CHARGE TRANSFER AT THE INTERFACE BETWEEN COMPLEX OXIDE THIN FILMS

Jaap Geessinck

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CHARGE TRANSFER AT THE INTERFACE BETWEEN COMPLEX OXIDE THIN FILMS

PROEFSCHRIFT

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Chapter 1

Relevance of oxide interfaces

1.1 General introduction

The phenomenon of charge transfer

In this thesis, the term ‘charge transfer’ refers to the phenomena where charge is being transferred at the interface between two different materials or molecules, excluding the movement of charges within the bulk of a material. Although interfacial charge transfer occurs at small length scales, this phenomenon affects a multitude of different processes; from photosynthesis to hydrogen production and solar-panels, which are examples that will be briefly discussed in the following sections.

The distinction can be made between spontaneous charge transfer and charge transfer that needs an external stimulus. An example of the latter is the process of photo-induced electron transfer, in which a photon excites an electron that is subsequently transferred from donor-molecule to acceptor, resulting in a photo-induced reduction/oxidation [1]. Such charge transfer reactions, stimulated by light, are at the basis of photosynthesis in plants, where sunlight is absorbed by plants to convert CO_2 and H_2O into O_2 and carbohydrates, such as sugar [2].

Similarly, multiple other chemical reactions often rely on the transfer of charges between substances. For example in the electrochemical splitting of water [3]–[5], where hydrogen is produced from electricity by converting water into molecular oxygen and hydrogen: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$. In this system, charge transfer plays a crucial role; electrons are transferred from the cathode to the water (reduction) in order to form hydrogen gas, combined with the transfer of electrons from water to anode (oxidation) to create oxygen [4]. Both steps could benefit from suitable catalysts that easily donate/accept electrons to improve this reaction efficiency [5].

Charge transfer also plays a major role in the operation of solar panels, when photovoltaic cells are formed by combining n-type (electron doped) and p-type (hole doped) semiconductors. In this pn-junction, band bending occurs at the interface, leading to a built-in potential [6]. When light is absorbed, the photons create electron-hole pairs (excitons). Due to the built-in potential over the

junction, the electrons and holes are separated and transferred across the interface to opposite sides of the junction. Power can be extracted when connections are made to both sides of the junction, allowing the electrons to recombine with holes via the external circuit.

Transition metal oxides

Electronic devices often rely on the workings of field effect transistors, in which an electric field is used to move charges inside a semