, attracting a lot of attention due to their Verwey transition to a correlated insulating ground state [2].

Nowadays, TMO constitute an integral part of our everyday life owing to their novel properties that find numerous applications in a variety of products. Due to their unique performance-cost characteristics, they constitute the cathode material in Li-ion batteries [3, 4] that are featured in every modern portable electronic device. In addition, this type of batteries serve as energy storage units in sustainable technology applications including electric vehicles, setting the foundation for a fossil fuel-free planet. For their contribution to their development, Goodenough, Whittingham and Yoshino were awarded the Nobel Prize in Chemistry in 2019.

The functionality of TMO is exploited in a variety of other applications, including catalysts for redox reactions [5], ferrites that are used as components in electrical
elements and data storage units [6] as well as solid-oxide fuel cells [7, 8]. Hence, it is clear that TMO, particularly those of perovskite structure, are materials with flexible properties that render them well-suited candidates for a wide range of future applications. In order to engineer these type of materials, it is desirable to acquire nanoscale control over the interplay of the individual spin, charge, lattice and orbital degrees of freedom. This is accomplished by achieving a high degree of control over their growth and an atomic-level insight into their properties.

Owing to recent advances in film deposition techniques, an unprecedented, atomic precision over the growth of TMO has been achieved. Through the excellent control of the deposition, TMO can be grown epitaxially in a finely tuned, layer-by-layer manner, allowing the on-demand fabrication of a plethora of compounds with diverse constituents. Particularly in the case of TMO that share a common perovskite structure, the high degree of epitaxy, combined with their structural compatibility, enables the integration of multiple, dissimilar materials into a single heterostructure. In the 2-dimensional limit, the interface gains an important role, often encompassing very interesting physics, and constitutes the driving force of many exotic phenomena. A prominent paradigm is the discovery of the 2-dimensional electron gas that is confined to the interface between two insulating oxides, LAO and STO [9, 10]. The very same interface exhibits magnetism [11] and superconductivity [12, 13]. These extraordinary findings opened a new chapter for TMO in condensed matter physics and paved the way for future discoveries.

It is therefore apparent that the nanoscale control over the growth of TMO constitutes an appropriate tool to engineer these materials, providing a highly flexible way to tune the various degrees of freedom in the crystal. However, in order to achieve full control of the emergent properties and design novel functionalities, it is essential to obtain a deep understanding of the rich interplay of the various physical forces that act on the atomic level, constituting the microscopic source of the observed quantities. As elaborated in detail later in this thesis, modern spectroscopies are powerful and versatile tools to gain knowledge on the quantum entities that represent the solid.

The subject of this thesis is the spectroscopic investigation of TMO thin films. Advanced X-ray spectroscopies constitute direct experimental probes of the electronic and magnetic structure of matter due to their interaction with the lattice and electrons. Moreover, these experimental techniques are element-specific and
selectively (non)-surface-sensitive, able to distinguish between the constituents of a compound and consequently highly suitable for the investigation of thin films. In this project, a broad variety of oxide materials is examined, using synchrotron-based spectroscopy methods aiming to investigate novel interfacial electron states, emergent ferromagnetism and correlated electron transitions.

Chapter 2 explores fundamental aspects of the structural and electronic properties of TMO, concepts in magnetism and gives an overview of the experimental tools that were employed for the growth and the investigation of the thin films in this study. Chapter 3 discusses results on the novel interfacial charge transfer states that emerge at the isopolar interface between LaCoO$_3$ (LCO) and LaTiO$_3$ (LTO) as a direct result of an interfacial band offset. Chapter 4 describes an alternative pathway to achieve charge tuning and subsequent emergent magnetism in the polar LaMnO$_3$ (LMO) $|$ SrTiO$_3$ (STO) interface. Chapter 5 deals with the spectroscopic investigation and soft X-ray, lensless imaging of the Metal-to-Insulator Transition (MIT) in VO$_2$. 
Chapter 1. Introduction
Chapter 2
Experimental aspects

The present chapter reviews important aspects in terms of the general theoretical background concepts as well as the relevant experimental methods. In the first part, the unique characteristics of the perovskite structure along with criteria for its stability are introduced. This is followed by a discussion of the taxonomy of correlated electron systems on the basis of the balance between the relevant electronic energy scales around the Fermi energy that leads to distinctive ground states. Next, a brief overview of basic principles of magnetism in atoms and crystals is provided.

The second part of this chapter describes fundamental aspects of the experimental techniques that were employed for the material growth by research partners in the University of Twente. Above all, a brief account of the technique that enables the growth of perovskite TMO with an atomic level precision is given. Next, the discussion focuses on the inherent suitability of spectroscopic techniques that renders them powerful experimental tools for the investigation of matter. In this section, the working principle of the core-level spectroscopies is described as well as the way in which these encode an abundance of information on the electronic and magnetic properties and other collective phenomena.

The fabrication of the thin films was carried out by members of the Inorganic Materials Science and Interfaces & Correlated Electrons groups at the MESA+ Institute of Nanotechnology, University of Twente, Enschede. The bulk of the spectroscopy measurements were carried out at synchrotron facilities, namely at Diamond Light Source (Didcot, UK), BESSY II (Berlin, DE) and SOLEIL (Paris, FR).
Chapter 2. Experimental aspects

2.1 Theory

2.1.1 The Perovskite Structure

Perovskite TMO constitute a broad family of compounds, encompassing those with the chemical formula $ABO_3$, where $A$ is a rare earth or alkaline earth element and $B$ is a transition metal ion. In the ideal cubic structure of the space group $Pm\bar{3}m$, shown in Figure 2.1(a), the sixfold O-ligand coordination defines an octahedron which encloses the $B$-ion, while the $A$-ion is surrounded by four $BO_6$ octahedra in a cubic arrangement.

The octahedral arrangement of the oxygen atoms that is commonly found in TMO forms a highly flexible electronic environment that promotes electron correlations, giving rise to a plethora of emergent phenomena. In the ideal perovskite structure, the symmetric Coulomb field has a direct impact on the electronic structure of the 3d shell, lifting the fivefold degeneracy of the energy levels and splitting them into two states: the triple degenerate, $t_{2g}$ state, and the double degenerate, $e_g$ state, which are separated in energy by the strength of the (octahedral) crystal field, $10Dq$, as shown in Figure 2.1(b). The degeneracy of these states can be further lifted in the presence of additional structural distortions, including Jahn-Teller effects [14]. As explained in detail in the next section, the choice in the distribution of the electrons among the available states in this type of energy configuration leads to very interesting correlated phenomena.

The freedom in the choice of $A$ and $B$ ions enables the realisation of many materials, each one having its unique characteristics. A measure of the deviation of the perovskite structure from the ideal arrangement and predictor of its stability is the Goldschmidt tolerance factor $\tau$ which quantifies the mismatch of the $A$-O and $B$-O bond length difference in terms of the ionic radii [15] $R_A$, $R_B$, $R_O$, given as follows:

$$\tau = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$$

The degree of deviation of $\tau$ from unity is a measure of the mismatch of the bond lengths and is consequently linked to the distortion of the perovskite. Generally, a relatively high accuracy of the predictor is achieved in the range $0.8 < \tau < 1$ [16], while modern approaches have improved its accuracy [17].
2.1. Theory

Figure 2.1: (a) Schematic of an ideal, non-distorted cubic $\text{ABO}_3$ (space group $\text{Pm\bar{3}m}$, $\tau=1$) perovskite crystal structure showing the cubic arrangement of the rare earth ions ($A$-site) with the transition metal ion ($B$-site) being enclosed by the oxygen octahedron. In reality, ions are much bigger resulting in large filling factors (b) energy schematic of the $O_h$ octahedral crystal field lifting the degeneracy of the 3d energy levels and splitting them into groups: the $t_{2g}$ and the $e_g$ states that are separated in energy by 10Dq.

2.1.2 The Mott Transition

In regards to the electronic properties of TMO with partially-filled (sub)shells, conventional band theory predicts a conducting ground state owing to the unpaired, free valence electron(s). In spite of this expectation, the strong electron-electron interactions render some of these compounds insulating. This observation can be understood, within the approach of localised states, as a direct result of the rich interplay of the various electronic degrees of freedom around the Fermi energy.

Strongly correlated oxide insulators can be classified on the basis of the energy balance of the Coulomb energy interaction between 3d electrons, $U_{dd}$ and the charge transfer energy cost $\Delta$ required for an electron to hop between the anion and the cation. According to the Zaanen-Sawatzky-Allen classification [20], the energy scale landscape around the Fermi energy allows a distinction on the basis of the nature of the insulating gap and the lowest possible excitations, as shown in Figure 2.2. In Mott-Hubbard insulators, such as those containing early 3d shell elements, $U_{dd}<\Delta$ and the energy band gap $E_g \propto U_{dd}$ with the dominant electron interactions occurring between the 3d transition metal sites. On the other hand, in charge transfer insulators, as in the case of systems containing heavier 3d ions, $U_{dd}>\Delta$ and $E_g \propto \Delta$. In
Chapter 2. Experimental aspects

Figure 2.2: Energy configuration schematic [18] close to Fermi energy \( (E_F) \) of a) Mott Hubbard and b) charge transfer insulators on the basis of the Coulomb energy interaction between 3d electrons, \( U_{dd} \) that splits the d-states into the upper/lower Hubbard band and the charge transfer energy \( \Delta \). c) Zaanen-Sawatzky-Allen [19] taxonomy of TMO, featuring the charge transfer/Mott-Hubbard regime above/below \( \Delta = U_{dd} \).

In this case, the energetically cheapest excitations occur from the p-band to the upper Hubbard band entailing electrons hopping within the unit cells. A precise determination of the \( U_{dd} \), \( \Delta \) and the relevant energy scales can be achieved by systematic modeling of experimental 2p core-level spectra [19, 21].

The Mott insulating state of TMO can be suppressed via appropriate tuning of a parameter that causes electrons to turn from localised to itinerant. This can be achieved by either enhancing the electron bandwidth by means of external or chemical pressure (bandwidth control) or tuning of the d-band count by non-stoichiometric doping, or either electrostatic or chemical gating (filling control) [22]. Prototypical materials in which the Mott transition can be controlled by bandwidth tuning include hole-doped versions of d\(^1\) titanates, including LaTiO\(_3\) (LTO) [23] and vanadates [24]. Additional pathways to control the Mott transition is pressure (ruthenates) [25] and in thin-films, where epitaxial strain becomes important, the orbital occupancy (vanadates) [26].

In the case of VO\(_2\), the Mott-Hubbard nature of the MIT observed close to room temperature constitutes a long-standing dispute in condensed matter physics. This
2.1. Theory

The subject is treated in detail, along with recent experimental observations in Chapter 5.

2.1.3 Electronic reconstructions in heterointerfaces

Having discussed fundamental structural and electronic characteristics of TMO, the present section moves on to describe ways in which the combination of two materials can affect their properties. The interface between two electronically dissimilar materials exhibits interesting and potentially technologically relevant properties. In fact, the precise control over the growth of crystals along with their reduced dimensionality, boosts the role of the interface, giving rise to emergent phenomena that are not present in the parent compounds.

In the following, two pathways to achieve internal electronic reconstruction are briefly discussed. The first charge rearrangement mechanism emerges as a direct result of the polar discontinuity in polar/non-polar interfaces while the second stems from the band mismatch of a pair of materials that contain transition metal elements of different electronegativity. In this project, both concepts are put to the test in different material combinations. The precise experimental implications are discussed in the experimental Chapters 3 and 4.

Band alignment as a design principle for functional heterojunction engineering constitutes a well-established concept in semiconductor physics. In metal-semiconductor heterointerfaces [27], an energy mismatch between the Fermi levels of the two constituents with respect to the energy of the vacuum is realised. In an ideal Schottky diode, the height of the energy barrier depends on the energy difference between the work function of the metal and the electron affinity of the semiconductor. This leads to band bending on the side of the semiconductor imposed by the boundary condition of matching the Fermi level of the metal. In reality, the height of the energy barrier is insensitive to the work function of the metal and the band bending “pins” the Fermi levels at an energy that depends on the band-gap of the semiconductor [28]. Similar rules predict vacuum level energy aligning via band bending in semiconductor - semiconductor interfaces [29].

Along these lines, the band mismatch between a pair of TMO can be viewed as a direct result of the difference in the workfunction of its constituents, which is the amount of energy required for an electron at the highest occupied energy level to be
removed by reaching the vacuum level \[30\]. At the interface of such \(ABO_3 \mid AB'O_3\) structure, the shared oxygen framework can be argued to impose an O2p band alignment condition, causing an analogous mismatch at the Fermi energy level. A way for the system to compensate for the incipient band mismatch is to transfer electrons across the interface, between the layers. Density Functional Theory (DFT) can be used as a predictor of the magnitude and the direction of a possible charge transfer \[31, 32\]. In contrast to the polar catastrophe concept, this band-driven internal electron transfer can also occur at isopolar interfaces, being relatively insensitive to electrical potentials and chemical doping. Experimentally, valence band PES has been used for the determination the energy offsets for a number of systems \[33–37\].

Chapter 3 examines band alignment-driven charge transfer in detail in the isopolar \(LaCoO_3 \mid LaTiO_3\) interface with the aim of achieving full control over the Co valence via interfacial engineering.

A second manner to achieve internal charge transfer in TMO is the avoidance of a polar catastrophe. As mentioned in the introduction, a renowned paradigm in interfaces of TMO is the 2-dimensional electron gas, which, above a critical thickness, emerges at the interface between the two insulating oxides \(LaAlO_3 \mid SrTiO_3\) \[9, 10\]. This electron self-doping that is observed in the LAO|STO systems is believed to stem from the uncompensated electric potential that is accumulated in the polar LAO film which consists of consecutive \((La^{3+}O^{2-})^{1+}\) and \((Al^{3+}O_2^{2-})^{1-}\) layers that are grown on charge neutral \((Ti^{4+}O_2^{2-})^0\) and \((Sr^{2+}O_2^{2-})^0\) layers. Although the iconic picture of polarity-driven interfacial self-doping is an inspiring idea, it is widely accepted that a pure polar catastrophe is not occurring in many real systems \[38\], in which an uncontrollable potential build up is often avoided by the off-stoichiometry route, namely \(A\)-site intermixing \[39\] and oxygen vacancies \[40\]. Chapter 4 contains a detail discussion of several experimental aspects of the polar discontinuity and the way in which the ensuing reconstruction manifests itself in the \(LaMnO_3 \mid SrTiO_3\) heterointerface as well as the concomitant thickness-dependent emergent ferromagnetism.

\subsection*{2.1.4 Magnetism in ions and solids}

This section describes basic concepts and background on magnetism which are covered in detail in standard textbooks \[41, 42\]. Magnetism is a manifestation of the
quantum nature of matter, being directly linked to the angular momentum of the electron. The total angular momentum of an electron is the vector sum of the orbital angular momentum and spin angular momentum. For an electron that orbits around a nucleus, the spin and orbital momenta are coupled by the spin-orbit interaction, an effect that is heavily dependent on the atomic weight. In light elements, the spin-spin and orbital-orbital interaction of the constituent electrons are the strongest and can be combined individually to yield the total angular momentum (Russell-Saunders coupling). On the other hand, in heavier atoms, the spin-orbit interactions become dominant for each electron, forming a net total angular momentum (jj coupling).

A useful physical constant that is commonly used to quantify the magnetic properties of a system is the Bohr magneton ($\mu_B$), a unit that expresses the fundamental magnitude of the magnetic moment carried by the circular motion of an electron of mass $m_e$ and elementary charge $e$. The Bohr magneton ($\mu_B$) is given by [41]:

$$\frac{e\hbar}{2m_e} \equiv -\mu_B$$

Since elements contain multiple electrons, certain quantum mechanical rules apply to the way in which these are distributed amongst the available energy levels. In the case of a transition metal atom or ion in free space, these are allocated to the degenerate levels of the outer d-shell, taking into account that the occupation of the same quantum state by two electrons is forbidden by Pauli’s exclusion principle. The criteria that have to be met for the choice of the quantum numbers J, L, S in the ground state of an atom are given by Hund’s rules that impose the requirements of (i) maximum spin multiplicity (S), (ii) maximum orbital angular momentum value (L) and (iii) lowest/highest total angular momentum value (J) for shells that are less/more than half-filled shells. Consequently, in view of the fact that filled shells have opposite spin constituents and evenly distributed values of orbital angular momenta resulting in $J=0$, only incomplete shells contribute to ferromagnetism. The estimation of the effective magnetic moment of a certain electronic configuration of an ion depends on the Landé g-factor $g_j$ that constitutes a quantum mechanical correction of the classical expression for an electron in a magnetic field that takes
into account electromagnetic interactions and is given by [41]:

$$g_j = \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)}$$

A magnetic field in free space, expressed in terms of a magnetic field intensity \(\vec{H}\) causes a magnetic flux density \(\vec{B}\) which depends on the magnetic permeability of the vacuum \(\mu_0\) as follows:

$$\vec{B} = \mu_0 \vec{H}$$

A solid system, being a macroscopic entity that consists of a large number of magnetic dipoles, responds to the presence of magnetic field by proportionally developing an internal magnetisation \(\vec{M}\), with the the proportionality coefficient being the magnetic susceptibility \(\chi\). Depending on the nature of the material, the magnetisation \(\vec{M}\) can have a different direction from the driving field \(\vec{H}\). Thus, the flux density is given by:

$$\vec{B} = \mu_0 (\vec{H} + \vec{M}) = \mu_0 (\vec{H} + \chi \vec{H}) = (1 + \chi)\mu_0 \vec{H}$$

The sign of the magnetic susceptibility \(\chi\) describes the magnetic response of a material: \(\chi > 0\) for a paramagnet and \(\chi < 0\) for a diamagnet. For a ferromagnet, \(\chi >> 1\) and the system exhibits magnetic hysteresis. Some materials can exhibit physical properties that are characteristic of ferromagnetism due to the existence of canted antiferromagnetism or of ferrimagnetism. Finally, in ferromagnetic systems, the demagnetisation factor can become significant and should be taken into account. The demagnetizing field stems from the accumulation of (virtual) magnetic monopoles at the boundary of a finite size system. These develop a demagnetizing field that opposes the direction of the magnetisation, tending to reduce its size. It can be deduced that the demagnetisation effects are absent in thin films that facilitate in-plane magnetisation [42].
2.2 Methods

2.2.1 Pulsed Laser Deposition (at MESA+ Institute)

Recent advances in film deposition techniques have enabled an unprecedented control over the growth of ultra-thin crystals that extends down to the unit cell level. A physical vapour deposition technique enables the controlled growth of thin films of crystals, providing a highly flexible way to fabricate a vast variety of materials is Pulsed Laser Deposition (PLD) [43].

PLD has been widely employed in the case of perovskite TMO, due to its effectiveness in producing complex structures consisting of interlocking perovskite building blocks that are combined on the nanoscale. The atomic control over the growth of thin films allows the nanoscale manipulation of matter and constitutes a powerful tool for its systematic investigation, while the reduced dimensionality of these structures assigns a substantial role to the interface and allows the individual degrees of freedom in a crystal to be tuned with high precision. The wide range of possible material combinations that can be implemented in this way leads to novel, functional properties and opens endless possibilities for future applications.

This is particularly exemplified in the family of $ABO_3$ perovskites TMO. Besides sharing a common crystal structure, these compounds can be chosen to have compatible lattice constants, therefore constituting interlocking pieces of matter. Therefore, using PLD, it is possible to combine them epitaxially in a single heterostructure. The purpose of this section is to provide a short description of the relevant growth principles. The fundamental elements of such an instrument are depicted in Figure 2.3.

Ideal oxide heterostructures consist of pure, structured and flat individual atomic layers that are combined to give well-defined and abrupt interfaces. This requires a way to monitor the growth real-time in a layer-by-layer manner that is achieved by integrating a Reflection High Energy Electron Diffraction (RHEED) apparatus into the PLD setup. The RHEED gun directs high energy electrons on the sample which interfere with the lattice giving diffraction spots on a phosphor-coated screen. A rotating target carousel allows the facilitation of multiple targets, enabling the efficient growth of different materials in a single session.
Figure 2.3: Working principle of RHEED-assisted PLD: a pulsed laser impinges on a target located in a UHV chamber, transferring energy that drastically raises the local temperature, resulting in the ablation of the target and the formation of an atomic molecular plasma plume. The plume, in-turn, is deposited onto a substrate that is heated to appropriate temperatures. The process is monitored on a layer-by-layer basis using RHEED oscillations.

Firstly, an atomically flat substrate is required for the epitaxial growth to be initiated. The single termination is commonly achieved by selective, wet acidic etching procedures which yield a well-defined step terrace surface, a result that can be confirmed by atomic force microscopy [44]. In the case of STO, a chemical etching procedure to achieve TiO$_2$ single-termination is commonly practised [45]. The substrate is then placed in the sample heating stage, located in an Ultra High Vacuum (UHV) chamber, where a heater elevates the temperature to the deposition temperature. The main process that drives the film deposition is the ablation of the target which is achieved by focussing a high fluence, pulsed laser beam onto the target that consists of the starting material that will be deposited [43]. A series of focusing optics forms a high flux beam that transfers sufficient energy to the target, breaking the chemical bonds. This ablation process results in the evaporation of the material into a plasma plume which expands due to the strong, local pressure gradient. The uniformity of the plasma plume is achieved by optimising the beam spot and the rotation of the target. The source is typically an excimer (e.g. KrF, 248 nm) or solid-state laser e.g. (Nd:YAG, 1064 nm), while the wavelength is tuned to different harmonics, depending on the desired output power.
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The distinctive features of PLD renders it an unique thin film deposition technique, especially applicable to the growth of complex oxide heterostructures. Firstly, assuming appropriate choice of laser fluence and careful conditioning of the target, the ablation process preserves the stoichiometry of the removed material of the target. Nevertheless, possible differences in the sticking coefficient of the atoms on the surface could cause non-stoichiometric deposition. Secondly, reactive deposition is straightforward and is carried out by the introduction of low pressure background oxidants such as O$_2$ to the chamber. In addition, the growth can be monitored down to the monolayer limit by observing intensity oscillations in the RHEED diffraction spots which stem from the alternating smooth/rough surface morphology of the film as each layer is deposited. Finally, consecutive deposition from multiple target materials is a straightforward task and can be carried out in the same growth run. These unique characteristics make PLD an extremely popular film growth technique in the field of complex oxide heterostructures.

2.2.2 Synchrotron radiation

Since their discovery, X-rays have been widely used for the investigation of the fundamental structure and properties of matter, finding applications to material systems that range from solids, liquids and gases to complex assemblies such as proteins and biological entities [46]. Light-matter interaction arises when X-rays with typical wavelength comparable to the characteristic lengthscale of the interatomic distances in matter, collide with a solid. These fundamental properties render soft and hard X-ray spectroscopies a powerful investigation tool, widely employed in the scientific and industrial world.

Particularly in thin film studies, the suitability of these methods lies in their tunable surface-sensitivity and element-specificity. In materials that contain 3d transition metal ions, the intense and fairly complicated light-matter interaction leads to distinctive spectral features, giving direct access to their atomic properties and allowing both their quantitative and qualitative evaluation, ranging from details on the electronic configuration and crystal environment to collective phenomena such as magnetism and Jahn-Teller distortions. The deconvolution of the complex physical parameters of such systems contributes to the deeper understanding of the properties and helps enable the exploitation of their novel functionalities.
In this section, emphasis is given to the method of producing radiation with wavelengths in the X-ray regime used in this thesis. This type of radiation can be described complementarily as electromagnetic waves with wavelength $\lambda$ in the range 10 nm to 0.01 nm or as photons with energy $E$ in the range of 100 eV to 120 keV. The wavelength $\lambda$ is linked to the photon energy $E$ via the relation $E = \frac{hc}{\lambda}$, where $h$ is Planck’s constant and $c$ the speed of light. Because of the lack of a universal classification, the boundary between soft and hard X-rays is not well-defined. On the basis of their attenuation, soft X-rays can be seen as photons that ionize air, thus having no significant capability of traversing outside vacuum. This corresponds roughly to wavelengths that are larger than 2 nm or energies smaller than 600 eV. On the other hand, hard X-rays with wavelengths shorter than 2 nm, can easily transmit through the atmosphere and if they carry substantially large energy, even through matter. The need for tunable, high photon flux X-ray sources led to the construction of specialised facilities, the modern third-generation synchrotrons and free electron lasers, which are capable of producing X-ray beams of unprecedented intensity.

Electromagnetic radiation with wavelength in the X-ray region is produced when electrons that are thermionically emitted from a filament are accelerated, to collide with a metal anode. The high energy electron bombardment of the target results in the abrupt deceleration of those electrons from the other charged particles of anode, leading to bremsstrahlung emission. This type of radiations is spread over a continuum in the wavelength domain. Kramers’ law provides a quantum mechanical description of the bremsstrahlung emission in the framework of Bohr’s model of the atom [47]. Besides the continuous, low intensity spectrum, there is a second type of feature in the emission spectrum of such sources, which consists of high intensity peaks at characteristic energies that depend on the material of the anode. These stem from photons released at distinctive energies during the decay of core-holes which are formed by electron scattering processes in the shell of the target atoms via the electron bombardment.

A conventional laboratory X-ray source employs this characteristic radiation because it is well-defined in energy and has very high intensity compared to bremsstrahlung emission that is characterised by being of low intensity and continuous in wavelength. A widely used anode material is Al that emits high flux Kα radiation which corresponds to the decay of the Al1s core-hole, at 1486.6 eV with a natural, core-hole
2.2. Methods

lifetime determined bandwidth of \( \approx 0.5 \text{ eV} \) \cite{48}. To gain better energy resolution this Al:K\(_2\) is often further monochromatised using a diffraction process involving a single crystal or crystals as an effective grating for the X-rays.

Third generation synchrotron facilities produce very intense radiation of tunable wavelength and selective polarisation using a circular particle accelerator that accelerates an electron particle beam close to roughly the speed of light \cite{49}. A schematic of such facility is shown in Figure 2.4. These relativistic electrons reside in a storage ring and are steered through multiple sections via consecutive bending magnets in order to maintain a closed orbit. Each bending magnet changes the straight path of the particle beam causing spectrally continuous synchrotron photon emission at the point of deflection in a forward path. In present day facilities, an even higher photon flux, desirable for high resolution experiments, is achieved by the addition of insertion devices such as undulators or wigglers which consist of periodic arrays of electromagnets. These devices cause extra oscillations in the trajectory of the electrons in an otherwise straight section of the storage ring, resulting in the production of high intensity photons in a narrower spectral region (for undulators such as those used in this research) compared to the output of a bending magnet in the wavelength domain. Depending on the initial design and the demands, a synchrotron facilitates a number of experimental stations. At each beamline a series of focusing optics steers the beam to the chamber, where the experiment takes place.

2.2.3 (Hard X-ray) Photoemission Electron Spectroscopy

A widely used technique for the chemical and physical analysis of matter on an elemental basis is (Hard X-ray) Photoemission Electron Spectroscopy (HAXPES). The working principle of this technique originates in a fundamental manifestation of the light-matter interaction, namely the photoelectric effect \cite{50}. This effect stems from an energy exchange process that is triggered when photons of sufficient energy collide with a solid, thereby exciting electrons that are normally bound to the core of the atoms in the target material. The excited electrons move through the solid and some of them, after a cascade of possible scattering events, depending on how deep below the sample surface they were created, reach the surface of the sample, having adequate energy to overcome the work function of the material \( \phi_s \), which is the energy that is required for them to enter vacuum in the form of photoelectrons.
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Figure 2.4: Schematic of a third generation synchrotron radiation source. Relativistic electrons that reside in a storage ring enter straight sections where an insertion device (such as an undulator) causes them to oscillate, producing an high flux beam of radiation present as a series of partially monochromatic harmonics. A monochromator (single or double crystal(s)) is used to produce a well-defined in wavelength (monochromatised) beam of small bandwidth, before a series of focusing optics guides the beam to the experimental chamber. Typical distances are shown. Taken from Ref. [46]
In UHV conditions, the photoelectrons travel freely until they reach the analyser, a device that is used to determine their kinetic energy, and, in some cases their angular distribution. The spectrometer has its own material-specific work function \( \phi_d \). In respect to the energy level of the vacuum, the energy that is spent in order for the photoelectrons to lead to a current in the analyser, is \((\phi_d - \phi_s)\). Both the analyser and the sample are electrically connected to ground, so as to have their Fermi levels aligned. The workfunction of the analyser is determined by measuring known photoelectron resonances or the Fermi edge of metals \([51]\). Hence, for incident light of energy \( E_{\text{photon}} \) and based on energy conservation arguments, the only unknown remaining quantity, \( E_{\text{binding}} \), can be determined with very high precision via the following equation:

\[
E_{\text{kinetic}} = E_{\text{photon}} - E_{\text{binding}} - \phi_s - (\phi_d - \phi_s) \Rightarrow \\
E_{\text{kinetic}} = E_{\text{photon}} - E_{\text{binding}} - \phi_d
\]

A typical (HAX)PES spectrum consists of intensity peaks that are resolved as a function of binding energy, being therefore characteristic of a chemical species. The lineshape of the peaks has a Voigt profile as a result of the convolution of gaussian and lorentzian broadening caused by the resolution of the instrument combined with the finite lifetime of the core-hole.

An important aspect of the photoemission process is the inelastic character of the scattering that the excited electrons are subjected to in their trajectory in the solid. This scattering mechanism accounts for the finite Inelastic Mean Free Path (IMFP) of the photoelectrons defined as the characteristic length scale on which the signal is attenuated by a factor of \(1/e\) compared to the incident value. A systematic investigation of experimental data showed that IMFP tends to be a kinetic energy-dependent quantity, generally being relatively insensitive to the material itself. This results in a rather universal IMFP curve as a function of the electron energy \([52]\). An established way to estimate the IMFP, for electron energies in the range of 50 to 2000 eV, is the TPP-2M equation \([53]\) which takes into account several material-specific parameters including the density of the solid, the number of valence electrons and the energy band gap.
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![Figure 2.5: “Universal” curve of the IMFP (nm) of the photoelectrons as a function of electron energy (eV) [50, 53]. Overlay of calculated IMFP (nm) of LCO and LMO using the formula given in ref. [53]](image)

Figure 2.5: “Universal” curve of the IMFP (nm) of the photoelectrons as a function of electron energy (eV) [50, 53]. Overlay of calculated IMFP (nm) of LCO and LMO using the formula given in ref. [53]

For the materials of interest, discussed in chapters 3 and 4 (LaCoO$_3$ and LaMnO$_3$), the TPP-2M equation yields the curves that are shown in Figure 2.5. It can be deduced that for a shallow core electron, close to the Fermi energy, that is excited with a standard Al:K$_\alpha$ laboratory source ($E_{\text{kinetic}}$=1486 eV) the estimated IMFP for LCO and LMO are 24 and 28 Å respectively. In other words, assuming the take-off angle of the photoelectron is along the surface normal, 63% of the PES signal stems from approximately the 7 uppermost unit cells of the film and 95% of the signal from the top-most 21 unit cells. At glancing take-off angles, the surface-sensitivity is further enhanced, reducing the effective probing depth by a factor of $\sin \theta$, where $\theta$ the emission angle with respect to the surface. This surface sensitivity means that an atomically well-defined surface that is clean of adsorbates and other contaminants in a UHV environment constitutes a necessity for reliable PES experiments. At the synchrotron, the IMFP can be significantly enhanced via the utilisation of high photon energy radiation in HAXPES experiment, thus enabling HAXPES to probe buried interfaces.

The atomic nature of the photoionization process renders (HAX)PES a substantially suitable technique for the elemental investigation of matter. The systematic examination of a spectrum, besides signalling the existence of a certain chemical species in a sample, enables the quantification of its stoichiometric composition and
the chemical state of its constituents. In principal, a reduction/increase in the oxidation state of an element causes a respective change in the binding energy of a core-level, referred to as a chemical shift. However, other atomic phenomena occur concomitantly upon the formation of core-holes, which can complicate or even scramble the spectrum. These are particularly prominent in the partially-filled 3d-shell transition metals \([54, 55]\) in which the interaction of the core-hole with the unpaired electrons leads to complex multiplet splittings, rendering the componental fitting of valence contributions all but impossible. As discussed in the following section, XAS offers an alternative route to measure the d-electron count in TMO.

### 2.2.4 X-ray Absorption Spectroscopy

A well-established technique for the investigation of the electronic and magnetic properties of matter on an elemental level, is X-ray Absorption Spectroscopy (XAS). In the classical picture, a solid absorbs the incident light with its intensity \(I(x)\) exhibiting attenuation which is proportional to the penetration depth, that is the path length \(x\) from the surface. For a infinitesimal sheet of material of thickness \(dx\), the intensity \(I(x)\) can be computed as follows:

\[
-dI = I(x)\mu dx \Rightarrow \frac{dI}{I(x)} = -\mu dx
\]

where \(\mu\) is a proportionality coefficient known as the absorption coefficient. In the general case, \(\mu\) is a wavelength-dependent quantity, showing a decreasing tendency for increasing photon energies. The absorption coefficient is directly proportional to the absorption cross-section, a property of the material. Assuming that the intensity of the beam at the surface of the solid is \(I(x = 0) = I_0\), the above differential equation can be solved to yield the Beer-Lambert law:

\[
I(x) = I_0 e^{-\mu x}
\]

In the atomic picture, the absorption coefficient exhibits intense enhancement at specific energies that correspond to core-level resonances. At these energies, the incident photon energy coincides with the characteristic energy for a transition from a core to a formerly unoccupied state. The requirement for strong spatial overlap
between the core level wavefunction and that of the unoccupied level into which the core electron is promoted makes XAS an element and orbital specific probe.

A schematic of the working principle of the two core hole creation mechanisms is shown in Figure 2.6 (a). As mentioned in the previous section, in the photoemission process, the incident light has energy higher than $E_{\text{binding}}$ of the core level of interest (including $\phi_s$), resulting in the ionization of the core electron which then exits the crystal and enters the vacuum. In contrast, at the X-ray absorption edges, the incident photon energy is strongly absorbed exciting in-turn core-level electrons from the ground state to the low lying available unoccupied states of the correct symmetry.

In case in which there is a strong Coulomb interaction between the core hole and the excited electrons “added” to the unoccupied states, the spectral variation of the unoccupied density of states collapses into a narrow line. This is dubbed a “white-line” (heavily exposed spectral line on a photographic film that is placed on the path of the transmitted beam). In proximity to the absorption edges, various other spectral structures make their appearance. The immediate surrounding (few tens of eV) of the absorption edge is the focus of Near Edge X-ray Absorption Fine Structure (NEXAFS) whereas the Extended X-ray Absorption Fine Structure (EXAFS) region includes spectral features that may extend over hundreds of eV.

The core hole is a short-lived entity that ceases to exist when an electron that belongs to a higher energy level fills its place. During this process and in view of the energy conservation requirements there is an excess of energy that is released either in the form of a photon, in a process known as fluorescence decay or in the form of another electron that leaves the solid, as a result of Auger decay. Both decay channels, shown in Figure 2.6 (b), lead to the formation of new core-holes that collectively contribute to an avalanche of events. In general, the lower characteristic energy of core level excitations in lighter elements favours Auger decay over fluorescence decay.

There are multiple ways to measure the absorption spectrum of a material. A straightforward method of detection is carried out in transmission geometry wherein the incident beam is shone on a thin sample and the outgoing beam is measured at the backside with a photodiode, shown schematically in Figure 2.7 (a). This enables the determination of the ratio $I/I_0$ that is directly proportional to the absorption coefficient $\mu$. In the soft X-ray regime and in view of the exponential attenuation
2.2. Methods

Figure 2.6: Energy level scheme of the core hole (a) formation and (b) decay mechanisms. (a) PES is based on the photoionisation process, whereby the occupied electron state is excited by an incident photon to an energy level above the vacuum level, thus exiting the material and entering the vacuum (N-1 electron final state), while in XAS the incident photon excites the electron to an unoccupied state above the Fermi energy (N electron final state overall, but interpretable in some cases as N+1 electron for the formerly unoccupied states). (b) the two decay pathways of the core hole: in fluorescence, an electron occupying a higher energy level fills the core hole accompanied by the simultaneous emission of a photon while in Auger decay, the core hole is filled with the simultaneous emission of an Auger electron from another occupied electronic state.
Figure 2.7: Detection methods in XAS (a) Direct, whereby the incident beam is transmitted through a nm-thick sample, while the outgoing beam is measured at the back side and (b) indirect in which the fluorescence/Auger decay of the core holes is measured close to the sample. Alternatively the sample is connected to the ground and the compensating (drain) current is measured by an amperometer of the light intensity, absorption measurements in transmission require a particularly thin (~10-50nm) sample that is homogeneous in the direction of the beam propagation which is sometimes impractical.

Furthermore, the XAS spectrum can be measured either by employing an electron analyser that measures the Auger products of the core decay or in Fluorescence Yield (FY) mode, shown in Figure 2.7 (b). In the FY configuration, photon-sensitive elements such as photodiodes or Charge Coupled Device (CCD) cameras are placed close to the sample, measuring the photon decay of the core holes. In this case, the probing depth is significantly large, typically exceeding 100nm, since the photons emitted during the core-hole decay have a significantly longer path length in the solid than electrons with comparable energy. Despite being a bulk sensitive probe, FY suffers from self-absorption effects, i.e. the attenuation of the emitted light by the absorber itself. Depending on the concentration of the absorber in the sample, these effects distort the absorption spectrum, producing photon energy dependent artifacts, particularly at the main peaks [56].

Alternatively, XAS can be carried out in Total Electron Yield (TEY) mode. This is achieved by connecting the sample to the ground and using a picoammeter to determine the flow of charges that move to the sample from ground, so as to compensate for all the photoelectrons, Auger electrons and secondary electrons that
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due to the self-amplification nature of the electron avalanche processes behind the secondary electron cascade, TEY XAS enables the acquisition of a very strong signal that is typically 2 to 3 times orders of magnitude larger than other methods [58]. Therefore, TEY can provide a high fidelity representation of the absorption spectrum, in view of the fact that fluorescence decay is strongly influenced by self-absorption and final state effects that cause distortions in the FY spectrum [59, 60].

2.2.5 Fermi’s Golden Rule

For atomic transitions taking place in a quantum system, the initial state $\psi_i$ is different to the final state $\psi_f$. Based on perturbation theory, for an incident photon of energy $\hbar \omega$ the rate of transition probability $w$ is given by the Fermi’s Golden Rule [50, 61]:

$$
\omega \propto \frac{2\pi}{\hbar} |\langle \psi_f | T | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar \omega)
$$

where $E_f$ and $E_i$ the energy of the final and initial state respectively and $T$ a transition operator that is related to the interaction Hamiltonian $H_{int}$. It can be shown that for one photon processes (such as XAS and PES) [50]:

$$
T = H_{int} = (\tilde{e} \cdot \tilde{p}) e^{i(k \cdot r)}
$$

where $\tilde{e}$ the electric vector of the light, $\tilde{p}$ the electron momentum and $r$ the transition operator. In the dipole approximation, only the first two terms in the Taylor expansion of $e^{i(k \cdot r)}$ are kept. It turns out that the quadrupole contribution (third term in the expansion) is smaller by a factor of $10^{-4}$ and can often be neglected.

An additional requirement for a transition to be allowed is imposed by the parity of the initial and final states that should be taken into account. In view of the fact that the dipole operator is of odd parity, the parities of the initial and final states have to be antisymmetric, enabling the term $|\langle \psi_f | T | \psi_i \rangle|^2$ to give non-zero value. For a quantum system of total angular momentum $\tilde{J}$, orbital momentum $\tilde{L}$ and spin momentum $\tilde{S}$ and respective quantum numbers $m_j$, $m_l$ and $m_s$ this leads to the following criteria:

$$
\Delta J = 0, \pm 1
$$
\[ \Delta L = \pm 1 \]
\[ \Delta S = 0 \]
\[ \Delta m_l = 0, \pm 1 \]
\[ \Delta m_s = 0 \]

The above, so-called selection rules are dictated by the Fermi’s Golden Rule, imposing requirements to the atomic transitions on the basis of the initial/final quantum states and rendering some transition prohibited. For example, in this picture, an electron occupying a p state can be excited only to an unoccupied s or d state. In addition, in the dipole approximation, spin flipping is not allowed.

### 2.2.6 X-ray Magnetic Circular Dichroism

A powerful technique that allows in-depth magnetic characterization of a system is X-ray Magnetic Circular Dichroism (XMCD), proposed by Schütz et al. [62] (the sum rules were derived by Thole et al. [63] and were experimentally verified using soft X-rays by Chen et al. [64, 65]). This method is based on polarization-resolved XAS and has unique properties over any other magnetic measurement technique [66] of being element-specific and therefore capable of retrieving selectively the magnetic contribution of a certain chemical species and being ultra-sensitive to subtle magnetic moments as small as 0.01\(\mu_B\) via the sum-rules [63].

As mentioned in the previous section, there are multiple ways to measure the (polarisation-dependent) absorption spectrum of a (magnetic) system. Although FY can be used to determine the XMCD [67], there are various effects that render the calculation of the spin and orbital moments less reliable [68–70]. The difference between a pair of XAS spectra measured with circular polarisation of opposite helicities is directly linked to the magnetisation. This dichroism spectrum is sensitive to subtle magnetic moments and allows the decomposition of the spin and orbital contribution of the probed population [63, 65]. The spin and orbital contribution to the total magnetic moment can be estimated by the following equations:

\[
\mu_{\text{spin}} = -\frac{3P - 2Q}{R}n_h \tag{2.1}
\]
2.2. Methods

\[ \mu_{\text{orbital}} = -\frac{2Q}{3R} n_h \]  

(2.2)

where \( R \) is the integral of the average XAS spectrum after subtraction of a background (for example in the form of an arctan function at each edge), \( P \) is the value of the XMCD integral of the dichroism at the L\(_3\) edge and \( Q \) is the value of the integral of the dichroism at the L\(_2\) edge. In systems that contain transition metal elements with incomplete 3d shells, there are limitations in the application of the sum rules that depend on the chemical species under investigation as well as the crystal environment [71].

Figure 2.8 (a), (b) and (c) show example cases of XMCD patterns calculated by subtraction of a pair of XAS spectra that were measured using circularly polarised light of opposite helicities, along with their integrals in Figure 2.8 (d), (e) and (f). These model spectra correspond to three distinctive physical cases. In Figure 2.8 (a), the integral of the XMCD over the L\(_3\) edge is equal to the L\(_2\) edge but it has an opposite sign. This leads to \( Q = 0 \), hence \( \mu_{\text{orbital}} = 0 \) (no orbital moment, only spin). Figure 2.8 (b) shows a special case in which the L\(_2\) \( Q = \frac{3}{2} P \), hence, \( \mu_{\text{spin}} = 0 \) (no spin moment, only orbital). Generally, a typical XMCD measurement of a system that contains both orbital and spin magnetic moments, resembles the spectrum of 2.8 (c) which consists of a superposition of the first two cases.

As described above, the sum rule analysis for the determination of the spin and orbital magnetic moments involves the integration of the XMCD signal over a broad energy range. In some cases, this method can be sensitive to a background of extrinsic origin that may appear in the measurement. Panels (b) and (c) in Figure 2.9 show the effect of a linear and a non-linear background respectively on the XMCD pattern of (a). Figure 2.9 (e) and (f) show the respective deviations in the integral of the XMCD compared with the ideal case shown in (d). A linear background can be easily removed from the XMCD by fitting a linear function in the pre-edge region. To ensure high accuracy, the measurement should be started at sufficiently low photon energies, well before the main edge. A non-linear background of polynomial form is more difficult to removed from the XMCD signal. This type of background is commonly affecting XAS measurements that are carried out in beamlines that are not specialised in absorption measurements. In the next section, the precise data analysis steps that were used in this work are described in detail.
Chapter 2. Experimental aspects

Figure 2.8: Application of the sum rules for the determination of the spin and orbital contributions to the magnetic moment of a 3d-ion: (a) and (b): two special cases of schematic XMCD patterns at the L_{2,3}-edges that yield only spin and orbital moment respectively, (c) general form of XMCD of a system that contains both orbital and spin moment, (d)-(f) respective integrals used in the sum rule analysis. The vertical dashed line in each graph marks the midpoint of the energy separation between the L_3, L_2 edges at which the P value was determined. Black arrows at the high energy side indicate a point located after the L_2 edge at which the Q value was determined. In real systems a typical XMCD spectrum, shown in (c) consists of a superposition of (a) and (b) (see text for details)
Figure 2.9: Effect of background artifacts in the determination of the spin and orbital contributions to the magnetic moment of a 3d-ion via the sum-rules: (a) ideal XMCD signal being zero before, after and in-between the absorption edges and same signal superimposed with (b) linear and (c) non-linear (polynomial) background. Dashed lines show the background that needs to be removed to retrieve the real XMCD pattern of (a). Graphs (d)-(f) show differences in the XMCD integrals of (a)-(c) that stem from these extrinsic backgrounds.
2.2.7 XAS and XMCD data treatment

This section gives an overview of the XAS and XMCD data analysis steps that were used in this work. A proper data treatment routine is essential for reliable valence fingerprinting and accurate determination of the spin and orbital contribution to the magnetic moment. The monochromator at synchrotron end-stations that are specially designed for absorption experiments is equipped with a “fly”-mode that allows the grating to move in a continuous manner, while an encoder records its actual position. This feature dramatically reduces the duration of a typical photon energy sweep compared with the process of moving the monochromator in steps. In this way, the acquisition of XAS spectra on a energy scale that extends over tens of eV takes no more than a few minutes. Figure 2.10 shows an example of the data analysis steps that were followed to extract the XAS and XMCD spectra used for valence fingerprinting and sum rule analysis in the following chapters.

Panel (a) of Figure 2.10 shows a set of six raw drain current measurements (vertically shifted for clarity) that were recorded consecutively employing $\sigma^+\sigma^+\sigma^-\sigma^+\sigma^+\sigma^-$ circular polarisation respectively in the presence of a magnetic field of 6 T, at a temperature of 10 K and with the X-ray beam incident at an angle of 20° in respect to the surface of a film that contains a layer of LCO of thickness 4 uc. Panel (b) of Figure 2.10 shows $I_0$ mirror current data that are divided out from the data of panel (a), to account for intensity fluctuations of the incident beam. Panel (c) of the same figure shows data recorded by the encoder of the plane grating monochromator that are used to assign the correct photon energy for each point of panels (a) and (b). The result of the above procedure along with interpolation is shown in panel (d). In the same panel (d) a linear pre-edge fit (dashed line) is calculated for each spectrum, while panel (e) shows the result of the background subtraction. Panel (f) shows the same spectra collapsed (not shifted for clarity). The average of those was employed for the XAS valence fingerprinting. Panel (g) shows a zoom-in region of the $L_3$ absorption edge of the same individual spectra, exhibiting magnetic contrast at the low energy shoulder and at the maximum of the absorption$^1$. Panels (h) and (i) show the calculation of the R and P, Q values respectively. For the sum rule analysis, the R value is computed after subtracting an arctan background function

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$^1$The first scan for each collection of measurements is considered a sample conditioning scan and is not taken on board the subsequent XAS/XMCD analysis
2.2. Methods

at the absorption edges of the unpolarised XAS spectrum, while the P, Q values at a region between and after the absorption edges of the XMCD spectrum.
Chapter 2. Experimental aspects

Figure 2.10: XAS and XMCD data analysis routine: (a) TEY drain current set of data measured with $\sigma^+ (+)$ and $\sigma^- (-)$ circular polarisation shifted for clarity accompanied by (b) mirror current $I_0$ data and (c) photon energy values recorded by the encoder of the plane grating monochromator. (d) XAS data divided by $I_0$ and interpolated according to the photon energies values of (c). A linear pre-edge (dashed line) is subtracted from each spectrum (e) XAS spectra after background subtraction (f) shows a superposition of all the individual spectra, the average of which is used in the valence fingerprinting analysis. (g) Zoom-in of the $L_3$ of a pair of polarisation-dependent XAS spectra (h) Determination of the R value used in the sum rule analysis (i) Determination of the P, Q values used in the sum rule analysis (see text for details)
Chapter 3

Co valence transformation in isopolar LaCoO$_3$ / LaTiO$_3$ perovskite heterostructures

We report charge-transfer up to a single electron per interfacial unit cell across non-polar heterointerfaces from the Mott insulator LTO to the charge transfer insulator LCO. In high-quality bi- and tri-layer systems grown using PLD, XAS, XMCD and STEM-EELS are used to probe the cobalt 3d-electron count and provide an element-specific investigation of the magnetic properties. The experiments show the cobalt valence conversion is active within 3 uc of the heterointerface, and able to generate full conversion to 3d$^7$ divalent Co, which displays a paramagnetic ground state. The number of LTO/LCO interfaces, the thickness of an additional, an electronically insulating “break” layer between the LTO and LCO, and the LCO film thickness itself in tri-layers provide a trio of control knobs for average charge of the cobalt ions in the LCO, illustrating the efficacy of O2p-band alignment as a guiding principle for property design in complex oxide heterointerfaces.

Chapter 3. Co valence transformation in isopolar LaCoO$_3$ / LaTiO$_3$ perovskite heterostructures

sized the samples and performed lab XPS and data analysis. M.S.G., G.A.K., J.G., S.K.M., S.S., and X.V. carried out the synchrotron work, with the data analysis done by G.A.K. and M.S.G., while P.B., T.-L.L., and C.S. provided essential user support at the synchrotron. N.G., D.K., J.F., and J.V. carried out TEM-EELS experiments and their analysis. M.S.G. and G.A.K. wrote the manuscript and all authors contributed to the discussion and revision of the manuscript.
3.1 Introduction

As introduced in Chapters 1 & 2, complex oxides of the transition metals are of great importance and interest from both a technological and a fundamental science point of view. Technologically, LiCoO$_2$ has underpinned the development of the now eponymous Li-ion battery [72], ferrites are indispensable in transformer cores and inductors, and oxide piezoelectric materials, such as PZT and their Pb-free analogs, are enablers of ultrasound imaging [73, 74]. With regard to fundamental science, complex oxides show an interplay between strong electron correlations, band behavior, and a rich repertoire of ordering phenomena in the spin and orbital sectors, making them an enduring focus of theoretical and experimental investigation [21, 75].

The maturity of epitaxy-based thin-film growth techniques provides opportunities to improve experimental control over the properties of these systems, leading to emergent interfacial properties such as conductivity [9], magnetism [11] and superconductivity [12, 13]. A central concept in the field is the role played by nature’s response to an incipient polar catastrophe at interfaces, which can be seen as an ultimate driver of interfacial charge transfer [76], providing an elegant and powerful new mechanistic paradigm for doping at a distance in an interfacial system. In practice, the response of real materials to the presence of a potentially polar interface can also be rooted in the relatively facile creation of oxygen vacancies in perovskite transition metal oxides [40], meaning in some systems the in-built potential of a polar overlayer is observed [77] and in other cases, such as the LAO|STO system, it is not [38]. In addition, strain and the GdFeO$_3$ (or octahedral tilting) distortion of the cubic $ABO_3$ perovskite can also be either transmitted or blocked between a bulk substrate and an overlayer [78]. All of these and other properties constitute a number of tools that can be used to design interesting and potentially useful functionalities in complex oxides [79]. As the dominant, silicon-based electronic materials universe makes clear, the interface can indeed be the device [80] fostering added interest in (ultra)thin oxide films and their interfacial properties.

A family of fundamentally intriguing and technologically relevant materials is cobaltates. This is exemplified in the case of LCO whose electronic properties have been a long-standing puzzle in condensed matter physics. In its ground state, LCO is a $d^6$ charge transfer insulator with a non-magnetic $t_{2g}^6e_g^0$ ($S=0$) LS electron config-
Chapter 3. Co valence transformation in isopolar LaCoO$_3$ / LaTiO$_3$ perovskite heterostructures

Temperature-induced changes in the resistivity and susceptibility in LCO [81] are well-understood features in the framework of the gradual thermally-activated occupation of the $t_{2g}^4e_g^2$ (S=1) HS state which results in a mixed-spin system with an accompanying insulator-to-metal transition at high temperatures [82–84]. An IS state $t_{2g}^5e_g^1$ (S=1/2) is suggested [85] to bridge the gap at intermediate temperatures and explain the discrepancy between the low and high temperature but the experimental evidence for this state remains elusive [86]. Bulk, long-range FM interactions were not found in the context of single crystals [87] and low temperature signs of ferromagnetism are attributed to spin-state surface effects related to the Co ion coordination [88].

In thin film form, the epitaxial strain imposed by the substrate is known to prevent the full occupation of the $d^6$ LS state in the ground state and measurable magnetic moments at low temperature are attributed to a finite $d^6$ HS occupation [89, 90], while more recent literature attributes the insulating ferromagnetic ground state to oxygen vacancy ordering [91–94] and spin-state ordering [95–97]. In electron-doped cobaltate species whereby coexistence of $d^7$ $t_{2g}^5e_g^2$ (S=3/2) HS with $d^6$ LS electrons takes place, a spin blockade state is realised [98]. In this case, the hopping of the $e_g$ electron from the $d^7$ HS ion to the $d^6$ LS is forbidden because it would convert the former to $d^6$ IS and the latter to $d^7$ LS, which is an energetically unfavourable configuration. On the other hand, the hole-doped variance of LCO hosts double exchange ferromagnetism [99].

3.2 Scope of this work

As discussed in Chapter 2 of this thesis, one method to tune and control d-state occupation in TMO is via charge transfer, and recently, a broadly applicable principle was introduced, enabling the design of oxide heterointerfaces in which charge transfer is predicted [32]. The idea here is that both the octahedral backbone and the A-site sublattice in an $ABO_3$ perovskite can be considered continuous across an $ABO_3|AB’O_3$ heterointerface. As a consequence, the O-2p-related bands of the two materials should align in energy. Depending on the relative energy alignment and separation of the metal ($B$ or $B’$) 3d and O-2p states in each compound, this can lead to charge transfer becoming favorable in the heterointerface, and also in
the case of isopolar heterointerfaces. The observation [37] of divalent Fe at isopolar interfaces between LTO (ground state 3d$^1$) and LaFeO$_3$ (ground state 3d$^5$) was an important inspiration for the development of the O-2p band alignment picture [32]. The band alignment argument presents a clear driving force for nature to avoid a d$^6$ LCO|d$^1$ LTO interface. Recently, the propensity of LTO to overoxidize was highlighted [100] and this can be seen as an alternative route for Ti to take on a 3d$^0$ configuration in the LCO|LTO interface.

Here, the successful generation of interfacial, valence-transformed, divalent cobalt ions in LCO is reported. This charge state is realized without any cationic chemical doping or visible change in the crystal structure, and is operative at the nanoscale: concentrated within 3 uc of the LCO|LTO interface. By tuning the LCO thickness and number of interfaces, the average Co valence can be altered between di- and trivalent. This electronic transformation of the Co 3d$^6$ to a 3d$^7$ state goes hand in hand with significantly increased paramagnetic polarization in external magnetic fields.

We present detailed spectroscopic and Scanning Transmission Electron Microscopy (STEM) data from a variety of LCO/LTO interfacial systems. These data not only characterize the cobalt valence transformation but also enable a discussion of the two main mechanistic routes for Co-3d$^6$ generation, namely O-2p band alignment driven charge transfer from LTO, and/or (overoxidation) underoxidation of the (LTO) LCO layers.

As we will present in detail below, key facets of the experimental data support the picture where electronic charge transfer is important, while other data point to the presence of oxygen nonstoichiometry. Therefore, while accepting the reality of oxygen off-stoichiometry effects in real-life perovskite transition metal oxides, these experimental findings support the design guidelines involving O-2p band alignment as a driving force for the generation of interfaces with tailored charge/orbital states [32]. Nanoscale, controlled electron transfer processes in oxides—in particular, in cobaltates—could also be very interesting in the context of sustainable energy technologies involving the oxygen evolution reaction, in which activity has been linked to an e$_g$ electron occupancy of unity [101].
3.3 Sample design and fabrication (at MESA\textsuperscript{+} Institute)

In the experiments reported here, ultrathin films of LTO and LCO were grown using PLD, in the Inorganic Materials Science (IMS) group’s laboratories in MESA\textsuperscript{+} Institute/University of Twente, on conducting 0.5 weight % Nb-doped, (100)-oriented STO substrates. The substrates were ultrasonically cleaned in acetone and subsequently ethanol, followed by a chemical etching procedure and finally annealing to achieve a well-defined, single TiO\textsubscript{2}-terminated surface \textsuperscript{102}. Intensity variations in RHEED were used to monitor the growth and assure uc level control over the film thickness. Subsequently, a 30 uc thick layer of LAO was grown. This served to (a) enable an accurate calibration of the PLD set-up as LAO grows very well in a layer-by-layer manner; (b) prevent formation of a polar-interface-driven charge transfer involving the LCO or LTO (both of which are polar) by separating them far from the non-polar STO, (c) mask the Ti states of the STO substrate in the soft X-ray absorption experiments and (d) discourage transport of oxygen from the STO substrate into the LTO film \textsuperscript{100}. After growth of the LTO, LCO or combinations thereof, a 5 uc LaNiO\textsubscript{3} (LNO) layer was added as a cap. The addition of this layer could be seen as a complication, yet it was a precautionary measure taken to hinder oxygen off-stoichiometry due to atmospheric exposure and to structurally “close” the perovskite structure of the top layer of the single- bi- or trilayer. An LAO cap was tried, but led to deleterious charging effects, particularly for the low temperature experiments probing the magnetic properties, and thus LNO was adopted throughout.

The growth of LCO and LTO film combinations poses a dilemma: in order to grow LTO, a low oxygen background pressure (typically well below 10\textsuperscript{-4} mbar) is desired, in order to avoid formation of unwanted phases like La\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} \textsuperscript{103} and over-oxidation of the LTO, which results in tetravalent Ti with 3d\textsuperscript{0} electronic configuration \textsuperscript{100}. On the other hand, good LCO growth prefers a higher oxygen background pressure (typically \sim 0.1 mbar), so as to avoid oxygen vacancies \textsuperscript{104}. Thus, while interfacing perfect, stoichiometric LTO and LCO in the computer \textsuperscript{32} is relatively straightforward, in the laboratory, true high-pressure LCO growth would aggressively over-oxidise the underlying LTO, resulting in an uncontrolled LTO qual-
3.3. Sample design and fabrication (at MESA+ Institute)

<table>
<thead>
<tr>
<th>Material</th>
<th>Fluence (J/cm²)</th>
<th>Substrate temperature (°C)</th>
<th>Laser repetition rate (Hz)</th>
<th>P(O₂) (mbar)</th>
<th>Laser spot size (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaAlO₃</td>
<td>1.3</td>
<td>750</td>
<td>1</td>
<td>2×10⁻³</td>
<td>2.3</td>
</tr>
<tr>
<td>LaTiO₃</td>
<td>1.9</td>
<td>750</td>
<td>1</td>
<td>2×10⁻³</td>
<td>2.3</td>
</tr>
<tr>
<td>LaCoO₃</td>
<td>1.9</td>
<td>850</td>
<td>2</td>
<td>2×10⁻³</td>
<td>2.3</td>
</tr>
<tr>
<td>LaNiO₃</td>
<td>1.9</td>
<td>750</td>
<td>1</td>
<td>2×10⁻³</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table 3.1: PLD growth parameters for the LAO, LTO, LCO, and LNO layers. P(O₂) denotes the oxygen background pressure during growth.

ity, and low-pressure growth aimed at stoichiometric LTO will not allow the growth of stoichiometric LCO with trivalent Co. Consequently, a third way was chosen here: namely, to grow both materials at an intermediate pressure of 2×10⁻³ mbar. The LTO thickness was kept below 5 uc, and the substrate-induced strain was used to help stabilize the 113-phase of LTO [103]. We note that all LCO reference samples grown without LTO were still grown at this intermediate pressure to facilitate comparison. Other PLD-parameters were optimized to obtain a flat and smooth surface after deposition and to form sharp interfaces. Ideally, additional trilayers in which the LTO thickness was varied with constant LCO thickness could be instructive. However, in practice, the formation of unwanted, non-113 LTO phases in these systems and the inability to fully reach the LCO layer using TEY XAS for thicker LTO layers form prohibitively severe complications to their study. An overview of all the growth parameters can be found in Table 3.1. Below we will experimentally justify the appropriateness of the chosen synthesis conditions.

A wide range of samples were grown, designed to test various aspects of the expected physical behaviour. As mentioned above, all possess a 30 uc LAO buffer layer and a 5 uc LNO capping layer and can be divided into four differing sample types as depicted in Figure 3.1. The four sample types are:

(a) LCO - containing no interface (0*IF)
(b) LTO|LCO - containing a single heterointerface (1*IF), a 4|x sample
(c) LTO|LCO|LTO - containing a double heterointerface (2*IF), a 4|x|4 sample
(d) LTO|LAO|LCO a single interface system including a “breaker” layer of LAO.

To exclude strain-related effects dominating the physics observed, a [2*IF] sample was also generated on an LAO substrate. Since the bulk (pseudocubic) lattice
constant of LCO is 3.78 Å at 4K and 3.84 at 1248K [105] the LCO would have a tensile strain of about 3% when fully strained on the STO substrates. For the samples grown on bulk (100) LAO substrates, LCO would have a compressive strain of about 1%.

3.4 Results

3.4.1 XAS Co valence fingerprinting

XAS was carried out at the Co-L$_{2,3}$ (and Ti-L$_{2,3}$) edges using soft X-rays from the I10 beamline at Diamond Light Source, Didcot, in the BLADE end-station. Both TEY and FY detection modes were employed simultaneously. As described in Chapter 2, the TEY signal exhibits an exponential falloff as a function of the depth into the sample. The IMFP, describing the characteristic lengthscale on which the signal is attenuated by a factor of 1/e compared to the incident value, is about 4 nm at the Co-L$_3$ edge [106] in TEY, meaning 95% of the signal is from within 12nm from the surface. The effective FY probing depth is comparable to the X-ray penetration depth, but FY data do present some complications for the use of XMCD sum rules [70], so the XMCD data analysis presented here concerns the TEY data. The experimental station combines a cryostat operated at a lowest temperature of
3.4. Results

10K with a superconducting magnet applying fields between $-14 \leq H \leq +14$ Tesla. The magnetic field is oriented along the incoming X-ray beam-path, facilitating element specific magnetometry based on XMCD experiments using the sum rules as described in Chapter 2 of this thesis. The base pressure of the measurement chamber is in the $10^{-10}$ mbar range. The L$_{2,3}$-edge XAS spectrum of a transition metal compound involves electronic transitions from the $2p_{1/2}$ and $2p_{3/2}$ core levels to unoccupied 3d states, and provides an ultra-sensitive fingerprint of the d-electron count, or valence of the system under investigation [107].

For ensuring maximally accurate XAS data, experiments were conducted at 10K by recording repeated blocks of spectra with alternating X-ray polarisation (e.g. $\sigma^+\sigma^-\sigma^+$ followed by $\sigma^-\sigma^+\sigma^-$). For the valence fingerprinting, the average of the spectra for the two circular polarizations is taken. For the majority of the data reported here, the X-rays were incident at a grazing angle of 20 degrees with respect to the surface of the film. Control experiments were carried out at higher temperatures, larger incidence angles and investigating different locations on the 5x5 mm$^2$ films. In all cases, the measured XAS spectra were normalized to the edge-jump, accounting for the number of holes in the 3d-shell, while a linear background that was determined well before the pre-edge region was subtracted.

As the right-hand panel (b) of Figure 3.2 shows, Co-L$_{2,3}$ XAS spectra from high-quality single crystals taken from [108] are very characteristic for whether the cobalt ions are trivalent (nominally d$^6$, in this case EuCoO$_3$ or Sr$_2$CoO$_3$Cl) or divalent (formally d$^7$, here CoO). There are some subtle differences between the LS and HS variants in the trivalent case, but there are two very prominent low-energy features in the divalent case, highlighted with yellow arrows that make a valence change from tri- to divalent experimentally very easy to spot.

Panel (a) of Figure 3.2 shows the core result of this research. The data from the thin (4 uc) film of LCO (blue) closely resembles a combination of the spectra of the two trivalent model compounds. We point out that the very tiny shoulder at the lowest energy in the blue trace of Figure 3.2 (a) could signal a nonzero divalent contribution, but this is too small to fit reliably (we estimate the divalent contribution to be less than 3%). Upon sandwiching a sample with 2 uc of LCO between LTO layers to generate two LTO/LCO interfaces (2*IF) (red), strong XAS intensity can be seen at the location of the two yellow arrows. Now the XAS fingerprint is almost identical to that of CoO: for this double-interface system 100% of the cobalt
Figure 3.2: Valency fingerprinting via Co-L$_{2,3}$ XAS shows complete transformation to divalent Co. (a) From top to bottom: no active interface (0*IF): 4uc LCO; double IF (2*IF): 4uc LTO|2uc LCO|4uc LTO; (2*IF) on LAO substrate: 4uc LTO|2uc LCO|4 uc LTO. Top two datasets measured at 10 K, lowermost at 100 K. (b) Spectra from single crystals of model compounds from Ref. [108]: from top to bottom: EuCoO$_3$ (Co$^{3+}$ LS) Sr$_2$CoO$_3$Cl (Co$^{3+}$ HS) and CoO (Co$^{2+}$, HS).
ions have been transformed into a divalent, d$^7$ electronic configuration. In the simplest picture this yields a single electron in an otherwise empty e$_g$ orbital manifold. The bottommost trace in Figure 3.2(a) (gray) shows that exactly the same result of complete valence transformation occurs also with the LCO under (mild) compressive strain, as this film stack was grown on bulk LAO. Figure 3.10 shows two methods for decomposing spectra to yield Co$^{2+}$ percentages, and they agree nicely. The effective error in valency determination is of order 5%, leading to an appropriate rounding of all divalent Co percentages in the rest of this chapter. From the data of Figure 3.2 it is already clear that the combination of ultrathin LCO sandwiched between LTO does not support regular trivalent cobalt ions, but rather a divalent state, in line with the theory predictions for this couple in Ref. [32]. As each of the Co ions in the 2 uc LCO film has picked up an extra electron, the obvious question arising is, from where? The two main possibilities are the following:

(i) Charge transfer of the 3d$^1$ electron from the LTO to the cobalt ions (as takes place in the DFT simulations [32], or

(ii) a Co valency change as a result of oxygen (or cation) nonstoichiometry in the LCO layer or anionic/cationic intermixing between the layers.

Obviously, this is an important issue to settle. To work out what is happening in these carefully PLD-grown single-, bi-, and trilayer systems with layer thicknesses in the few- uc level in an unbiased manner, a combination of atomic level structural determination and sensitive (and non-invasive) valency determination is required. This is precisely what is brought to bear on the problem using soft X-ray XAS, (HAX)PES and STEM techniques. As a next step, we discuss data regarding the following:

(i) the range within which the cobalt valency is altered in the LCO (from both XAS and STEM)

(ii) the valency of the Ti in the LTO (from XAS and XPS) and

(iii) the crystalline quality of the interfacial systems (from STEM).

For each set of data, we discuss the pros and cons for an explanation via charge transfer from LTO to LCO or via some degree of overoxidation (underoxidation) of the LTO (LCO). This approach allows the reader to form their own opinion of the relative importance of O-2p band alignment and oxygen vacancy effects in this system. At the close of this chapter we will gather together all the arguments, once all the different experimental results have been presented.
Chapter 3. **Co valence transformation in isopolar LaCoO$_3$ / LaTiO$_3$ perovskite heterostructures**

We now move to the range in the LCO over which this charge transfer effect is active. This can be probed by varying the LCO thickness in a 4 uc LTO/x uc LCO/4 uc LTO sandwich configuration. The Co-L$_{2,3}$ XAS valency fingerprints for these systems are shown in Figure 3.3 for x=2, 4, 6 and 36 uc together with a trace from a single-interface (1*IF) 4 uc LTO/4 uc LCO sample for comparison (the 4/2/4 data are the same as those shown in Figure 3.2 (a)).

Starting from the bottom of the stack of spectra in Figure 3.3: The 1*IF data in green already show the presence of significant divalent cobalt (model compound fits yield 30% divalent Co), linked to a single active LTO/LCO interface. Next up in Figure 3.3 is the 2*IF system shown in pink. Here the lowermost interface has been placed 15 nm below the film surface, and thus is essentially invisible in TEY-XAS due to its limited probing depth [106]. Thus, as regards the information depth of the experiment, the 4/36/4 sample should resemble a 1*IF system, as the data of Figure 3.3 show it does. This is a first indication for interfacial character of the charge transfer.

Moving to the centermost XAS spectrum, confining only 6 uc of LCO between the LTO (blue) brings both interfaces within measurement range, and the result is an increase to 40% divalent Co. As the central LCO layer gets thinner, the average divalent percentage increases: in the 4/4/4 sample half the Co ions are divalent, and as discussed in the context of Figure 3.2 (a), for 4/2/4 all the trivalent cobalt ions have received an additional electron, turning them divalent.

The deepest-lying LTO/LCO interfaces for x = 6, 4, and 2 vary from 5.7 to 4.9 to 4.2 nm below the sample surface, so it is a combination of the reduction of the distance in the LCO to the nearest active LTO/LCO interface and the limited range away from the LTO interface at which the charge transfer into the LCO is effective that are responsible for the strong growth in the overall divalent character.

These LCO-thickness-dependent data on trilayers also are in line with interfacial character of the Co valence transformation. The Co-L$_{2,3}$ XAS data from these trilayers suggest that each interface leads to a remarkably large transformation of the Co valence in the abutting LCO, equivalent to one additional electron in the LCO. In order to correctly interpret the origin of the electrons picked up by the Co ions, atomic-scale information is required on the structure and chemical makeup of the interfacial region.
Figure 3.3: Interfacial character of charge transfer. Co-L₂,₃ XAS spectra of 2*IF systems: 4 uc LTO/x uc LCO/4 uc LTO with x = 2, 4, 6, and 36 uc. The bottommost trace from a 1*IF 4 uc LTO/2 uc LCO sample shows the 4/36/4 system is similar to the single-IF case. The LCO thickness dependence clearly signals the interfacial character of the electron transfer. All data recorded at 10 K, and individual spectra are offset vertically for clarity.
Figure 3.4: STEM imaging and spectroscopy: (a) HAADF-STEM cross section showing excellent epitaxy and sharp interfaces. (b) and (c) show STEM EELS data from the same cross section. In (b) a downshift of Co-L\textsubscript{2,3} main feature close to the active IF, is consistent with interfacial Co(II). In (c) an upshift of interfacial O-K pre-peak in LCO is seen, also consistent with interfacial Co(II). In the central images of (b) and (c) the white lines schematically indicate the energy shifts occurring. All data recorded at room temperature and in the 2T field of the objective lens.

3.4.2 STEM-EELS real space confirmation

Scanning Transmission Electron Microscopy (STEM) using High Angle Annular Dark Field (HAADF) imaging was performed by the Electron microscopy for Materials Science (EMAT) team (Dr. Nicolas Gauquelin) in the University of Antwerp using a FEI Titan 80-300 microscope operated at 120 kV. The samples were prepared in a vacuum transfer box and studied while held in a Gatan vacuum transfer sample holder to avoid any influence of air on the film [109–111]. Electron Energy Loss Spectroscopy (EELS) measurements were performed using a monochromatic beam with a 120meV energy resolution. The Ti-L, Co-L edge, O-K and La-M\textsubscript{5} edges were acquired simultaneously (the La being used for energy calibration). The acquisition parameters were 0.25s/pixel, 0.4\AA/pixel and 0.05eV/pixel in the dual EELS mode. Collection angles for HAADF imaging and EELS were 70-160 mrad and 47 mrad, respectively.

Figure 3.4 (a) shows a HAADF STEM image from a cross-section of an LNO-capped LTO4|LCO36|LTO4 film stack grown on STO (substrate not shown). This particular sample was chosen as the upper and lower LTO|LCO interfaces were
3.4. Results

readily identifiable after focused ion beam-based cross-section preparation. From the image, the high quality of the samples is evident.

A 2D representation of the STEM-EELS spatial line-scan data across the two active IFs of the sample are depicted at the Co-L\textsubscript{3} and O-K edges in Figs. 3.4 (b) and 3.4 (c), respectively. These 2D spatial/spectroscopic maps, show a definite shifting of the energies of the low energy features of both the Co-L\textsubscript{3} edge (downward) and the O-K edge (upward) that take place inside the LCO, within ~3uc of the LTO|LCO interface. A glance at Figs. 3.2 or 3.3 suffices to see that the downward shift observed in the Co-L\textsubscript{2,3} STEM EELS data matches the spectral fingerprint of the divalent cobalt seen in XAS. Importantly, the STEM data show that in this 36 uc LCO film, the Co valence transformation takes place within a region within ~3uc of interface to the LTO. Thus on a qualitative level, the picture of electron-rich LCO near the LTO interface suggested from the data of Figure 3.4 is borne out in the STEM data.

We pause here in the data presentation to point out that the STEM data rule out prominent cationic non-stoichiometry or migration across the ABO\textsubscript{3}|AB'O\textsubscript{3} interface. Obviously, A-site cationic migration is a non-issue as La has been used throughout all layers in our heterostructures. For the B-site, it would be possible for Ti and Co to migrate across interfaces in both directions and take on different valence states. However, both the HAADF-STEM and the EELS data from multiple samples yield no indication - within the error margins of a single uc - that such migration occurs, and nor was significant cation non-stoichiometry observed in either material.

At this stage, it is useful to turn to the electronic states and valency of the Ti in the LTO in these heterostructures, which can be measured using core level photoemission and XAS. In Figure 3.11, the Ti-L\textsubscript{2,3} edges of the LTO layers in 2*IF samples composed of 2, 4 and 6uc of LCO between a pair of 4 uc LTO layers are shown, as well as those of STO. The intensity ratio of the first two (L\textsubscript{3}, t\textsubscript{2g} and e\textsubscript{g} related) structures are different in the trilayers compared to STO, but otherwise all four traces clearly signal Ti in the tetravalent (3d\textsuperscript{0}) state. On a qualitative level this can argue for the transfer of the 3d electron of the LTO to LCO, as predicted in Ref. [32]. However, on a charge-counting level the data reveal that more electrons are lost from Ti than are gained by Co. The 4/2/4 sample is the clearest example of this: 2 uc of LCO have a 3d\textsuperscript{7} (divalent) configuration, as shown in the data of Figure 3.2, yet
Figure 3.11 shows that 8 uc of LTO are in a 3d⁰ initial-state configuration. This fact immediately means that the interpretive slider on a scale from -on the one hand-(a) O-2p alignment driven charge transfer between stoichiometric LTO and LCO and -on the other hand- (b) oxygen nonstoichiometry induced valence changes (in both LTO and LCO) cannot lie fully at the “(a) only” end of the scale. This conclusion is only natural, given the intermediate oxygen pressure in which we chose to grow the samples: one could expect the formation of LaTiO³⁺ and LaCoO³⁻ as this has been seen in the growth of each material as a “stand-alone” system [100, 104]. We do mention here that the XAS traces from reference LCO films grown under identical conditions to the LCO in the bi- and trilayers show divalent Co only at the < 3% level, which would obviously not explain the high percentages of divalent Co in the heterostructures.

Returning to the LTO, in Figure 3.12 we use in situ XPS experiments (carried out by Jaap Geessinck in the IMS lab in MESA+ / University of Twente using monochromatized Al-Kα radiation and an Omicron 7-channeltron electron energy analyzer) to show that the Ti valence in an LTO film grown on LAO under the conditions given in Table 3.1, and then transferred without breaking vacuum from the PLD to the PES system, can be altered between essentially tetravalent to majority trivalent, depending on a UHV annealing protocol. These valency changes would be in line with the LTO overoxidation phenomena reported in Ref. [100]. From a solid-state chemistry point of view, the extra oxygen interstitials required to remove 6 Ti-3d electrons (2 electrons being hosted by the LCO layer) from the 2 × 4 uc of LTO in the 4|2|4 trilayer sample are not an easy “fit” in a space-filling representation of the 113-ABO₃ structure for the LTO and should result in some degree of structural deformation. Indeed, in LaTiO₃+δ with Ti⁺⁴, one could expect to see line defects belonging to the 227 phase [103], which we do not see in the STEM data. Analogously, if oxygen vacancies in LCO account for the presence of the entirely divalent Co population in the 4|2|4, the result would be the formation of the brownmillerite structure LaCoO₂.₅ [112] in the central LCO block, also something not supported by the STEM data presented here. Nevertheless, the PES experiments of Figure 3.12 do show alterations in Ti valence in our LTO films and this should also find a place in the interpretative framework for the data from the bi- and trilayer systems.

In addition to the issue of the true electron count in the LTO structures, the Ni-3d level in the LNO cap could act as an acceptor for electrons from the LTO, or indeed
from the LCO. LNO was not covered as an example in the DFT data of Ref. [32] and the use of LNO (chosen to avoid A-site migration issues) means there is a strong overlap of the La-M\textsubscript{4,5} lines with the Ni\textsubscript{2,3} features thus complicating Ni valence determination in XAS of the LNO layer. Consequently, both the electron-counting imbalance mentioned above and the smaller divalent Co contribution seen in thin, 1*IF samples relative to the expectation from the 3 uc charge transfer range from STEM could have a connection to the LNO. We freely admit that this is a potential complication; however, as mentioned in the introduction to this chapter, a cap was included to minimize the effects of atmospheric exposure and LNO was found to be a good candidate to enable charging-free, low-temperature TEY measurements.

Returning to the STEM data, we see a clean perovskite structure throughout the whole stack for all types of samples that we have presented in this chapter. For example, ordered defects have already been seen experimentally for 10\% oxygen vacancies, equivalent to a composition of LaCoO\textsubscript{2.7} [70]. Our STEM data are wholly devoid of the stripe- or line-like features that have been interpreted in the literature as Co spin-state ordering or O-vacancy ordering in LCO [70, 91, 92, 95, 96]. In epitaxial films one would also expect a measurable expansion of the LCO c-lattice parameter [113], something which is not seen in our STEM data. Ion milling to generate (S)TEM samples is ubiquitous, and also used in Ref. [70], which saw ordered vacancies in LCO. Thus, although milling-induced or STEM beam-induced alterations of the oxygen content cannot be excluded, the agreement between our XAS and STEM-EELS data suggests that ion-milling damage is not a leading-order factor in the data presented here.

### 3.4.3 (HAX)PES confirmation

HAXPES measurements were conducted at the I09 beamline at Diamond Light Source, Didcot, using a photon energy of 2.2 keV. The HAXPES spectra were recorded using an EW4000 photoelectron analyser (VG Scienta), equipped with a wide angle acceptance lens, with the X-rays incident at a grazing angle of 55°, so as to enable depth profiling analysis of the photoelectrons where appropriate. XAS spectra were also recorded at the I09 beamline at the Co L\textsubscript{2,3} edges from the same spot (30 µm \times 50µm) as was measured using HAXPES, so as to connect to the XAS data recorded at the I10 beamline. A portable UHV “suitcase” chamber was
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![HAXPES spectra](image)

Figure 3.5: HAXPES confirms Co(III)-d$^7$ ions in interface samples: HAXPES spectra of the Co-2p core level of (top to bottom) CoO (Ref. [55]); 2*IF LTO4/LCO4/LTO4 and 1*IF LTO4/LCO4 on LAO substrates and LCO 4 uc on a Nb:STO substrate (red, blue, and green, respectively); and bulk LCO (Ref. [114]). The thin-film data were recorded using $h\nu = 2.2\text{keV}$ at 250 K, and the yellow arrows highlight the shake-up satellites characteristic of octahedrally coordinated Co(II) ions. Individual spectra are offset vertically for clarity.

used to transfer some of the samples from the PLD system in Twente to Diamond Light Source in a pressure in the 10$^{-10}$ range, to investigate whether oxidation occurs during transport.

Figure 3.5 shows Co-2p HAXPES spectra of a 0*IF 4 uc LCO sample (Nb:STO substrate), 1*IF 4 uc LTO/4 uc LCO, and 2*IF 4 uc LTO/4 uc LCO/4 uc LTO, the latter grown on LAO substrates, together with reference spectra from bulk LCO and CoO from the literature [55, 114]. The Co-2p photoemission line shape is a result of numerous final-state charge-transfer and multiplet interactions and this cautions against a strict quantitative analysis. However, the absence or presence of characteristic satellite structures appearing at $\approx 6$ eV higher binding energy than the main spin-orbit-split main lines is a telltale sign of the Co valence. These features are indicated in Figure 3.5 using yellow arrows, and are a result of a so-called “shake-up” process in which ligand-to-metal charge transfer takes place, yielding a $|2p^5 3d^{n+1}L\rangle$.
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final state \([115]\). In octahedrally coordinated Co(III) systems such as bulk LCO, the charge transfer energy, \(\Delta\), required to do this is too great and no satellite is observed \([116]\), but in divalent Co(II) this is a salient feature of the spectrum \([117]\).

Looking at the data of Figure \ref{fig:3.5}, it is clear that the 1*IF 4/4 sample shows clear satellite intensity [and thus presence of Co(II) ions] and that this increases further in the case of the 2*IF 4/4/4 sample, following the same trend as seen in the XAS data. In line with this, for the 4 uc LCO film without an “active” LTO/LCO interface, no shake-up satellite is observable, just as for the bulk LCO spectrum from trivalent cobalt. Given the thinness of the cobaltate layers and the significant IMFP length of the photoelectrons under these conditions, no depth profiles could be extracted from the angle-dependent HAXPES data.

3.4.4 Testing the range of charge transfer in LAO “break” layers

This penultimate results section of this chapter presents a double-check of the range over which the charge transfer between LTO and LCO is active. The calculations of Ref. \([32]\) also suggested the possibility of modulation doping, in which there is spatial separation between the location of the (potential) conduction electrons and the dopants/structures that give rise to the charge transfer. Up to 5 uc of a transition metal oxide SrZrO\(_3\) buffer layer (what we call below a “break” layer) is suggested to be able to leave the interfacial charge transfer unaffected \([32]\). Given the very robust dependability of the PLD growth, generation of samples including such “break” layers provides a simple, combined test of both the interfacial nature of the charge transfer and the practical feasibility of modulation doping in such oxide heterostructures.

In Figure \ref{fig:3.6} the main Co-L\(_3\) XAS feature is shown for a series of 1*IF samples. The LTO4/LCO4 (red) and LCO4 (blue) have been discussed before, with the former showing 25% divalent Co and the latter <3%. The three traces in between possess a single IF, but with a varying number (here 1, 2, and 8) of unit cells of LAO slipped in between as an electronic break layer [see Figure \ref{fig:3.1} (d)]. As LAO is a wide band gap insulator, with no variable oxidation state cations, it is a highly effective charge transfer circuit breaker. The inset highlights the lowest energy divalent Co prepeak feature, and clearly shows what is happening: charge transfer at a level comparable
Figure 3.6: Testing “modulation doping” style charge transfer idea using LAO “break” layers: Co-L\textsubscript{3} XAS traces of 4 uc LTO/x uc LAO/4 uc LCO, with x = 0, 1, 2, 8. LAO interrupts the charge transfer, approaching the zero-active-IF 4 uc LCO system. The inset shows a zoom of the prepeak region.

to that in the LTO4/LCO4 system is maintained despite addition of a single uc of LAO as a break. However, already an LAO break of only 2 uc reduces the telltale divalent Co feature by a factor 2.5.

In the context of the LAO/STO interface possessing a 2D electron gas in the STO, the inclusion of a SrCuO\textsubscript{2} layer as an oxide ion supplier above 10 uc of LAO on STO removed the thermally activated defect donor states at the STO interface, boosting the mobility fivefold [118]. The success of this sample design involving the cuprate layer shows that oxide ions can be effectively transmitted by LAO over even 10 uc thicknesses. Thus, if the divalent Co seen in the bi- and trilayer samples were to be dominantly due to oxygen gettering by the LTO from the LCO, given the proven transmission of oxide ions through LAO [118] the strong reduction in divalent Co for the break-layer samples with LAO thicknesses of 2 and 8 uc would be hard to understand. However, if the divalent Co results from O-2p band alignment driven interfacial charge transfer, then the data of Figure 3.6 would seem to confirm the DFT-based expectation that the charge transfer can bridge a thin insulating barrier.
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Figure 3.7: XMCD shows boosted Co magnetic moment on formation of Co(III)-d^7 ions in interface samples: (a)–(d) TEY-XMCD signal (σ^+−σ^-) at the Co-L_{2,3} edges as a percentage of the maximum of the Co-L_3 absorption. Panels (e)–(h) show the integrals over the XMCD signals, normalized to the integral of the unpolarized absorption for the same data. Panels (a), (e) are for 0*IF: 4 uc LCO; (b), (f) are for 1*IF: 4 uc LTO/4 uc LCO; (c), (g) are for 2*IF: 4 uc LTO/4 uc LCO/4 uc LTO; (d), (h) are for 2*IF: 4 uc LTO/2 uc LCO/4 uc LTO. All data are measured at 10 K with the samples cooled in the fields shown.

3.4.5 XMCD data and sum rule analysis

In the final results part of this chapter, we turn to the spin state and magnetic properties of the Co ions in the LCO films. Obviously, there is no straightforward manner in which the individual Co^{2+} ions with Co 3d^7 configuration can be spinless. Measuring the magnetic properties of complex oxides in the form of ultrathin films as components in heterostructures on bulk substrates is a severe technical challenge for regular magnetometry. In such cases, the chemical specificity offered by XMCD [62, 119] offers not only exquisite sensitivity, but also, via application of XMCD sum rules [63], extraction of both the spin and orbital moments.

Panels (a)-(d) Figure 3.7 show XMCD data recorded in different applied magnetic fields for 0, 1 and 2*IF systems. Figure 3.13 shows exemplary raw σ+ and σ−XAS data that yield the XMCD signal. Each XMCD panel in Figure 3.7 is on the same y-scale in units of the % of the maximal Co-L_3 absorption. As is expected for
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<table>
<thead>
<tr>
<th>System</th>
<th>Co$^{+2}$ (%) from XAS</th>
<th>Orbital moment $m_l$ ($\mu_B$) from XMCD</th>
<th>Spin moment $m_s$ ($\mu_B$) from XMCD</th>
<th>Total moment $m_{tot}$ ($\mu_B$) from XMCD</th>
<th>Saturation magnetization $M_{sat}$ ($\mu_B$) from Brillouin function</th>
<th>Factor increase in $m_{total}$ cf. LCO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0*IF LCO4</td>
<td>&lt;3</td>
<td>0.15</td>
<td>0.33</td>
<td>0.45</td>
<td>0.48</td>
<td>0.53</td>
</tr>
<tr>
<td>1*IF 4</td>
<td>4</td>
<td>25</td>
<td>0.2</td>
<td>0.38</td>
<td>0.55</td>
<td>0.58</td>
</tr>
<tr>
<td>2*IF 4</td>
<td>6</td>
<td>4</td>
<td>40</td>
<td>0.26</td>
<td>0.5</td>
<td>0.52</td>
</tr>
<tr>
<td>2*IF 4</td>
<td>4</td>
<td>4</td>
<td>50</td>
<td>0.26</td>
<td>0.47</td>
<td>0.54</td>
</tr>
<tr>
<td>2*IF 4</td>
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<td>4</td>
<td>100</td>
<td>0.37</td>
<td>0.75</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 3.2: Magnetic parameters from XMCD sum rule analysis for -14 T applied field at 10 K.

a thin film system [86], the 0*IF 4 uc LCO sample is not perfectly low spin, with the data of Figure 3.7 showing an XMCD signal at the 7-8 percent level at the maximal field of 14T. Adding an active LTO|LCO interface (1*IF: LTO4|LCO4) alters the spectral form of the XMCD signal and it more than doubles in magnitude. Upon going to the [2*IF] systems LTO4|LCO4|LTO4 and LTO4|LCO2|LTO4, the XMCD signal is four- and six-fold enhanced compared to that of the single LCO layer. Thus, it is very clear that the controlled charge transfer between LTO and LCO is turning the interfacial cobalt ions into magnetically polarisable entities, in keeping with the odd number of electrons in their d-shell from the XAS lineshape analysis.

The XMCD sum-rules enable extraction of more quantitative information on the magnetic properties [63]. These involve the integration of the XMCD signal over the photon energy region of the Co-L$_2$ and L$_3$ edges, as explained in Chapter 2 of this thesis (see Figure 2.10) and Panels (e)-(h) of Figure 3.7 show these normalised XMCD integrals. Already without any further analysis, the fact that the XMCD integral shows a downward step at the L$_2$ edge and maintains a finite value thereafter, which, as illustrated schematically in Figure 2.8 earlier in the thesis, indicates that the Co ions possess both spin and orbital moments.

The spin and orbital moments extracted from the sum rule analysis are shown in Table 3.2. Increasing the number of active interfaces boosts both the spin and orbital
moments by factors equal to or exceeding 1.2 [1*IF], 1.5 [2*IF with LCO4] and 2.4 [2*IF with LCO2]) compared to 0*IF (LCO4). For all samples, the orbital moment is considerable, amounting to half of the spin moment, and is aligned parallel to the spin moment, meaning the g-factor exceeds 2 in these systems.

Grown under coherent epitaxial strain on bulk STO, the LCO layers in these systems are under in-plane tensile strain: c/a < 1. Studies of 10nm thick films of CoO grown either sandwiched between MnO on a Ag substrate or grown directly on silver [120] have shown that the 3d spin-orbit interaction prevents the collapse of the orbital moment [121] for HS Co 3d⁷ states when c/a < 1. We propose that this same mechanism is likely to be operative in the in-plane tensile strained LCO films presented here.

The data presented in Figure 3.7 and their analysis clearly point to the generation of spinful Co 3d⁷ entities as soon as one or more active LTO|LCO interfaces are introduced, with a total moment of 1.16 μB, and m_l/m_s of 0.5 for the fully divalent cobalt ions in LTO4|LCO2|LTO4.

In order to discuss the magnetic behaviour of the Co ions, Figure 3.8 presents the field and temperature dependence of the magnetisation extracted from the XMCD sum rules for a 0*IF LCO sample and two 2*IF systems: LTO4|LCO6|LTO4 and LTO4|LCO2|LTO4. The colour-coded solid lines are fits to: $M = M_{sat}B_J(x)$, where the experimentally determined $m_l/m_s$ ratio and the S expected from the valence observed in the XAS were used to calculate J using a Brillouin function:

$$B_J(x) = \frac{2J + 1}{2J} \coth \left( \frac{2J + 1}{2J} \right) - \frac{1}{2J} \coth \left( \frac{x}{2J} \right) \text{ with } x = \frac{g_J\mu_B J B}{k_BT}$$

The Landé g-value is:

$$g_J = \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)}$$

and we note that such a Brillouin function describes the spin physics of a collection of spins behaving paramagnetically [41].

The saturation magnetisation, $M_{sat}$, was varied to achieve optimal fits to the experimental field- (main figure) or T-dependence (inset) of the data. $M_{sat}$ is about 10% greater than the values connected to maximal(minimal) fields(temperatures) accessed experimentally. Simple inspection of Figure 3.8 shows the Brillouin function captures the essence of the field dependence and the strong decay of the magnetisa-
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...tion as temperature is raised for all the samples measured, indicating paramagnetic behaviour.

For the 0*IF system LCO$_4$, the 3d$^6$ HS (S=2) population provides the paramagnetic magnetic response that is also evident in the photon energy dependence of the L$_3$ XMCD signal for LCO$_4$ shown in Figure 3.7 (a) which is different to that of the samples with interfaces (Figure 3.7(b)-(d)), an additional argument on top of the valence fingerprint data that the spins in LCO$_4$ are not originating from Co$^{2+}$-3d$^7$ centres. Taking into account the experimentally determined $m_l/m_s$ ratio of 0.45, a good fit is achieved for a saturation magnetisation of $M_{sat}$(LCO$_4$) = 0.45 $\mu_B$ per Co atom. For the 2*IF systems LTO$_4$|LCO$_6$|LTO$_4$ and LTO$_4$|LCO$_2$|LTO$_4$, in which charge transfer has created divalent Co 3d$^7$ ions, there are two options:

i) a HS t$_{2g}^5$e$_g^2$ S=3/2 state

ii) a LS t$_{2g}^6$e$_g^1$ S=1/2 state

The Brillouin function fits in the main panel of Figure 3.8 are for HS 3d$^7$, the same spin state as in CoO (the latter is also HS as a thin film under either compressive or tensile in-plane strain [120]). Without exception, divalent cobalt oxides are quoted as HS in the literature, as their on-site Coulomb interaction energy, $U_{dd}$ (at the root of Hund’s first rule) is greater that the crystal field energy. In the mixed valent cobalt oxide La$_{1.5}$Sr$_{0.5}$CoO$_4$, successful modelling of the Co-L$_{2,3}$ XAS using a combination of the spectra from EuCoO$_3$ (LS Co3d$^6$) and CoO (HS Co3d$^7$) is provided as evidence that the divalent Co in La$_{1.5}$Sr$_{0.5}$CoO$_4$ is HS [122]. The fact that the XAS data from our bi- and trilayer samples can also be fitted in exactly the same way (see Figure 3.10) argues by analogy for the conventional HS spin state for the divalent Co 3d$^7$ here. Having said that, the Brillouin function fit for the field dependence for the LS 3d$^7$ state, only gives a marginally worse fit. The saturation magnetisations - using $m_l/m_s$ ratios of 0.52 for both [2*IF] samples - are 0.89 and 1.29 $\mu_B$, per Co atom for LTO$_4$|LCO$_6$|LTO$_4$ and LTO$_4$|LCO$_2$|LTO$_4$, respectively, as shown in Table 3.2.

The expected spin-only magnetic moment in a simple single-ion picture for HS Co 3d$^7$ would be 3 $\mu_B$ per Co, and under similar assumptions would be 1 $\mu_B$ for LS Co 3d$^7$. In this straightforward view, the LS configuration can be argued to yield a spin moment closer to the experimental spin-only value of 0.75 $\mu_B$ for the fully Co 3d$^7$ LTO$_4$|LCO$_2$|LTO$_4$ system. Arguments can also be made that the improved Goldschmidt tolerance factor for the smaller LS Co3d$^7$ ion [15] of (t=0.958)
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Figure 3.8: Magnetic field and temperature dependence of the cobalt element-specific magnetisation shows Brillouin-function behaviour. Shown is the field dependence of \(m_{\text{tot}}\), the sum of spin and orbital moments (coloured symbols), determined using the XMCD sum rules for 0*IF: 4 uc LCO (blue), and 2*IF: 4uc LTO|6uc LCO|4uc LTO (red) and 4uc LTO|2uc LCO|4uc LTO (green). The solid lines show fits using a Brillouin function (\(T_{\text{sample}} = 10\)K) for \(S\) values from the XAS valence analysis (\(S=3/2\) for HS Co 3d\(^7\); \(S=2\) for HS Co 3d\(^6\)) and \(L\) values matching the determined \(m_l/m_s\) values from the sum rules. The inset shows the temperature dependence of the sum of spin and orbital moments for the 2*IF system 4uc LTO|6uc LCO|4uc LTO (black symbols) measured in a field of -14 T. The lines show the Brillouin function behaviour expected for HS Co 3d\(^7\) HS (red) and LS Co 3d\(^7\) (green).
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compared to the HS one (t=0.915) could also help counteract the additional Coulomb repulsion cost of the LS state.

The inset to Figure 3.8 shows the temperature dependence of total magnetic moment of the 2*IF system LTO4|LCO6|LTO4 in the range of 10 to 180 K. Example XMCD spectra underlying the data-points of Figure 3.8 are shown in Figure 3.14 (a). The solid lines are from the Brillouin functions (red: HS 3d\textsuperscript{7}, S=3/2, m_l/m_s=0.53; green line: 3d\textsuperscript{7} LS, S=1/2, m_l/m_s=0.53) with M_{sat} = 0.89 \mu_B. The HS curve yields a better result than for the low spin state. Both fit curves show steeper decay of the magnetisation than do the data, and suggest a contribution to the experimental value of the total moment from another source that grows as temperature is raised. A natural candidate for this is a trivalent Co 3d\textsuperscript{6} HS contribution (S=2) growing from zero at 10K to of order 15% at 150K [86]. Seeing as 60% of the Co in the LTO4|LCO6|LTO4 system for which we have the detailed field- and temperature-dependent XMCD data is simply trivalent LCO, it is not unreasonable to suggest that this is the source of the additional magnetisation at higher temperatures.

In any case, the lack of remnant magnetisation in zero field, and the good description provided by the Brillouin function at low temperatures argues firmly against ferromagnetism in the case of these bi- and tri-layer interfacial Co spin systems. Here we note that thick LCO films grown on STO (d_{LCO}=60nm) using similar conditions to those given in Table 3.1 did exhibit ferromagnetism, observable both using VSM and element-specific XMCD magnetometry, in keeping with the literature for thicker LCO films. The present (ultra)thin cobalt oxide layers may simply be below the minimal thickness required to enable FM ordering, as has been reported for PLD-grown LMO films [123]. In keeping with this, supplementary Figure 3.14 (b) shows a lack of in-plane/out-of-plane anisotropy in the XMCD of the 2*IF system LTO4|LCO4|LTO4. It is also clear from Figure 3.8 that these interfacial systems are not generating a long range ordered antiferromagnetic ground state. Antiferromagnetic Co-Co correlations, however, have been cited as the cause of reduced moments for the paramagnetic, divalent Co sites in FM films of Co-doped ZnO studied using XMCD [124], and in thick, Ce-doped LCO films (also containing HS Co 3d\textsuperscript{7}), reduced moments are also reported [99]. Thus, antiferromagnetic correlations or local patches of antiferromagnetic order could be responsible for the reduced saturation magnetisation of the Co 3d\textsuperscript{7} ions from the XMCD analysis on these bi- and trilayers. Detailed angular and T-dependent x-ray magnetic linear dichroism measurements
would be required to examine possible (incipient) antiferromagnetic ordering while distinguishing these magnetic contributions from charge order/anisotropies in these non-cubic systems [125]. Such experiments go well beyond the remit of this investigation.

The bottom line of the XMCD experiments on the magnetic properties is that the interfacial charge transfer clearly increases the spin and orbital moments, with the Co 3d\(^7\) spins displaying paramagnetic behaviour.

The rich spin physics of cobalt oxides also sheds light on the lack of electrical conduction in these systems, also for cases with non-integer 3d electron counts. If the divalent Co 3d\(^7\) are in a HS state and neighbouring trivalent Co 3d\(^6\) are LS, then a process called spin-blockade prohibits hopping, suppressing conduction, as has been suggested in HoBaCo\(_2\)O\(_{5.5}\) [98], La\(_{1.5}\)Sr\(_{0.5}\)CoO\(_4\) [122] and Ce-doped LCO films [99]. For the 3d\(^7\) integer electron count in the 2*IF: 4uc LTO|2uc LCO|4uc LTO system, Mott physics most likely lies at the root of the insulating ground state.

Before concluding, we return to the key discussion of the microscopic origin of the remarkable charge transfer to create structurally unaltered, paramagnetically polarisable Co\(^{2+}\) at a 100% level across all LCO unit cells abutting LTO in high quality, non-polar oxide heterointerfaces. The data are very clear in that the Ti of the LTO is 3d\(^0\) and the Co of the LCO is 3d\(^7\) (divalent), supporting the DFT prediction that the LCO|LTO couple exists as 3d\(^7\)|3d\(^0\) and not 3d\(^6\)|3d\(^1\).

Electronic charge transfer or oxygen migration between the LCO and LTO (oxygen gettering by the LTO) are the two front-runner mechanisms for the observed behaviour, as both are sensitive to the number of active LTO|LCO interfaces present in the sample. Some aspects of the experimental data point to oxygen non-stoichiometry in the LTO, yet others argue against oxygen gettering effects between the layers as being dominant. In reality, a combination of these two mechanisms is most likely at work, so as to avoid the 3d\(^6\)|3d\(^1\) situation when interfacing LCO and LTO. Here we re-iterate the key experimental data relevant to the oxygen gettering discussion:

(i) The addition of an oxide ion permeable LAO break layer between LTO and LCO strongly suppresses the formation of divalent cobalt, arguing against oxygen gettering by LTO from LCO as the dominating factor.

(ii) The STEM data show that the altered Co valence is localized close to the LCO/LTO interface and that no oxygen vacancy ordering is present at sufficient
density in the LCO to explain the Co valence. The STEM data also do not show structural alterations such as line defects associated with crystalline domains of La$_2$Ti$_2$O$_7$ in the LTO or brownmillerite LaCoO$_{2.5}$ in the LCO.

(iii) Nevertheless, charge counting in the trilayers (such as the 4|2|4 and 4|4|4 systems) shows that more charge is lost from LTO than is gained by LCO. This would appear to signal over-oxidation of the LTO, something possible due to the relatively high oxygen partial pressure in the growth step, without the need for the LTO to getter oxygen from the LCO layer. The mechanism of over-oxidation remains unclear and should be subject of further investigation.

(iv) Electron transfer from the LTO to the LNO cap cannot be excluded as an additional channel by which a Ti 3d$^0$ configuration in reached in the LTO.

3.5 Conclusions and outlook

We have grown high-quality thin films of the charge transfer insulator LCO using PLD possessing either 0, 1, or 2 structurally abrupt, nonpolar interfaces to the Mott insulator LTO. The data clearly show that the O-2p band alignment based DFT prediction of a Co-3d$^7$/Ti-3d$^0$ electronic configuration is correct. The heterointerface, although nonconducting due to spin blockade physics for noninteger average charge states, provides a controllable population of interfacial, most likely HS, divalent Co.

The magnitude of the electron transfer for the bi- and trilayers is one electron per interfacial LTO/LCO unit cell, per interface in the structure. Therefore, the LCO film thickness and the number of LTO/LCO interfaces provide a pair of deterministic control knobs for the average valency of the LCO layer. Overoxidation of the LTO layer also plays a role in determining the Ti valence, yet the reduction in divalent Co signals via insertion of an oxide-ion-permeable yet electrically insulating “break” layer between the LTO and LCO points toward the charge transfer mechanism predicted in the DFT calculations. The interfacial 3d$^7$ Co ions formed by charge transfer exhibit significant orbital moment, likely due to a combination of the anisotropic crystal field and Co-3d spin-orbit coupling, and detailed XMCD investigations point clearly to their paramagnetic behaviour.

These experiments clearly affirm the O-2p band alignment concept as a successful design philosophy for the engineering of strongly correlated quantum materials [32],
without the need for the system to be responding to an incipient polar catastrophe, and without introducing cationic disorder connected to chemical doping. To be able to do this is of interest in controlling conductivity, magnetic states, and also (catalytic) chemical reactivity.

3.6 Supplementary Information

3.6.1 Data treatment of XAS spectra

The XAS spectra were collected using simultaneously TEY and FY modes. In a few cases, extrinsic, but well understood peaks made their appearance in the spectra. Firstly, the TEY signal of Co L-edge exhibited weak Ba-M\textsubscript{4,5} absorption the origin of which is elusive. This signal did not give rise to any dichroism and subtraction was achieved by measuring the Co L-edge of samples that did not contain any Co (namely LTO 4 uc), as shown in Figure 3.9. Secondly, the FY signal, used primarily to ensure that TEY is sufficiently representative of the bulk of the film, contained an AlK\textsubscript{α} peak that originated from 2nd order synchrotron radiation exciting the K-edge of Al contained in the LAO buffer layer. The same Co L-edge of a reference film containing no Co was used to subtract this feature, too. Further investigation showed that the SiC coated mirror in the soft X-ray beamline is adequate to strongly suppress this peak in contrast to the generally-used Au mirror.

3.6.2 Co valence fingerprinting using model compounds

Two methods were explored to determine the % of divalent Co 3d\textsuperscript{7} in the (0*IF), (1*IF), and (2*IF) structures. In a first iteration, the spectra were modelled using the data from single crystalline model compounds from Ref. [108]. An example of fits is shown in Figure 3.10 (a), with the percentages as given in the right-hand panel. The heterostructure spectra are quite well described in this manner, and the “stand-alone” LCO film shows more intensity at 778eV suggesting (in the light of Figure 3.10 (b) in the main body of the chapter) that the thin-film LCO has a greater HS admixture than the single crystal. We note the divalent pre-peak at 777eV is clearly a different feature to this shoulder, as can clearly be seen in the heterointerface samples.
Figure 3.9: Correction of Ba-M\textsubscript{4,5} signals in TEY and Al:K\textalpha{} fluorescence in FY. (a) TEY mode XAS data show very weak Ba-M\textsubscript{4,5} signals in the energy region of the Co-L\textsubscript{2,3} edge which are unrelated to the LCO layers. In the main figures, the Co-free, 4 u.c. LTO data are used to subtract this signal. (b) The FY data do not contain the Ba-M\textsubscript{4,5} features, but do show Al:K\textalpha{} fluorescence excited by second order light. Again, the LTO spectrum is used to correct the data. In the lowest trace, a beamline mirror was used which does not transmit the second order light, thus offering a clear control of the correction.
Figure 3.10: Decomposition of the Co-L\textsubscript{2,3} XAS data to extract tri- and divalent contributions. (a) Use of the spectra from the model compounds EuCoO\textsubscript{3} and CoO to fit the data from bi- and trilayer heterointerface samples. The same mixing percentages of the di- and trivalent model spectra are kept as used in the right-hand panel. (b) An analogous procedure – the one actually used to determine the valency figures given in the main body of the chapter – in which the data from the LCO\textsubscript{4} and LTO\textsubscript{4}[LCO\textsubscript{2}]LTO\textsubscript{4} systems are used a tri- and divalent model spectra, respectively, mixed as indicated in the figure.
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In atomic multiplet-based models for L$_{2,3}$ XAS of transition metal oxides, the exact spectral distribution of multiplets in Co-L$_{2,3}$ XAS (which ends up giving the shape of the overall spectrum) is sensitive to a number of fundamental parameters including Coulomb energies (dd and core-d), the charge transfer energy, covalence between the metal and oxygen levels as well as crystal fields and the local crystal symmetry.

It is asking a lot to expect the finer details of the multiplets from the bulk, model compounds to be strictly relevant for the ultrathin film systems here. For the divalent cobalt case, CoO is quite a different system structurally, to a LTO4|LCO2|LTO4 trilayer, grown coherently strained to STO. Therefore, in a second iteration, the series of Co-L$_{2,3}$ spectra were decomposed into tri- and divalent contribution using the Co L$_{2,3}$ XAS traces from LCO4 and the LTO4|LCO2|LTO4 trilayer as representatives of trivalent and divalent Co in the structural context of our thin film heterostructures. Figure 3.10 (b) shows the results of this process, which yield excellent agreement with the details of the multiplet structures. The numbers shown in Figure 3.10 (b) are given in Table 3.2 in the main body of the chapter.

3.6.3 Ti-L$_{2,3}$ XAS of trilayers

The valency of the Ti ions in the LTO layers in the investigated heterostructures was probed using both Ti2p HAXPES at the I09 beamline, and soft X-ray XAS at the Ti-L$_{2,3}$ edges at both the I09 and the I10 beamlines. The data from the I10 experiments are shown in 3.11 from (2*IF) from LTO4|LCO2|LTO4 (424), 444 and 464 samples. Due to charge transfer to LCO, the single 3d electron present in stoichiometric, defect-free LTO should be missing, yielding a Ti$^{4+}$ XAS spectrum, as seen in Figure 3.11. As discussed in the sample design section of the main chapter, and in the context of Figure 3.11. below, even though the growth conditions were carefully chosen to optimally grow both LCO and LTO with as few defects and vacancies as possible, in the post-growth, post-cool-down timepoint, a single film of LTO does not necessarily possess pure 3d$^1$ character for reasons explained in Ref. [100]. We reiterate the message of the main chapter here that the essential comparison is between the valence states of the Ti in LTO abutting LCO and the Co in LCO abutting LTO between the situation in experiment, and -for example- the DFT calculations of Ref. [32]. It is evident that the situation of a Ti/Co interface
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Figure 3.11: Ti-L_{2,3} XAS data from (2*IF) samples and STO reference. Shown are TEY data for 2 (green), 4 (blue) and 6 (red) uc of LCO sandwiched between a pair of 4 uc thick LTO layers. Their strong resemblance to the Ti^{4+} 3d^0 data from a STO reference from the literature [100] indicates a tetravalent configuration.

possessing 3d^1/3d^6 (i.e. tri/divalent valencies) is avoided, both in the computer and in practise.

3.6.4 Control of the Ti 3d electron count in LTO films through UHV heat treatment

Figure 3.12 shows in-situ Ti2p core level photoemission data recorded in the IMS lab-based XPS by Jaap Geessinck from a LAO 3uc / LTO 3uc / LAO 3uc film grown on LAO substrate in using identical growth parameters to those of the LTO layers in the bi- and tri-layer systems that form the core of this chapter. The Ti2p spectral shape of the as-grown film (blue) yields a d^0 character due to over-oxidation that took place in the relatively high growth pressure environment that was required to enable growth of LCO/LTO film combinations in agreement to recent results [100]. Subsequently the film was transferred in-situ to the XPS chamber in a pressure environment of 1 × 10^{-10} mbar. Having undergone thermal post-treatment in ultrahigh vacuum and at temperatures comparable to the deposition conditions, the LTO shows increased 3d^1 content expressed in the peak located
Figure 3.12: Ti-2p XPS data from a LTO film grown on LAO. The LTO is 4 uc thick, deposited on a 3 uc cell LAO layer itself grown on bulk LAO. The film stack of capped with a further 3 uc of LAO to yield LAO\textsubscript{bulk}|LAO\textsubscript{3}|LTO\textsubscript{4}|LAO\textsubscript{3}. Panel (a) on the left shows data after cool-down, transferred without breaching UHV (lowest trace), and at different post-anneal temperatures as indicated and after a final cool-down from 700\textdegree C. The characteristic 2p\textsubscript{5}3d\textsubscript{1} final state feature for Ti\textsuperscript{3+} is clearly present at low binding energies in the latter. Panel (b) on the right shows reversible behaviour during a heating/cooling cycle between 25 and 700\textdegree C.

at the low binding of each spin-orbit split component of the doublet. Still higher annealing temperatures further promote the stabilisation of the 3d\textsuperscript{1} configuration. After cooldown (uppermost trace in Figure 3.12 (a) , the film exhibits a dominant Ti\textsuperscript{3+} population, reflecting establishment of the relatively unstable stoichiometric state of LTO. In the right-hand panel of the figure, the data show how consecutive cycles of heating and cooling yield the same spectral signatures, highlighting the tendency of LTO to gain oxygen once at elevated temperature and in relatively higher pressures (10\textsuperscript{-9} mbar at 700\textdegree C, compared to 10\textsuperscript{-10} at room temperature). Restoration of the dominance of the stoichiometric valence was again achieved upon subsequent cooling. From these data it is clear that there is a reversible ingress/removal of additional oxygen from the LTO within the depth-scale of the XPS measurements.

We mention that the subjection of a LTO\textsubscript{4}|LCO\textsubscript{4}|LTO\textsubscript{4} trilayer, grown on LAO and capped with LAO - i.e. analogous to the LTO sample whose data is shown in

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Figure 3.13: Example X-ray absorption spectra used to extract XMCD data. Co-L$_{2,3}$ XAS data (TEY) for an LTO4 (left) and LTO4—LCO2—LTO4 sample (right), together with the XMCD signal (in green) as shown for different film systems in Figure 3.7 of the main results part of this chapter.

Figure 3.12: to in-situ annealing steps in UHV starting at 25°C and going via 175°C up to 400°C (i.e. all below the annealing temperatures used in Figure 3.12 for LTO) led to the appearance of a Ti$^{3+}$ feature in XPS signaling 3d electron occupation in the LTO but also an XPS signal at a binding energy matching cobalt metal, signaling the irreversible decomposition of the LCO under these conditions in the trilayer. These experiments support the chosen strategy of growth at an intermediate oxygen pressure.

3.6.5 XMCD contrast in raw XAS spectra

Figure 3.13 shows an example of the raw, polarisation-dependent XAS data from which the XMCD datasets shown in Figure 3.7 of the main results part of this chapter were extracted.
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Figure 3.14: Temperature and angular signatures of paramagnetic behaviour. Panel (a) Temperature dependence of the system LTO4|LCO6|LTO4 XMCD signal from measured at a field of -14T. These data underpin the data-points of Figure 3.8 in the main results part of this chapter. (b) Normal incidence (NI) vs. grazing incidence (GI) XMCD patterns of system LTO4|LCO4|LTO4 measured at both at 14 and -14 T fields. Essentially zero anisotropy is observed.

3.6.6 Temperature- and incidence angle dependent XMCD of trilayers

Figure 3.14 (a) shows the XMCD data of the double-interface system LTO4|LCO6|LTO4 measured at a field of -14T at different temperatures. These data form the basis of the magnetisation values shown in the inset of Figure 3.8 in the main results part of this chapter. In Figure 3.14 (b), a comparison between the grazing incidence (GI) and normal incidence (NI) XMCD data for the double-interface system LTO4|LCO4|LTO4 is presented, showing only very small deviations in the XMCD patterns despite probing magnetic polarisation either in (GI) or out of the film plane (NI).
Chapter 4

Emergent ferromagnetism in the polar LaMnO$_3$ / SrTiO$_3$ interface

Charge transfer and thickness-dependent emergent ferromagnetism was studied in the polar/non-polar interface formed by the Mott insulator LMO and the band insulator STO. LMO thin films with thicknesses in the range of 2 - 10 uc grown by PLD on Nb-doped STO substrates were investigated using HAXPES, XAS, STEM-EELS, XMCD, XLD and resonant magnetic scattering spectroscopies. The average valence of Mn was found to exhibit a systematic decrease in thinner LMO films, ranging from 2.9+ for 10 uc to 2.35+ for 2 uc, while layer-resolved STEM-EELS tracked the Mn$^{2+}$ content at the interface and surface. This finding does not fit in the framework of an ideal polar catastrophe mechanism and instead promotes the role of non-stoichiometry effects such as oxygen vacancies. Robust ferromagnetic moments on the Mn sites were probed for all LMO films, while a pronounced enhancement of their magnitude was linked to a critical thickness of 6 uc. This indicates the existence of magnetic dead layers at the interface and surface, attributable in part to electron-doping in the ultrathin limit. On the STO side, Ti was found to align oppositely to the Mn moments, which results from interfacial La/Sr intermixing driven by the polar mismatch between STO and LMO. The emergent ferromagnetism itself is understood as a strain-related effect.
4.1 Introduction

Mixed valence manganites have been studied intensively for the last 70 years, attracting a lot of interest due to the rich interplay between the orbital, lattice and spin degrees of freedom that constitutes the source of a plethora of emergent phenomena. The large family of magnanite compounds encompasses hole and electron doped genres of magnanese-based perovskite oxides. In their pioneering work [126, 127], Jonker and van Santen found that the introduction of tetravalent Mn to a nominally trivalent Mn compound by A-site substitution of La with Ca or Sr causes the system to become electrically conducting and ferromagnetic at the same time. In an effort to give a theoretical interpretation of this empirical relationship, Zener proposed [128, 129] the double exchange mechanism. In this process, the oxygen ion serves as a bridge, mediating a pair of simultaneous electron transfers, one hopping from Mn$^{3+}$ to O$^{2-}$ and the other from O$^{2-}$ to Mn$^{4+}$. This leads to the energetically favourable state in which the Mn$^{3+}$, Mn$^{4+}$ ions spontaneously order into a chessboard configuration whereby double exchange interactions occurring between neighbouring tiles constitute the driving force for ferromagnetism and electric conductivity.

A series of seminal papers [130–135] led to the formulation of the Goodenough-Kanamori rules which assign the sign of the exchange interaction between the mixed valence Mn ions, as well as the associated magnetic structure and ensuing crystal distortions, resulting in the rich magnetic and electric phase diagram of the hole/electron-doped manganites, shown in Figure 4.1. In its pure, stoichiometric phase, the super-exchange interaction mediates A-type antiferromagnetism in LMO whereby ferromagnetic planes align oppositely to each other along the c-axis [136]. This phase is accompanied by a long-range, cooperative Jahn-Teller distortion of the octahedra that results in alternating elongated and shortened Mn-O bonds in the ab plane and orbital ordering [137]. A canting of the moments is caused by the Dzyaloshinskii-Moriya interaction giving rise to measurable magnetic moments even in the stoichiometric case. Notably, as Figure 4.1 shows, even a minute amount of holes or electrons as dopants is sufficient to cause the system to exhibit ferromagnetism whilst still being insulating. Hence, bulk LMO typically shows measurable magnetic moments, rendering a clear distinction between stoichiometry-related ef-
4.1. Introduction

Figure 4.1: Phase diagrams of LMO showing the Curie $T_C$ and Neel $T_N$ transition temperatures as a function of dopant concentration: a) hole-doping (Ca) [138] and b) electron-doping (Ce) [139]. In both cases, an insulating ferromagnetic region is extends up to approximately 15% of dopant concentration. In hole-doped LMO, antiferromagnetism prevails for concentrations higher than 50%.

...effects and other phenomena very challenging if not impossible purely on the basis of the measured magnetic moment or the electrical resistivity. The insulating ferromagnetic region of the phase diagram extends up to the point where approximately 15% of La is replaced by hole or electron dopants. For increased dopant concentrations the double-exchange processes give rise to half-metallic conductivity, with an optimal doping of roughly 30%. For increased dopant concentrations the antiferromagnetic interactions prevail.

Renewed interest in manganites was sparked after the discovery of the colossal magnetoresistance effect [140] that signalled LMO’s thin film era. The colossal change in resistance in the presence of magnetic field can amount up to a three orders of magnitude increase in resistivity. This is a manifestation of the half metallic nature of the system, in which the bands are spin-polarised and the majority spin population is electrically and magnetically active [141]. Ferromagnetism in LMO films grown on STO substrates was widely thought to be of double exchange nature, a consequence of oxygen or $A$-site non-stoichiometry that contributes to mixed valence $\mathrm{Mn^{3+}}/\mathrm{Mn^{4+}}$ and $\mathrm{Mn^{2+}}/\mathrm{Mn^{3+}}$ states [142–144]. However, Wang et al. [123] discovered that ferromagnetism in LMO films is a thickness-dependent property, suggesting that the interfacial polar discontinuity between the polar LMO and the non-polar STO gives rise to a polar catastrophe similar to that of LAO/STO, resulting in internal electron doping of the interface and spatial separation of mixed...
valent Mn ions that favours double exchange interactions and consequently ferromagnetism. The experimentally verifiable direct implications of this concept are given in the following section.

4.2 Scope of this work

The existence of a universal so-called “critical thickness” is a key component of the polar catastrophe hypothesis. The LAO/STO interface is a prominent paradigm of such system that consists of insulating parent materials, yet exhibits, above a thickness of 4 uc, a 2-dimensional electron gas confined in a small region at the interface, as a result of the divergent potential that is accumulated due to the polar nature of LAO \[9, 10\]. In an ideal, perfectly sharp and stoichiometric polar/non-polar interface, the interfacial polar discontinuity is compensated by an electronic reconstruction.

Along the same lines, LMO consists of consecutive \((\text{La}^{3+}\text{O}_{2}^{2-})^{1+}\) and \((\text{Mn}^{3+}\text{O}_{2}^{2-})^{1-}\) layers of opposite charge which, if grown on top of the charge neutral \((\text{Ti}^{4+}\text{O}_{2}^{2-})^{0}\) and \((\text{Sr}^{2+}\text{O}_{2}^{2-})^{0}\) layers of STO, contribute to the development of a divergent electric potential in the LMO film that becomes increasingly greater with each additional layer, as shown in Figure 4.2 (a). In this way, a potential energy staircase is formed and, above the critical thickness, the accumulated energy exceeds the band-gap of LMO (1.3 eV \[145\]), leading to an internal electronic reconstruction in the LMO, whereby electrons are moving from the surface to the interface. The relatively small band gap energy of LMO compared to that of STO (3.2 eV \[146\]) confines the transferred electrons to the LMO side of the electronically reconstructed interface accounting for the lack of conductivity, in contrast to the LAO/STO interface where the electrons are transferred to the STO side due to the large band gap energy of LAO (5.6 eV) \[9\]. The electronic re-arrangement that is argued to take place in the LMO film results in the spatial separation of the LMO in regions consisting of mixed valence Mn ions and this was suggested to be the source of double exchange ferromagnetism above the critical thickness \[123\]. In the following, multiple methods by which the above picture can be put to the test are discussed.

Rigid conduction and valence band shifts of the LMO layer below the critical thickness are predicted to stem directly from the uncompensated divergent potential
4.2. Scope of this work

Figure 4.2: The polar catastrophe concept in the LMO/STO interface: (a) consecutive \((\text{La}^{3+}\text{O}^{2-})^{1+}\), \((\text{Mn}^{3+}\text{O}^{2-})^{1-}\) layers of opposite charge that are deposited on top of the \((\text{Ti}^{4+}\text{O}^{2-})^{0}\), \((\text{Sr}^{2+}\text{O}^{2-})^{0}\) charge neutral layers cause the development of an non-zero average electric field \(E\) in the LMO layer which in-turn gives rise to a divergent potential \(V\) which becomes increasingly larger with thickness. Above a critical thickness, electronic reconstruction takes place and electrons are transferred internally from the surface to the interface, causing \(E\) and \(V\) to oscillate around zero (b) in the reconstructed LMO layer, a spatial separation of mixed valence Mn ions is realised with the surface of the stack being hole-doped and the interface, electron-doped.

[123] and constitute a first property of the interface for which experimental validation can be sought. In the LAO/STO interface, this type of polar discontinuity-induced shifts were experimentally found to be an order of magnitude smaller than expected [38], because the system finds alternative routes around the potential build-up [147–149]. On the basis of simple dielectric constant considerations, the internal electric field of the LMO was estimated at 0.85 eV/nm (0.33eV/uc) [123], yielding a critical thickness of 6 uc. A more recent study found, using DFT, that the effective electric potential in the LMO layer is 0.177 eV/Å (0.69 eV/uc) [150] that yields a critical thickness of 2 uc. Taken at face value, this suggests two critical thicknesses: one for electronic reconstruction and one for ferromagnetism with the latter only emerging in thicker samples. The origin of these “dead” layers in thinner samples can be linked to the high degree of electron doping that exceeds the ferromagnetic region of the phase diagram, such as that shown in Figure 4.1 (b). However, the pronounced absence of any core level shifts in the range of thicknesses 1-6 uc has been attributed to the
lack of electric potential build-up in the LMO layer [151], pointing to accumulation of oxygen vacancies at the surface.

The depth dependence of the mixed valence state constitutes a second property of the system that can be investigated experimentally. As shown in Figure 4.2 (b), assuming pure electronic reconstruction driven by the interfacial polar discontinuity, the transferred electrons reduce the valence of Mn in the interface region, resulting in a mixture of Mn$^{2+}$/Mn$^{3+}$ ions, whereas at the surface, the removed electrons contribute to a hole-doped region that consists of Mn$^{3+}$/Mn$^{4+}$ ions. Experimentally, electron accumulation at the interface was reported in the context of reduction of the average Mn valence [150]. However, this study failed to fully address the lack of Mn$^{4+}$ ions at the surface. Another study [152] suggested a spatially separated Mn$^{2+}$/Mn$^{3+}$-Mn$^{3+}$/Mn$^{4+}$ mixed valence state with the Mn$^{4+}$ signal at the surface being minute.

A third experimental parameter that can be experimentally assessed is the thickness-dependent ferromagnetism and the way this fits into the electronic reconstruction picture. Scanning SQUID microscopy measurements provided spatial evidence for a magnetic transition from an antiferromagnetic to a ferromagnetic state [123] or a less abrupt transition to a inhomogeneous state in which, above the critical thickness, metallic ferromagnetic patches nucleate in an antiferromagnetic background [153]. A natural connection can be made with the magnetic and electric dead layers observed in hole-doped LSMO [154], an effect triggered by a similar polar discontinuity mechanism. LSMO alleviates the build-in electric potential via formation of oxygen vacancies in the (La,Sr)O layers which result in electron accumulation at the interfacial MnO$_2$ layer [155], as well as cation intermixing [156].

Finally, the strain imposed by the substrate is a fourth property of the system that typically plays a significant role in thin films. As discussed earlier, in bulk, stoichiometric LMO, a combination of cooperative Jahn-Teller distortion (electron-phonon coupling) and orbital ordering accounts for the insulating A-type antiferromagnetic ground state. Several studies, based on calculations, showed that the compressive strain of STO is adequate to suppress the “fragile” Jahn-Teller mode and induce ferromagnetism in the system [157–159]. Furthermore the lack of strong magnetism below 6 uc has been predicted to be an effect of the open surface [160]. Hence, the investigation of the strain conditions of the LMO layer is crucial in order to establish the precise circumstances under which ferromagnetism emerges.
In this work, a combination of synchrotron-based spectroscopies and microscopic imaging experiments were carried out on thin films of LMO. As described in detail below, a combination of these techniques constitutes an ideal tool to investigate the effect of the polar mismatch on the valence and the magnetism of the system. The ability of these experimental methods to directly probe the electronic and magnetic structure of matter in conjunction with their element-specificity and surface-sensitivity constitute unique traits that render them highly appropriate for the investigation of the LMO/STO interface. An attempt is made to systematically address potential inadequacies of the previous studies that were reported above with the ultimate goal of revealing the underlying mechanism that mediates thickness-dependent magnetism in high quality LMO thin films of various thicknesses which were grown using RHEED-assisted PLD on Nb:STO, (001)-oriented, TiO₂-terminated substrates [123]. In this study, the following experiments were performed:

(i) Synchrotron-based valence profiling using the element-specific and surface-sensitive characteristic spectral features of XAS and HAXPES experiments that were carried out aiming to draw a distinction between the idealised picture in which polar catastrophe occurs in a perfectly abrupt and stoichiometric interface (as shown in Figure 4.2 (a)) compared to realistic conditions in which non-stoichiometry, oxygen vacancies and inter-diffusion effects play a role.

(ii) Real-space STEM-HAADF imaging in EELS mode that was focused on the valence spatial distribution, the abruptness and degree of intermixing of the interface. In these experiments, conducted by the team at EMAT, University of Antwerp, the layer-resolved atomic columns are imaged in a valence sensitive manner, providing unique real-space insights, revealing possible ways in which the polar build-up could be avoided by change in the stoichiometry at the interface. These microscopic characteristics constitute excellent predictors of the magnitude of the polar reconstruction.

(iii) High magnetic field XMCD and resonant X-ray scattering experiments at low temperature to investigate the emergent ferromagnetism associated to a “critical thickness”. This type of magnetic contrast stems from the interaction of polarised X-rays with magnetic moments, being characteristic to specific chemical species and extremely sensitive, even to minute magnetic moments. XMCD provides a very complimentary approach to scanning SQUID microscopy which provides a micrometer spatial image of emanating magnetic fields.
(iv) Linear polarisation XLD experiments that were performed intending to investigate the thickness dependence of the crystal field and possible orbital ordering in the LMO films. This type of measurement enables the determination of the effect of strain imposed by the substrate.

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4.3.1 XAS Mn valence fingerprinting

XAS experiments were carried out at the Mn-L$_{2,3}$ absorption edges in TEY mode, at the BLADE endstation of the I10 beamline at Diamond Light Source, Didcot. To maximise data quality and exclude time-dependent artefacts, the spectra were measured in blocks of alternating X-ray polarisation e.g. ($\sigma^+\sigma^-\sigma^+$ and $\sigma^-\sigma^+\sigma^-$) at an incidence angle of 20 degrees with respect to the surface of the film (thus sensitive to in-plane magnetic polarisation), at a temperature of 10K and pressure in the range of 10$^{-10}$ mbar, while additional control experiments were performed such as measuring multiple spots on the 5×5 mm$^2$ film and at different incidence angles. The spectra used for valence determination correspond to the mean TEY signal measured with circular right and circular left polarisation. The XAS spectra were normalised to the edge jump, accounting for the estimated number of holes, while a linear pre-edge was subtracted from data starting at energies well before the absorption edge, as explained in Chapter 2.

The L$_{2,3}$-edge XAS spectrum of a transition metal compound corresponds to electron transitions from the 2p$_{1/2}$, 2p$_{3/2}$ to the unoccupied 3d states [107]. The XAS spectral patterns of atomic multiplets and their position in energy are very characteristic of the d-level electron count at the Mn L$_{2,3}$-edge, enabling the quantification of the valence via comparison to model compounds. Literature XAS reference spectra of high-quality single crystals [108] are shown in Figure 4.3 (c), exhibiting clear spectral changes for nominally Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ ions. These L$_{2,3}$-edge XAS features enable a quantitative analysis of the Mn valence of the LMO films with thicknesses in the range of 2 to 10 uc which are presented in the left panel of Figure 4.3 (a).

The multiple valence contributions can be resolved by the reconstruction of each measured spectrum from weighted combinations of Mn$^{2+}$ and Mn$^{3+}$ reference spec-
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Figure 4.3: Valency fingerprinting reveals the strong electron doping of thinner samples: a) Mn L\textsubscript{2,3}-edge XAS spectra of LMO films of 2,3,4,7 and 10 uc. b) reconstruction of the experimental spectra using linear combinations of Mn\textsuperscript{2+} and Mn\textsuperscript{3+} literature data of model compounds (the percentage shown corresponds to the Mn\textsuperscript{2+} content. The effective error in the valency determination is of the order of 5%, hence values are rounded). c) literature spectra of MnO (Mn\textsuperscript{2+}), LaMnO\textsubscript{3} (Mn\textsuperscript{3+}) and SrMnO\textsubscript{3} (Mn\textsuperscript{4+}) single crystals\[108\] that were used in the quantitative analysis of the LMO data.

X-ray absorption (arb. units)

635 640 645 650 655 660
Photon energy (eV)

635 640 645 650 655 660
Photon energy (eV)

635 640 645 650 655 660
Photon energy (eV)

tra, as shown in Figure 4.3 (b). Besides the strong Mn\textsuperscript{3+} portion of the signal, in agreement with the formal valence, a pronounced, characteristic Mn\textsuperscript{2+} low energy peak at approximately 640 eV is observed in thinner films. This feature decreases systematically for increasing thickness, being almost absent for LMO 10 uc. Thus, a first summarising statement can be made that a Mn\textsuperscript{2+} population is present in all LMO films with its percentage exhibiting a systematic decrease in thicker films\[1\]. A second clear statement is that the data do not support inclusion of a Mn\textsuperscript{4+} component for all of the samples measured. Consequently, the XAS spectra can be understood as a solely combination of Mn\textsuperscript{2+} and Mn\textsuperscript{3+} components while Mn\textsuperscript{4+} is absent in all samples.

The above result constitutes a first important clue about the effect of the polar discontinuity on the Mn valence. Firstly, the clear presence of Mn\textsuperscript{2+} below the critical thickness reported in [123], indicates alternative mechanisms at work than the ideal polar reconstruction mechanism. Secondly, the same conclusion is supported

\[1\]We do note that the LMO7 data have a larger Mn\textsuperscript{2+} feature than expected when comparing to the 6 uc data.
by the lack of Mn$^{4+}$ ions for samples above the critical thickness (or indeed any thickness). As mentioned in the previous section, this charge re-arrangement would result in the internal electron transfer from the upper part of the film to the bottom and the coexistence of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ ions that supports double-exchange electron hopping. Hence in that case, the average valence is expected to remain Mn$^{3+}$ but with the mixed valence ions redistributed in the way shown in Figure 4.2 (b). Due to the exponential drop-off of the XAS signal in TEY mode one would expect for films above the “critical thickness” to have a predominant Mn$^{4+}$ character. However, this is not the case and XAS verified the realisation of a Mn$^{2+}$, Mn$^{3+}$ mixed valence state, with the Mn$^{4+}$ ions being absent.

Thirdly, the observed thickness-dependent average valence variation is not strictly associated with a critical thickness of 6 uc [123], but is in good agreement with previous studies that suggested monotonic variation with thickness [150, 151]. The divalent character of Mn is extremely pronounced in LMO 2 uc amounting to approximately 65% of Mn$^{2+}$. In view of the fact that XAS is sensitive to the average valence in the probing depth, this observation points towards the accumulation of Mn$^{2+}$ entities at the surface [151] or interface to the STO[150], with the Mn$^{3+}$ then putatively in the centre of the films, hence increasing in thicker samples. This raises the question of a possible relation between the observed strong electron-doping with the thickness-induced magnetic transition. Before moving on to discuss the possible link between the Mn valence and the possible presence of magnetically inactive layers, a quantified overview of the valence trend as a function of the LMO thickness along with supplementary HAXPES data is given in the following section.

4.3.2 HAXPES data and valence quantification

HAXPES measurements were conducted at the I09 beamline at Diamond Light Source, Didcot, using a EW4000 photoelectron analyser (VG Scienta) equipped with a wide angle acceptance lens. The samples were transferred in-situ from the PLD system in Twente to the beamline, using a portable UHV suitcase operating in a pressure in the range of 10$^{-10}$ mbar, to prevent oxidation or contamination from the ambient environment. The photon beam used was linearly polarised, incident at an angle of 55 degrees with respect to the sample surface.
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Figure 4.4: HAXPES confirmation and quantification of the observed Mn\(^{2+}\) entities in LMO thin films: a) Mn3s HAXPES spectra of in-vacuo transferred LMO films with varying thickness: 2,3,4,6,7 and 10 uc exhibiting valence-dependent decreasing exchange splitting in thicker films that signifies the strong reduction of the Mn valence in thin samples b) Mn2p HAXPES spectra showing signs of a well-screened state at low energies that increases for thicker samples. The LMO 2 uc spectrum also exhibits MnO-like features (satellite at \(\approx 647\) eV marked with a red arrow and broadening of the main peak). All samples were transferred in-situ using the UHV suitcase and measured at a photon energy of a) 2.2 keV b) 3 keV at 250 K c) Combined Mn3s HAXPES and XAS valence quantification as a function of thickness showing the prominent Mn\(^{2+}\) character of the thin LMO films. The spectral information fits a model in which a layer of 1.25 ± 0.25 uc thickness contains solely Mn\(^{2+}\).

Spectral features of core level HAXPES can be sensitive to the valence of the constituent element. The Mn3s core level, having no angular momentum \((l=0)\), exhibits a doublet of multiplet character that stems from exchange interaction between the 3s and the 3d shell [161]. Hence, the energy splitting \(\Delta E_{3s}\) depends on the net valence spin of Mn via an effective exchange integral that takes into account intrashell correlation effects. Therefore, the Mn3s splitting enables the quantification of the Mn valence in the broad family of Mn compounds by a comparison to a universal trendline that links the \(\Delta E_{3s}\) to the Mn valence for a number of compounds with various formal compositions [162]. For the valence quantification, the following formula was employed [163]:

\[
v_{Mn} = 9.67 - 1.27\Delta E_{3s}[eV]
\]
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The Mn3s core-level HAXPES spectra as a function of the thickness of the LMO layer are depicted in Figure 4.4 (a). A systematic decrease in the spectral splitting $\Delta E_{3s}$ for increasing LMO layers was observed, reflecting the tendency of the thinner samples for reduced Mn valence as a result of the increasing Mn$^{2+}$ content, in agreement with the XAS results. Using the above formula, an estimate of the formal, average Mn valence can be made on the basis of the measured spectral splitting $\Delta E_{3s}$. This result, along with a comparison with the XAS valence expectation are depicted, as a function of the thickness of the LMO film, in Figure 4.4 (c). The observed trend is compared to models of the valence expectation for LMO films that would contain effective thicknesses of 0.5, 0.75, 1, 1.25, 1.5, 1.75 and 2 uc of Mn$^{2+}$. Due to the lack of Mn$^{4+}$ in the samples, it can be therefore deduced that the observed electron-doping equals to a layer of $1.25 \pm 0.25$ electrons per uc. This effect could be associated to an internal electron re-arrangement or other non-stoichiometric contributions such as oxygen depletion. This important open question along with information on the spatial distribution of these Mn$^{2+}$ ions are examined in the following section.

Along the same lines, the electron doping of LMO and the concomitant Mn$^{2+}$, Mn$^{3+}$ species coexistence gives rise to a weak Mn$^{3+}$ well-screened state, evident on the low binding energy side of the Mn2p core-level, as shown in Figure 4.4 (b). The well-screened state stems from the screening of the core hole by the valence electrons. A strong Mn$^{3+}$ well-screened state has been associated with conductivity in hole-doped LSMO [164, 165]. In our case, there is lack of conductivity in the LMO films, and this feature is attributed to the Mn$^{2+}$, Mn$^{3+}$ coexistence. Finally, the Mn2p spectrum of an LMO 2uc film, shown in 4.4 (b), exhibits MnO-like features (satellite at $\approx 647$eV as well as broadening of the main peak) that stem from the dominant Mn$^{2+}$ character [166].

Figure 4.5 shows Sr3d, La4d, Mn3s and Ti3s HAXPES spectra of LMO thickness of varying thickness: 2, 3, 4 and 7 uc. These spectra were normalised to the La4d spectral weight (from the LMO layers), and are aligned such that the binding energy of the Sr3d features from the STO substrate exactly match in each case. If a potential build up were to take place in the LMO, then the LMO’s core levels would progressively shift and broaden, when referenced to the substrate Sr core level feature. It can be deduced that no core level shift can be resolved within the resolution of the instrument. Besides that, the measured spectra exhibit identical lineshapes.
Figure 4.5: HAXPES Sr3d, La4d, Mn3s and Ti3s core level spectra of in-vacuo transferred LMO films with varying thickness: 2, 3, 4, 6 and 7 uc exhibiting lack of core level shift related to a potential build-up within the resolution of the instrument. Chemical species that belong to the substrate scale according to the nominal thickness of the film while spectral features show similar lineshapes. All samples were transferred in-situ using the UHV suitcase and measured at a photon energy of 3 keV at 250 K.
and lack of overlapping shifted components indicating the common chemical environment among the films. In addition, the peak intensity that originates from the substrate exhibits decrease that is consistent with the thickness of each film, indicating the high degree of “closure” of the LMO films, suggesting good layer by layer growth.

As mentioned previously, a core level shift for chemical species that belong to the LMO layer referenced to a signal stemming from substrate elements is anticipated for samples below the “critical” thickness, in which an uncompensated potential staircase is realised. This, however, does not occur in a magnitude anything like that predicted by electrostatic considerations for an ideal polar LMO/STO interface. In reality, this effect might be too small to reliably assess with instruments of finite resolution because the system is able to find alternative ways to alleviate the polar discontinuity. Similar results have been reported for the polar LAO/STO interface [38].

4.3.3 STEM-EELS real space confirmation

Depth-resolved information on the atomic arrangement and stoichiometry of the thin films was gained by layer-resolved EELS and STEM-HAADF imaging experiments conducted by Dr. Nicolas Gauquelin at the EMAT laboratory of the University of Antwerp. The data are presented in Figures 4.6 and 4.7 respectively. Due to sample preparation constraints, the LMO films were capped with an LAO 7 uc layer prior to cross-section generation. The LAO cap on top of the LMO film was chosen because (i) it is robust to off-stoichiometry (ii) it preserves the polar nature of the structure as well as (iii) preserving the A-site element.

Figure 4.6 shows Mn L$_{2,3}$-edge EELS spectra resolved for individual atomic columns for two samples (a) LMO 3 uc / LAO 7 uc (below the LMO critical thickness [123]) and (b) LMO 9 uc/ LAO 7 uc (above the critical thickness). The spectral features are representative of the Mn valence and can be interpreted in the same way as in the XAS analysis of Figure 4.3. In both samples, starting from the bottom STO interface, increased spectral weight at low energies was observed in the first layer(s). In the middle layer(s), Mn restores to its bulk trivalent character. In these capped samples, some Mn$^{2+}$ spectral weight is again visible in the LMO abutting the LAO interface. These STEM-EELS data provide crucial additional information
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Figure 4.6: Layer resolved STEM-EELS tracks electron doping at the STO interface: Mn L_{2,3}-edge EELS spectra of LAO-capped LMO films a) LMO 3 uc/ LAO 7 uc and b) LMO 9 uc/ LAO 7 uc showing characteristic low energy Mn^{2+} features being prominent at the STO interface and partially at the LAO interface and c) comparison of sum of EELS spectra to XAS of LMO 3 and LMO 10 uc (without cap)

as regards the location of the Mn^{2+} centres: for the uncapped sample type relevant to the XAS and HAXPES experiments presented here, the STEM data clearly point to the STO/LMO interface. This is also the location of the polar discontinuity. In the STO/ LAO interface this has been argued to lead to oxygen vacancies in LAO [149] and STO substrate [40]. By analogy oxygen vacancies in the LMO layer at the STO interface could give rise to the observed Mn^{2+} ions. In Figure 4.6 (c), an attempt to compare the sum of EELS spectra with XAS spectra of LMO films without cap is made. For the thicker LMO 9 uc/ LAO 7 uc, the valence-sensitive spectral features are reproduced with reasonably good accuracy when compared with the XAS spectrum of LMO 10 uc, whereas for the thinner LMO 3 uc samples, the XAS fingerprint points to increased Mn^{2+} content in the system with the open surface.

Figure 4.7 shows element-specific HAADF-STEM imaging that resolves the individual Mn, La, Sr and Ti atomic columns for the same pair of samples from which EELS data were shown in Figure 4.6: (a) LMO 3 uc / LAO 7 uc and (b) LMO 9 uc / LAO 7 uc. Although an overall high degree of epitaxy can be deduced from these images, some aspects point towards the non-abruptness of the interface at the point of the polar discontinuity.
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Figure 4.7: STEM imaging: EELS-resolved HAADF-STEM mapping of a) LMO 3 and b) LMO 7 uc with LAO 7 uc cap showing La diffusion into STO and A-site Sr/La intermixing in the STO side of the heterostructure. The Mn interdiffusion in both sides of the LMO film is not exceeding 1 uc.

Firstly, an A-site interdiffusion of La into STO was observed in both samples at the polar STO/LMO interface. This type of La, Sr intermixing is a well known result of the polar discontinuity at the LAO/STO interface [39] in which Sr$_{1-1.5x}$La$_x$O charge neutral layers are formed [167]. Secondly, diffusion of Mn in the STO side is not exceeding 1 uc in both samples, while the weak Mn signal at the LMO/LAO interface suggests reduced Mn content at the top of the stack. However, it is not possible to generalise this latter observation to uncapped samples, such as those measured with XAS and HAXPES. Given hypothetical stoichiometric oxygen content, both La and Mn deficiency would cause the hole-doping of the LMO layer resulting in Mn$^{4+}$ ions. However, a Mn$^{3+}$, Mn$^{4+}$ mixed valence state was not observed in the XAS, HAXPES or EELS experiments for the same samples. In any case, the dominant non-stoichiometric valence contribution is Mn$^{2+}$.

In summary, the important findings along with the direct conclusions that can be drawn from the combined XAS, HAXPES and STEM-EELS study are discussed below:

(i) No sign of Mn$^{4+}$ was observed in capped and uncapped samples of all thicknesses. Therefore a direct polar-induced electronic reconstruction mechanism that
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would result, above the critical thickness, in a spatially separated coexistence of Mn$^{4+}$, Mn$^{3+}$, Mn$^{2+}$ ions is excluded. In addition, the same lack of Mn$^{4+}$ argues against a substantial role for the $A$-site intermixing at the STO side that was observed in STEM imaging experiments and suggests that a different doping mechanism is at work to prevent the polar catastrophe, one having a more pronounced effect on the electronic configuration of the system.

(ii) A significant portion of the Mn ions in the thinner films was found to be in the divalent state. In LMO 2 uc this Mn$^{+2}$ population amounted up to 65% of the total no. of Mn ions, while it showed a relatively systematic decrease down to 10% for the LMO 10 uc sample. Through quantitative analysis of the XAS and HAXPES data, a working hypothesis of a constant 1.25 uc thick Mn$^{2+}$ contribution can be formulated. Hence, this thickness-dependent variation of the average valence stems from this roughly constant Mn$^{2+}$ contribution, offset against differing amounts of trivalent Mn in the rest of the LMO. Depth-information on the location of the divalent ions was gained by STEM-EELS experiments on LAO-capped samples, pointing to the spatial concentration of Mn$^{2+}$ at the interface (polar discontinuity) and partially at the interface to the cap.

Even though the lack of Mn$^{4+}$ provides clear evidence for the absence of a straightforward, polarity-induced electronic reconstruction within the LMO film itself above a critical thickness of order 5 uc, the Mn$^{2+}$ entities, being prominent in the thinner films do have interfacial origin. We link these to electron accumulation at the interface stemming from extrinsic factors with non-stoichiometry being the most likely candidate. The non-stoichiometry origin of Mn$^{2+}$ can be attributed either to $A,B$-site ion excess or oxygen vacancies. The present data do not show signs of excess $A,B$-site ions in the LMO film, making the latter more probable, in particular when taking into account the existing literature on the LAO/STO interface. It is known that oxygen vacancies play an important role in the polar LAO/STO interface, compensating for the polar discontinuity both in the surface and interface [147–149]. Such O vacancies can be also responsible for in the the lack of core level shifts observed below the critical thickness [38, 149].

Summarising the spectroscopic data from XAS, HAXPES and STEM-EELS, it can be said that although the need to deal with the polar character of LMO constitutes the fundamental driving force for the formation of Mn$^{2+}$ ions, stoichiometry factors play a crucial role in inducing the electron doping observed in the LMO film.
4.3.4 XMCD data and sum rule analysis

Given the renewed interest in ultrathin LMO due to the observation of a thickness dependence ferromagnetic behaviour [123], and given the microscopic information we now have on the presence of 3d$^5$ Mn$^{2+}$ ions, it is now of great interest to turn to the question of the magnetic properties of these (ultra) thin films.

The BLADE endstation of the I10 beamline at Diamond Light Source, Didcot, combines a cryostat operated at a lowest temperature of 10K with a superconducting magnet applying fields between -14 and +14 Tesla. The magnetic field is oriented along the incoming X-ray beam-path, facilitating element specific magnetometry based on XMCD experiments. The XMCD experiments were conducted at 10 K and care was taken to minimize any potentially time-dependent artifacts by recording groups of spectra with opposite helicities in trios ($+$ and $-$). Here, we note that the superconducting split-coil magnet of the cryostat of the I10 endstation has a small remanent field of $\approx$0.008 T.

The XMCD spectra of LMO films with thicknesses 3, 4, 5, 6 (two samples), 7 and 10 uc are shown in Figure 4.8 (a)-(f). These experiments were conducted in the presence of various magnetic fields (-2, -1, 1 and 2 T) as well as in the absence of magnetic field (0 T) in order to probe both the saturation$^2$ and remanent magnetic moments respectively. In all measurements, the magnetic field was carefully set at various points along the hysteresis loop taking into account the magnetisation history of the sample while the remanent state at 0 T was approached both from a negative and a positive field to ensure, as an extra sanity check, that the sign of the XMCD contrast flips accordingly. Before moving to the discussion of the sum rule analysis it is immediately evident that in the presence of a magnetic field (blue, cyan, red and yellow traces in Figure 4.8), the Mn moments lead to comparable XMCD contrast from one sample to the next, whereas, in the absence of the field (green and pink traces in Figure 4.8), a strong enhancement of the signal is observed for samples above the thickness of 6 uc.

Here we note that performing a sum rule analysis on the XMCD data at the Mn L$_{2,3}$-edge can lead to intrinsic errors in the determination of the magnetic moments [71]. On top of that, the Mn L$_{2,3}$-edge shows magnetic contrast over a broad energy region at the high photon energy side, being well-separated ($\approx$10eV away) from

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$^2$The saturation field in these films is below 1T [123, 153]
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Figure 4.8: XMCD shows strong thickness-dependent enhancement of the remanent magnetic moments (green and pink traces) and comparable polarisable moments in the presence of field (blue, cyan, red and yellow traces): (a)-(f) TEY XMCD signal \((\sigma^+ - \sigma^-)\) at the Mn \(L_{2,3}\)-edges as a percentage of the maximum of the Mn \(L_3\) absorption. Panels (g)-(l) show the integrals of the XMCD signals normalised to the integral of the unpolarised absorption from the same data. Panels (a),(g) are for LMO 3 uc; (b),(h) for LMO 4 uc; (c),(i) for LMO 6 uc #1; (d),(j) for LMO 6 uc #2; (e),(k) LMO 7 uc and (f),(l) for LMO 10 uc. The shadowed region indicates the region of the XMCD signals in which the integral becomes very sensitive to the background subtraction (which was carried out in a fully consistent manner for all spectra; see text).

The Mn \(L_2\) peak. This renders the high energy part of the integral of the XMCD signal very sensitive to the background subtraction. This region is indicated by grey shading in Figure 4.8. In addition, the Mn \(L_2\) and \(L_3\) edges exhibit a certain degree of overlap due to relatively small spin-orbit splitting. To deal with this issue, we chose to employ an identical background removal procedure in all XMCD spectra which involved the subtraction of a linear background fitted between the first and last points in each spectrum (located well away in energy from the main absorption edges). Hence, the \(P\) value used in the XMCD analysis was evaluated at the lowest point of the XAS spectrum between the main \(L_3\) and \(L_2\) features \((\approx 649 \text{ eV})\).

Using the integrals shown in Figs. 4.8 (g)-(l), the spin and orbital contribution to the total magnetic moment derived from the sum rule analysis \([63, 65]\) as a function of the LMO thickness and is shown in Figs. 4.9 (a) and (b). The first observation is that the orbital moments appear to be quenched across the board as shown in Figure

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Figure 4.9: Emergent, thickness-dependent ferromagnetism and quenching of the orbital moments probed by ultra-sensitive, element-specific magnetometry: (a) magnetic field dependence of the orbital (triangles) contribution to the magnetic moment and the total magnetic moment (circles) (b) thickness dependence of the total magnetic moment (circles) showing a strong enhancement of the total magnetisation of the system linked to a critical thickness of 6 uc. This amounts to a 4.5 times jump in the remanent magnetisation (0T, green markers) and a lesser through still significant increase for both 1 T (cyan markers) and 2 T (yellow markers). Dashed lines indicate span ranges of applied fields containing “missing” applied fields compared to the other datasets.
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4.9 (a) by the triangles. This can be deduced by the low values of the integrals at the high energy side in Figure 4.8 (g)-(l) (as a reminder, one can compare with the schematic shown in Figure 2.8) and this is expected for this type of 3d ions in a cubic ligand field [168]. In addition, in the XMCD spectra for $B = \pm 1, 2 \text{ T}$, a significantly non-zero polarisation is seen across all LMO film thicknesses, as shown in Figure 4.9(b). However, when the external magnetic field is removed, the residual magnetic moments show a much more pronounced jump around a critical value of 6 uc. Remarkably, the magnetic moments of films that have exactly a thickness of 6 uc are located in the middle of the transition, highlighting its abruptness.

Further insight into the effect the LMO magnetisation has on the STO substrate could be gained by carrying out XMCD spectroscopy in specular reflectivity mode at the UE46 beamline at BESSY II, Berlin. In this experiment, X-rays were incident at a few degrees with respect to the surface of the film while a photodiode detector recorded the reflected light in an angular region of about 30° that is allowed by the physical shape of the split-coil superconducting magnet. Then, the detector was set at the scattering angle of the maximum magnetic contrast (in this case $\theta = 22^\circ$). At this fixed angle, and at a temperature of 7 K, the magnetic field was swept, and, employing the two different X-ray energies, one possessing maximal $L_3$ XMCD contrast for the Mn edge and one for the Ti edge, element-specific hysteresis loops can be recorded as shown in Figure 4.10. The loops were calculated using the following formula:

$$X R M S_{\text{contrast}} = \frac{I_{CR} - I_{CL}}{I_{CR} + I_{CL}}$$

In view of the fact that the formal Ti valence in STO is $d^0$, there is no straightforward way for magnetic moments to arise. In LMO/STO superlattices, Ti magnetism was attributed to interfacial charge-transfer and orbital occupancy alternations that can lead to ferromagnetic or antiferromagnetic coupling [169]. One other explanation involves the formation of $d^1$ Ti$^{3+}$ ions by non-stoichiometry factors such as oxygen vacancies in the top region of the substrate, in a similar way to that seen in LAO/STO [40].

To conclude this section on XMCD-based magnetometry, the ultra-sensitive and element-specific character of the experiments carried out on LMO films including a variety of samples both below and above the “critical” thickness along with quantification of the moments via sum rule analysis have revealed the following:
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Figure 4.10: Element specific magnetic hysteresis showing anti-parallel coupling of Ti moments to Mn in a LMO 7 uc film: Field dependence of the reflected resonant X-rays at the scattering angle of the maximum magnetic contrast (in this case $\theta = 22^\circ$), at the photon energy of the maximum of the XAS contrast (642 eV for Mn and 458 eV for Ti)

(i) Robust remanent Mn ferromagnetic moments exist for all thicknesses in the range 2 to 10 uc. Nevertheless, strong enhancement of the magnetisation and in particular the remanent magnetisation is associated to the LMO thicknesses exceeding 6 uc. Assuming that the thickness-dependent emergent ferromagnetism is of double-exchange nature, an optimum doping of $x=0.3$ is expected to maximise the magnetic moment. This corresponds to a thickness of 4-7 uc. On the other hand, ferromagnetism is expected to vanish when the formal stoichiometry is recovered. Interestingly, neither of the above is observed. Therefore, we suggest that the system exhibit magnetic “dead” layers such as in the case of LSMO, alleviating the interfacial polar mismatch via the non-stoichiometry route [154–156].

(ii) Interfacial antiparallel coupling of the Ti moments to the Mn. In view of the fact that STO nominally has an empty d-shell and the gap of STO is relatively large, this observation again points towards the non-stoichiometry at the interface that was seen in the XAS and TEM-EELS experiments.

Consequently, our results argue against a sole “polar catastrophe”-driven double-exchange mechanism, mediating ferromagnetism via Mn$^{2+}$-O$^{2-}$-Mn$^{3+}$ and Mn$^{3+}$-O$^{2-}$-
Mn$^{4+}$ interactions. As mentioned in the introduction, the fragility of the cooperative Jahn-Teller distortion found in pure LMO constitutes an important aspect of the puzzle that is examined in detail in the following section.

### 4.3.5 XLD Results

XAS experiments using linear polarised X-rays were carried out at the UE46 beamline, at BESSY II, Berlin. The XLD is the difference in a pair of XAS spectra that were recorded using horizontally and vertically polarised radiation so as to probe out-of-plane (OOP) vs. in-plane orbitals (IP). XLD is very sensitive to the orbital occupancy of the 3d states and was employed in the past for the investigation of the orbital occupation and orbital ordering mostly in hole-doped manganite (LSMO) crystals [170–173] and films [154, 174–176] as well as LMO films [150, 169].

In our experiments, in view of the fact that the sample was mounted vertically in the cryostat, the electric field of the LV polarisation of the light was incident parallel to the film’s surface (p-polarisation, sensitive to IP). On the other hand, the electric field of the LH polarisation of the light was incident perpendicular to the surface of the sample (s-polarisation, sensitive to OOP). Hence, for c-axis normal to the surface in (001)-grown films, the XLD was calculated as follows: $\text{XLD} = \frac{\text{XAS}_{LV} - \text{XAS}_{LH}}{E_{||c} - E_{\perp c}}$, or IP-OOP.

Figure 4.11 shows the XLD patterns of (a) LMO 2, 4 and 7 uc thickness, measured at 250 K and (b) LMO 2 and 7 uc measured at 5 K. In all cases the XLD signal is shown as a percentage of the maximum $L_3$ absorption. The XLD pattern showed no remarkable change as a function of the thickness of the LMO layer and/or the temperature, suggesting no pronounced change in the orbital occupancy of the LMO. This finding argues against a link between the “critical” thickness of 6 uc for ferromagnetism and an alternation of the Mn orbital occupation or crystal field.

Over and above the lack of film thickness dependence of the XLD data, the XLD pattern provides information as regards the directionality of the orbital occupancy. Due to the physics of the XAS process, a positive/negative XLD signal indicates an excess of in-plane/out-of-plane unoccupied states and hence a preferential out-of-plane/in-plane electronic occupation. In Figure 4.11 (a) and (b), it can be seen that in all XLD traces the negative area is dominant across the Mn $L_{2,3}$-edge as a whole. This observation indicates the preferential occupation of the in-plane 3d orbitals.
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Figure 4.11: Lack of thickness-dependent alteration in the orbital occupancy probed by XLD experiments: XLD spectra normalised to the maximum Mn L$_3$ XAS absorption of (a) LMO 2, 4 (uc) below the critical thickness) and 7 uc (above the critical thickness) at 250 K and (b) LMO 2 and 7 uc at 5K, exhibit similar spectral features.

4.4 Conclusion and outlook

In conclusion, valence tuning and thickness-dependent emergent ferromagnetism were investigated in LMO thin films of thicknesses in the range of 2 - 10 uc grown by PLD on Nb-doped STO substrates, using HAXPES, XAS, STEM-EELS imaging, XMCD, XLD and resonant, soft X-ray magnetic scattering spectroscopies. The main findings of this study are summarised below:

(i) The average valence of Mn was found to exhibit a systematic decrease in thinner LMO films, ranging from 2.9+ for 10 uc to 2.35+ for 2 uc. The way in which the average Mn valence scales with thickness, along with layer-resolved imaging which could track the Mn$^{2+}$ content at the interface and surface indicates that approximately 1.25 uc are purely divalent. No “critical” thickness behaviour between the existence of non-magnetic and ferromagnetic states nor any Mn$^{4+}$ was observed in any of the films. This finding argues against the existence of a polar-driven electronic reconstruction (self-doping) mechanism. On the other hand, the data point towards non-stoichiometry effects that are particularly pronounced in the thin
limit. Oxygen vacancies at the location of the polar discontinuity are a prime suspect in agreement to previous literature [147–149].

(ii) Robust ferromagnetic moments on the Mn sites were detected for all LMO thicknesses, also for zero applied field. However, the magnitude of the (always non-zero) ferromagnetic magnetisation in LMO did exhibit a type of critical thickness behaviour with a pronounced enhancement of the remanent magnetisation being linked to a thickness of 6 uc. This can be understood in terms of magnetic “dead” layers at the interface and surface, a well-known effect in manganites [154–156]. This is supported by the observed, strong electron-doping in the ultrathin limit. In addition, Ti ions in the STO substrate were found to magnetically couple oppositely to the Mn moments. This points again to non-stoichiometry effects, particularly oxygen vacancies, leading to a subtle, yet non-zero Ti 3d occupation. Lastly, the strain that is imposed on the LMO film cannot be excluded as a driving force for ferromagnetism as predicted in the literature [157–159].
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Chapter 5

Imaging the Metal-to-Insulator transition in VO$_2$

Vanadium dioxide (VO$_2$) is a much-discussed material for oxide electronics and neuromorphic computing applications. Here, the metal-insulator transition (MIT) in this non-magnetic, complex oxide is the object of study. The focus of this chapter is on soft X-ray absorption spectroscopy conducted in transmission geometry, and lensless imaging of the MIT in real space, exploiting coherent soft X-rays. The ultimate aim is to combine such lensless imaging (then conducted in a ‘single-shot’ mode using an X-ray laser) with pump-probe excitation of the system so as to generate the first stop-motion movie of this exemplary complex oxide MIT in both time and (real) space. As the ability to pass soft X-rays through a high-quality, epitaxial VO$_2$ film is key to this goal, the first part of this chapter is based on research showing the feasibility of such transmission geometry measurements. This work is part of a collaboration between the QMat group in Amsterdam with our partners in MESA+ (University of Twente), EMAT (University of Antwerp), and SLAC/University of Uppsala, together with CSNSM/University of Paris-Sud, BESSY and synchrotron SOLEIL.

The first half of this chapter covers selected parts of the publication$^1$. It shows how oxide nanosheets can be used to generate high-quality, epitaxial VO$_2$ films on

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soft X-ray transparent substrates, and relates the XAS and XLD data resulting from their investigation, which prove the quality and suitability of this form of VO$_2$ for more complicated lensless imaging experiments.

The second part of this chapter, on the lensless imaging experiments is currently being written up for submission, in close collaboration with the EMAT group (University of Antwerp). These data show the spatial relationship between the metallic and insulating phases during the temperature driven MIT, pointing to initial nucleation of one phase in the other along directions perpendicular to the rutile c-axis of the VO$_2$, followed by growth of these “stripe-like” domains along the VO$_2$ dimer direction (i.e. along c-rutile).
5.1 Introduction

Vanadium dioxide (VO$_2$) has been drawing attention since the discovery of its Metal-Insulator Transition (MIT), signaled by a several orders of magnitude resistivity change close to 340 K [177, 178]. Given these remarkable properties, it may not be a surprise that VO$_2$ is a leading candidate material for the development of oxide devices for both low power electronics (high off-resistance), either in a more conventional field effect type of device or alternatively, in neuromorphic electronic architectures [179, 180] as a memristive material. It has been known that the MIT occurs alongside an abrupt, first-order structural phase transformation from a metallic, tetragonal rutile (R) phase (P4$_2$/mmm) to an insulating, monoclinic (M1) phase (P2$_1$/C). Recent work [181] points out that this transition from insulator to metal is preceded by a purely electronic softening of Coulomb correlations within the V–V singlet dimers that characterize the insulating state, setting the energy scale for driving the near-room-temperature insulator–metal transition in this paradigm complex, correlated oxide.

Up to now, most studies of epitaxial VO$_2$ thin films have used Al$_2$O$_3$ and TiO$_2$ single crystal substrates to control film orientation and strain [182, 183], bringing along challenges of cost, limited size, and incompatibility with the current Si-based technology for future VO$_2$-based devices. However, direct deposition of VO$_2$ on glass or Si substrates with a native amorphous silicon dioxide layer leads to a polycrystalline film with predominant (011)$_{M1}$ orientation [184], whereas VO$_2$ is favourably grown (010)$_{M1}$-oriented when a buffer layer of Pt(111) is used on a Si substrate [185]. Epitaxial growth of VO$_2$ with (010)$_{M1}$ orientation is possible on epitaxial layers of yttria-stabilized zirconia - YSZ(001) - on Si(001) [186, 187].

Ideally, one would wish for direct control over VO$_2$ film orientation on Si or even on arbitrary substrates at will, without any concessions being made on the VO$_2$ film quality. In the context of this chapter, this would mean the ability to grow epitaxial VO$_2$ on soft X-ray transparent substrates such as commercially available Si$_3$N$_4$ membranes. Oriented growth is not only an important enabler for the fundamental study of the mechanism of the VO$_2$ MIT [188], but also for potential applications for next-generation transistors [189], memory metamaterials [190], sensors [191] and novel hydrogen storage technology [192]. Recently, various metal oxide films have
been successfully grown on glass and Si substrates using epitaxy on the so-called oxide nanosheets [193–196]. Oxide nanosheets are essentially 2D single crystals with a thickness of a few nanometers or less, and lateral size in the micrometer range. They can be made spanning a wide range of crystal lattices and 2D structural symmetries [197], allowing for new possibilities to tailor the important structural parameters and properties of thin films on arbitrary -and thus also technologically relevant- bulk substrates. Successful implementation of nanosheets in fact means that the choice of the bulk substrate becomes a free parameter that can enter the engineering cycle of each individual application.

5.2 Full control of film growth on nanosheets

This section describes a way to achieve control over the orientation of VO$_2$ on nanosheets that act as templates for heteroepitaxial thin film growth. This method has been developed at MESA$^+$ Institute, University of Twente. The precise experimental procedures and characterisation details are reported elsewhere [198].

In the research presented here, T$_{0.87}$O$_2$ (TO) nanosheets have been identified as being ideal templates for the orientation of thin films of the important complex oxide VO$_2$ on varying substrates. Monolayers of nanosheets were deposited on Si substrates and alternatively on 20 nm thick Si$_3$N$_4$ TEM grids using the Langmuir–Blodgett method. Then, utilizing PLD, single-phase VO$_2$ thin films were grown epitaxially on TO nanosheets with $(011)_{M1}((110)_R)$ orientation of the low temperature monoclinic M1 phase (high-T rutile phase). The high structural and orientational quality of the VO$_2$ made possible by the nanosheet epitaxy was proven using TEM (EMAT, University of Antwerp) and X-ray diffraction (MESA$^+$, University of Twente) across the MIT. In addition, both transport (MESA$^+$, University of Twente) and soft X-ray spectroscopic probes of the MIT (carried out by QMat, University of Amsterdam) showed data of excellent quality, matching those for VO$_2$ grown on bulk single-crystalline substrates. Importantly, the use of a nanosheet-coated Si$_3$N$_4$ membrane as a PLD substrate allowed soft XAS and the lensless imaging experiments reported later in this chapter to be carried out in the fully bulk-sensitive and highly direct transmission mode. Finally, the nanosheet-approach
5.2. Full control of film growth on nanosheets

Figure 5.1: Temperature-dependent identification of the VO$_2$ structural phases using X-ray diffraction (a) XRD patterns of VO$_2$ on a) TO measured at 303 K (M1 phase) and 403 K (R phase). Data from MESA$^+$ Institute (University of Twente). The three peaks labeled “*” originate from the Inconel alloy 625/718 clamps holding the sample on the diffractometer heating stage. The VO$_2$ Bragg peaks can be indexed using the film orientation discussed in the text. (b) Sketch of the structural transition in VO$_2$ showing the dimerisation, below the transition temperature, of the V-atoms along the c-rutile axis (3 uc are shown, abc coordinates refer to the rutile structure). Taken from [26].

is shown to provide a high degree of control of the crystallographic orientation of the VO$_2$ film.

Figure 5.1 (a) presents the XRD data measured below and above $T_{\text{IMT}}$ (Insulator-to-Metal Transition temperature) of VO$_2$ films grown on monolayers of TO. At 303 K, the peaks seen at 2$\theta$ values of $\approx27.9^\circ$ and $\approx57.7^\circ$ in Figure 5.1 (a) are from the (011)$_{\text{M1}}$ and (022)$_{\text{M1}}$ VO$_2$ reflections respectively. These arise across the $T_{\text{IMT}}$ due to the structural transition of VO$_2$, during which the V-atoms move to form dimers parallel to the c-rutile axis as shown in Figure 5.1 (b). These XRD data confirm the excellent orientational integrity of the VO$_2$ films at the macroscopic scale, a conclusion confirmed by TEM data [198].

One of the motivations for choosing VO$_2$ for this study was its dual role as a model system for both understanding strongly correlated MIT, as well as its tunable/switchable large resistance change near room temperature [179]. Consequently,
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Figure 5.2: (a) Transport characterization of the metal–insulator transition of VO$_2$. Resistance ratio ($R_{\text{R phase}}/R_{\text{M1 phase}}$) of VO$_2$ films grown on TO as a function of temperature. For the M1 phase, the resistance was $2.6 \times 10^5 \Omega$ for TO nanosheet-templated VO$_2$. The resistance in the VO$_2$-R phase was a factor 810 times lower than in the M1-phase for TO nanosheet-templated VO$_2$ growth (b) sketch of the electronic band structure, showing partially occupied $d_{||}$ states at $E_F$ for $T > T_{\text{IMT}}$ and the opening of an energy gap ($\approx 0.6$ eV) for $T < T_{\text{IMT}}$ as a result of the splitting of the $d_{||}$ into bonding and anti-bonding states. Adapted from [26].

The transport behaviour of VO$_2$ grown using PLD on nanosheet templates is of great interest, and these data are shown in Figure 5.2 (a). Defining the midpoint of the transition in the resistance curve measured upon heating as the phase transition temperature, $T_{\text{IMT}}$, our data for the TO nanosheet templated films show transition temperatures close to the canonical value of 341 K for bulk VO$_2$ single crystals [177, 178]. The $T_{\text{IMT}}$ of the films with (110)$_R$ texture (rutile $c$-axis in-plane) grown on TO nanosheets was 347 K. These values are in agreement with what has been found in the literature on the orientation dependence of $T_{\text{IMT}}$ on different bulk TiO$_2$ substrates [199, 200].

Figure 5.2 (b) depicts the respective changes in the occupation of the V3d and O2p bands close to the Fermi energy, $E_F$. Above the $T_{\text{IMT}}$, the $\pi^*$ and $d_{||}$ states (parallel to c-rutile) are partially filled and the system is metallic. Below the $T_{\text{IMT}}$, the $d_{||}$ states split into bonding $d_{||}$ and anti-bonding $d_{||}^*$ states and an insulating gap of $\approx 0.6$ eV appears at $E_F$. Moreover, the $T_{\text{IMT}}$ in VO$_2$ is related to the V-V distance along the rutile $c$-axis, which affects the orbital overlap and the metallicity in the rutile phase [201, 202].
5.3. Results

Under compressive strain, the $T_{\text{IMT}}$ of a 24 nm thick (001)$_R$ VO$_2$ film grown on a bulk TiO$_2$ substrate decreased to 330 K, while it was the same as the bulk VO$_2$ value of 341 K for a fully relaxed 74 nm thick film [26]. When the rutile c-axis is under tensile strain, similar to using TiO$_2$ (110) single crystal substrates, $T_{\text{IMT}}$ is seen to increase further to 350-369 K [199, 200]. Therefore, as $T_{\text{IMT}}$ for VO$_2$ grown on TO nanosheets is higher than that of strain-free, bulk VO$_2$, this indicates that the R-VO$_2$ c-axis (2.86 Å, when unstrained) is under a degree of tensile strain in the [010] direction of the TO nanosheet which has $b = 2.97$ Å. The steep-sided hysteresis curve for the TO-templated VO$_2$ argues for its quality, as grain-to-grain percolation effects that play a role in the transport are sensitive to roughness and reduced structural coherence [198].

5.3 Results

5.3.1 Soft X-ray Absorption

Having proven the excellent crystalline quality of VO$_2$ grown on nanosheets, spectroscopy in the soft X-ray regime is now used to benchmark the epitaxial samples grown on TO nanosheets and provide comparison of the sample quality to what is known in the literature. The nanosheet approach enables deposition of high-quality VO$_2$ on Si$_3$N$_4$ membranes that are soft X-ray transparent, opening a route to conducting XAS in transmission. This yields a bulk-sensitive and direct measure of the absorption that can directly be correlated with local measurements carried out in the TEM. The majority of previous XAS studies of VO$_2$ have used indirect methods such as TEY to monitor the XAS [181, 203–206].

Linking to the transport data presented in Figure 5.2, XAS at the vanadium-L$_{2,3}$ (2p to 3d transitions) and oxygen-K (1s to 2p transitions) absorption edges also directly probe the insulator-to-metal transition (IMT), and are readily accessible using soft X-rays provided by a synchrotron light source. In correlated transition metal oxides such as VO$_2$, the ability of soft X-ray spectroscopy to provide detailed information on the manifold and coupled degrees of freedom (e.g., lattice, spin, charge and orbital) using the transition metal-L$_{2,3}$ and O-K edges have been studied extensively [181, 203–207].
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Figure 5.3: XAS in transmission. V-L$_{2,3}$ edge of nanosheet-supported VO$_2$ recorded in transmission at the temperatures shown for grazing incidence of the linearly (horizontal) polarized X-rays. Subtle yet clear differences in the spectral features mirror alterations in the electronic structure, reflecting changes in orbital energies as the V-d$_{\parallel}$ states split (see Figure 5.2 (b)) and an energy gap opens in the insulating, low temperature phase. The details of the difference spectrum agree very well with published polarization-dependent V-L$_{2,3}$ XAS from VO$_2$ grown epitaxially on bulk single crystalline substrates [26]. Panel (b) shows the O-K edge recorded at normal incidence as a function of temperature. The insets (whose data points are colour-coded to match the spectra from which they are taken) show the T-dependence of the two main absorption features signalling the MIT. Increasing leading edge intensity (black arrow/inset) tracks the closing of the insulating gap as the rutile phase is reached, and a different aspect of the same physics yields to the decrease of the d$_{\parallel}^\ast$ feature at 530.6 eV (gray arrow/inset). The identity of the different peaks, together with a schematic representation of the corresponding density of states is given in Figure 5.2 (b).
5.3. Results

Panel (a) of Figure 5.3 shows V-L$_{2,3}$ edge data both for the metallic (rutile) and insulating (monoclinic) phases for the TO nanosheet templated VO$_2$. As reported by Aetukuri et al. [26], the changes seen to occur across the MIT are related to the orbital occupation, and in particular they underscore the transformation of the 3D rutile situation to one in which V-dimers form along the direction of the rutile c-axis (see Figure 5.1 (b)), leading to shifts and splitting of electronic states related to the orbitals polarized in this direction, referred to as the d$_\|$ states. For grazing incidence of the linear horizontally polarised X-rays (E$_{\perp c_{\text{rutile}}}$) the temperature dependent changes shown in Figure 5.3 (b) agree excellently with published data on grown on single crystalline, bulk substrates [26], attesting to the quality of the nanosheet templated VO$_2$ thin films. Closer examination of the insets yields that the bulk (transmission) XAS shows an onset of the MIT on warming at 340 K, and that $\approx$40 K of further heating are required to complete the conversion to the rutile phase. The transport data shown in Figure 5.2 (a) from fully analogous VO$_2$ films show an earlier onset and faster completion of the transformation on heating. This can be understood straightforwardly as resulting from the percolative nature of the transport probe on the one hand and to the bulk-sensitive, volume-fraction-driven absorption of soft X-ray radiation on the other hand.

One of the clear order parameters for the MIT is the opening of an energy gap in the insulating phase. This can be clearly seen in XAS at the O-K edge, as shown in Figures 5.3 (b) and 5.4 (b), (c), and reported in the literature recently [181]. With reference to the electronic structure schematic shown in Figure 5.2 (b), the most marked spectroscopic changes in the O-K edge spectra while entering the metallic phase are due to the closure of the gap, and the disappearance of the unoccupied d$_\|^{*}$ states, the latter present in the monoclinic phase due to a splitting of the highly directional d$_\|$ states. The insets to Figure 5.3 (b) show how these changes to the gap [d$_\|^{*}$ states] leads to an increase [decrease] of the XAS absorption at the characteristic energy of 529.1 [$530.6$] eV.

Figure 5.4 (a) illustrates the experimental configuration used for polarized XAS in transmission. For the TO-nanosheet-templated VO$_2$ films, the rutile c-axis is in the film plane, and its in-plane orientation varies from one nanosheet to the next. The synchrotron X-ray beam is large enough (at the beamline/end-station used for these experiments of size $\approx 200 \times 100$ $\mu$m) to average over a large number of nanosheets, meaning that we can consider vertically polarized radiation (LV) at
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Figure 5.4: V orbital occupancy across the MIT. a) Schematic of soft X-ray absorption experiments on TO-nanosheet-supported VO$_2$ thin films grown on 20 nm thick silicon nitride TEM windows. Linearly polarized synchrotron radiation impinges in grazing incidence, as indicated (the transmitted beam is measured using a diode downstream of the sample, not shown). The c-axis of the (110)$_R$-VO$_2$ film is oriented differently in each of the nanosheet domains, but is always in the plane of the film. Therefore, LH fixes $E \perp c_{\text{rutile}}$ and LV polarization probes a mix of $E \perp c_{\text{rutile}}$ and $E \parallel c_{\text{rutile}}$. Polarization-dependent measurements at the O-K edge above and below the transition for both b) grazing and c) normal incidence show the in-plane polarization of the unoccupied portion of the highly directionally aligned $d_{\parallel}$ states.
grazing incidence to yield an unpolarised spectrum. Horizontally polarized radia-
tion (LH) aligns the E-vector perpendicular to the film plane and hence E_L|rutile is
always realized, regardless of the direction of the in-plane orientation of the rutile
c-axis in each individual nanosheet-templated epitaxial grain. In Figure 5.4 (b),(c),
polarization-dependent XAS spectra are shown for both grazing and normal inci-
dence of the beam, respectively. As is clear from the earlier discussion, for normal
incidence (Figure 5.4 (c)), whether LV or LH radiation is used makes no difference to
the absorption spectra, as in all cases a mixture of E_{||}c_rutile and E_Lc_rutile is the result.
For grazing incidence (Figure 5.4 (b)) and LH radiation, the E vector is E_Lc_rutile,
compared to mixed E_{||}c_rutile and E_Lc_rutile for LV. This is of high relevance for future
experiments such as those outlined in the next section. The major advantages are
the presence of: i) the O-K leading edge shift at $\approx 529$ eV, ii) the directional d_{||}* states in the monoclinic phase at $\approx 530.5$ eV, and iii) the $\sigma*$ states in the rutile phase
at $\approx 531.5$ eV which all show up clearly in the transmission XAS measurements, also
without the need of a full suite of polarization- dependent measurements.

5.3.2 Coherent Lensless Imaging using HERALDO

The significant temperature-dependent soft X-ray transmission contrast at the
d_{||}* state features in the O-K edge shown in Figure 5.3, combined with the ability
to work in transmission, means such nanosheet templated VO_2 films are ideal for
advanced soft X-ray techniques such as lensless imaging of the MIT with spatial
resolution of <100 nm. Such techniques involve holographic reconstruction of the
real-space patterns formed during the MIT, and can be carried out on similar TO
nanosheet templated samples on Si_3N_4 membranes. Figure 5.5 shows a schematic
for such an experiment, and Figure 5.6 shows the build-up of the holography mask
used.

Coherent lensless imaging using Holography with Extended Reference Auto-
correlation by Linear Differential Operator (HERALDO) was carried out in TO-
nanosheet-templated VO_2 thin films grown on TEM grids. The soft X-ray lensless
imaging experiments were conducted using the COMET end-station at the SE-
XTANTS beamline^2 of the SOLEIL synchrotron in Paris, France. The working prin-
ciple of this type of imaging is the phase retrieval of a differential holographic encoded

\[ \text{synchrotron-soleil.fr/en/beamlines/sextants} \]
Figure 5.5: Lensless imaging of the MIT of VO$_2$. Schematic of a soft X-ray holography experiment on nanosheet-supported VO$_2$ thin films that incorporate a gold mask structure. Illumination with coherent X-rays yields a far-field diffraction pattern, and using a differential filter and fast Fourier transform it is possible to reconstruct a real space image of the different phases of VO$_2$ during the MIT. At an X-ray free electron laser, sufficient intensity in a single ultrafast flash of X-rays would also allow a pump-probe version of this experiment, so enabling a stop-motion film to be built up of how VO$_2$ switches on both the fs timescale and nm length scales.

Besides the improved speed that such algorithm provides, coherent imaging using HERALDO shows improved resolution compared to conventional Fourier transform holography techniques due to the dependence of its resolution on the sharpness of the edge of the reference aperture (not the aperture itself) as well as the flexibility of its shape [209]. Coherent lensless imaging using HERALDO combined with the selectivity of X-rays has been demonstrated in single-shot femtosecond imaging experiments [210] and has been employed for time-resolved studies of magnetic vortices [211].

In this thesis, the focus is on the information gained about the MIT of VO$_2$ and not on the physics of the holographic technique or reconstruction algorithm(s). In this sense we are - in the jargon of the synchrotron - simply “users”. We are grateful to Dr. Horia Popescu and Dr. Nicolas Jaouen (both of SEXTANTS beamline...
5.3. Results

Figure 5.6: Sample mask for lensless imaging experiments in transmission: (a) Si TEM grid (top view) with a 200 nm-thick square Si$_3$N$_4$ window, (b) sample stack on TEM grid (side view) (c) thicknesses of sample stack window

SOLEIL) for their provision of reconstruction algorithms and advice in their use. Also Dr. Igor Vaskivskyi (University of Uppsala) played a key role in the reconstructions from the far field hologram to the “raw” real-space reconstruction. Further image processing was conducted for this thesis.

The structure of the sample is shown in Figure 5.6. The starting point is a round TEM Si grid which has a 200 nm-thick square Si$_3$N$_4$ window of lateral dimensions 0.5 x 0.5 mm. On the TEM grid, TO nanosheets and a 50 nm thin film of VO$_2$ are deposited, at MESA$^+$ Institute, following the same procedure described in the previous section. To enable coherent X-ray imaging using HERALDO a mask created on the backside of the sample. The rest of the TEM grid and VO$_2$ structure remains opaque to the X-ray beam. The mask enables the definition of the object aperture as well as the extended object (slit) that acts as holographic reference. The mask that covers the sample stack is 660 nm thick and consists of 60 alternating layers of 10 nm Au / 1 nm Cr, in order to maintain a flat surface required for the Focused Ion Beam (FIB) processing, as well as to allow “counting” of how far the milling has proceeded.

The next step is the FIB patterning that, for the samples from which the data are presented here, was carried out at Centre de Sciences Nucléaires et de Sciences de la Matière. Using FIB, the object hole and the extended object, were formed on top of the photomask as shown in Figure 5.7 (b). The object aperture is a 2 µm in diameter round hole that exposes the VO$_2$ sample while the extended object that acts as a holographic reference is a straight slit, formed by removal of the material
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Figure 5.7: Focused Ion Beam (FIB) milling of the Au/Cr mask: The window reveals the VO$_2$ film, whereas the slit goes right through the whole structure (including the VO$_2$, the nanosheets, and silicon nitride, too). (a) Schematic of circular object hole and linear reference slit including dimensions (b) SEM image showing a clear, sharp aperture with no remanent re-deposited material in the structure from the whole stack. The slit is thicker close to the surface but is not exceeding 30 nm. Figure 5.7 (a) shows the topology of the structures.

In order to determine the spectroscopic behaviour of the sample, conventional XAS and XLD measurements were carried out through the 2 µm object hole, at normal incidence, at low (300 K) and high (365 K) temperature, employing both LH and LV polarisation of the incident beam, shown in Figure 5.8. A very large XLD contrast is deduced for both low and high temperatures. This XLD result is strikingly different to the one shown in Figure 5.4 (c). In the previous case, no photomask was present causing the XLD signal to be smeared out stemming from averaging over the spatial extent of the X-ray beam (tens of µm) that covers multiple nanosheet domains with each one having random in-plane c-axis orientation of the (110)$_R$-VO$_2$ film. Carrying out this experiment through an object hole of 2 µm ensures -with some good fortune in this case- that a single nanosheet is exposed because their characteristic lengthscale is larger than 5 µm [198]. In addition, the large XLD contrast implies that the c-axis orientation of the (110)$_R$-VO$_2$ phase matches one of the linear polarisations.

For the temperature-dependent lensless imaging experiment across the MIT, the difference of the polarisation-averaged XAS spectrum between low and high temperature becomes important. The photon energy for imaging was chosen at the maximum of the temperature-induced variations of the XAS signal that coincides with the d$_{II}^*$ feature at $\approx$531.7 eV, marked in Figure 5.8 with a dashed line. In
addition, far-field holograms were recorded at the pre-edge, at $\approx 529.4$ eV, to allow normalisation of the real-space image reconstructions. Employing both linear polarisations, a pair of holograms were recorded using a CCD camera (exposure time 1 second, readout time 5 seconds) at both photon energies. A typical hologram is depicted in Figure 5.5, showing an Airy disk as a result of the passing of the X-ray beam through the object hole along with a typical diffraction pattern stemming from the single, reference slit.

The IMT was imaged at these photon energies during the heating cycle. At each temperature step, the recorded holograms were reconstructed using HERALDO, i.e. applying a linear differential filter to the field autocorrelation [208]. The post-reconstruction analysis procedure was initiated with the circular cropping of the images to about 70% of their original size in order to reduce artifacts visible at the edges of the object hole. Next, a 2-dimensional, third degree polynomial background was fitted and subtracted from each image. Subsequently, the images were normalised to the pixel that contained the maximum value and for each polarisation, the image taken at the pre-edge energy was subtracted from one taken at the
Figure 5.9: Lensless imaging the MIT on VO$_2$ using soft X-rays: Real-space images reconstructed using HERALDO from far field holograms as a function of temperature during heating, revealing the emergence of the rutile metallic phase of VO$_2$ as dark filaments propagating in a wavefront manner. Right hand side shows heating cycle resistivity data taken from Figure 5.2 from a similar sample (VO$_2$ on TO nanosheets)

$d_\parallel^*$ photon energy. Finally, the images recorded with the two polarisations were averaged to give one picture at each temperature.

Figure 5.9 shows the reconstructed of real-space images for a temperature window consisting of ten steps across the IMT upon heating. On the right hand side of the same figure, the heating cycle resistivity data taken from Figure 5.2 for a similar sample (VO$_2$ on TO nanosheets) are shown, along with numbered marks that highlight the position on the hysteresis curve at which each image was taken. It must be noted that the resistivity measurement was carried out on a different sample and in a different apparatus, using a different thermometer. In addition, resistivity reflects a “global” property of the sample and depends on the sum of the resistivities of all nanosheet-templated VO$_2$ films and the way in which these nanosheets are connected to each other. Nevertheless, a low sample-to-sample variation has been observed in the VO$_2$ films grown by our collaborators under similar strain conditions and thus the resistivity data can be used as an approximate guide to track the IMT.
5.3. Results

The metallic rutile phase of VO$_2$ is imprinted in the images of Figure 5.9 as high intensity (black) features that emerge during the heating cycle, recorded at thermodynamic equilibrium, coinciding with regions of the sample at which the absorption is low (see Figures 5.3 (b) and 5.8). The top left picture (no. 1), corresponds to a temperature of 332.5 K, before the MIT, and is dominated by a normal distribution of low intensity pixels that represent the monoclinic insulating phase of VO$_2$. At the centre of this image, three black dots are observed (highlighted using yellow arrows in this figure) with size of $\approx 50$ nm. These are attributed to nucleation sites at which the metallic phase initially grows.

Further increasing the temperature to 335 K (picture no. 2) leads to the emergence of distinctive thin black (rutile metal) filaments whilst increased intensity is concentrated around the nucleation centres. The lateral dimension of these filaments is larger at the nucleation centres ($\approx 100$ nm). Following increasing temperature steps from 337.5 K (picture no. 3), the system enters the steep downturn in resistivity up to 347.5 K (picture no. 7), at the middle of the IMT. Between 337.5 K and 347.5 K, it can be seen that these filaments monotonically increase in size, with the central filament propagating in both directions in a wavefront manner. At the middle of the IMT, at a temperature of 347.5 K (picture no. 7), the maximum XAS spatial contrast is evident, owing to the maximization of the phase coexistence. Further increasing the temperature to 350 K (picture no. 8) and 352.5 K (picture no. 9), the rutile metallic phase spatially dominates the field of view, and the XAS contrast starts to fade. At 357.5 K (picture no. 10), the system settles in the rutile metal phase and only a pair of lighter stripes is noticeable. These features are interpreted as late-switching insulating regions of the sample. Below, the important observations are summarised.

The real-space HERALDO imaging experiment carried out using coherent soft X-rays in transmission, has provided insight into the spatial characteristics of the IMT in VO$_2$ films grown on TO nanosheets. Firstly, the lengthscales associated to the phase segregation and propagation were determined and found to be resolvable at the tens of nm scale. The initial phase of the rutile metal formation takes place at nucleation centres which precede the IMT. These nucleation sites can be understood in terms of intrinsic point defects, particularly oxygen vacancies, which can act as a source of free electrons, locally changing the electronic structure and causing lower transition temperatures [212]. Upon heating, these nucleation sites gradually
develop anisotropically, connecting to each other in a thin, filamentary manner. At this point, assuming early switching defect-rich regions and late switching normal of the sample, a purely electronic (isostructural) MIT cannot be excluded, especially at the border of the defect-normal regions [212].

Further increasing the temperature leads to the growth of the metallic filaments beyond the field of view, and their growth in the perpendicular (in these images, vertical) direction. It has been reported [213] that their length may extend over several µm. Finally, the orientation of the filaments in respect to the crystallographic axes was investigated. The large XLD observed in the object hole of this VO₂ film (Figure 5.8) argues for an alignment of the rutile c-axis with the linear polarisation of the light. In such a picture, the nucleation centres get initially connected along an in-plane direction perpendicular to the rutile axis. The subsequent (vertical) growth of the metallic filaments, which gradually occupy the entire field of view, takes place as fronts growing in the c-rutile direction, along which the dimers associated with the insulating gap & split off of the d||* states are being destroyed as the VO₂ becomes a metal.

**5.4 Conclusion and outlook**

To conclude, we have shown that nanosheets can act as templates for heteroepitaxial growth of high-quality VO₂ thin films on arbitrary substrates. This approach can be employed to enable fabrication of samples suitable for spectroscopy experiments in transmission including soft XAS and X-ray Fourier transform holographic imaging. Specifically, XAS on the V-L and O-K edges has been used to track the MIT at specific energies associated with the collapse of the gap in VO₂. Moreover, angular-dependent XLD measurements on the O-K edge revealed the in-plane orientation of the d|| states, parallel to the E-vector for LV polarisation in Figure 5.8, with this direction corresponding to the c-rutile axis. This results argues for the high quality of the nanosheet templated growth and the suitability of these films for holographic lensless imaging of the MIT in VO₂ in transmission such as coherent soft X-ray imaging conducted using HERALDO. The part of the sample that was exposed in the object aperture in these experiments, corresponded to the part of a single nanosheet template, resulting in very large temperature-dependent XAS and
XLD contrasts. The imaging experiment, conducted during heating revealed the real-space image of the rutile metal emerging at nucleation sites and expanding in a filamentary way first perpendicular to and then parallel to the $c_{\text{rutile}}$ axis into the rest of the film. The ambition is to carry out this experiment in ultrafast mode and enable a real-space movie with fs time resolution and the 50 nm spatial resolution demonstrated here, so as to reveal new aspects of the IMT in this important test-case material for oxide-based devices.
Chapter 5. Imaging the Metal-to-Insulator transition in VO$_2$
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List of Publications

This thesis is based on the following publications:


The following publications present work that was carried out by the Amsterdam QMat group involving the thesis author during the period of his PhD and MSc, but which are not taken up in this thesis:

• Y Pan, AM Nikitin, GK Araizi, YK Huang, Y Matsushita, T Naka, A De Visser, Rotational symmetry breaking in the topological superconductor Sr3Bi2Se3 probed by upper-critical field experiments, Scientific Reports, 6, 28632 (2016) (DOI:10.1038/srep28632)

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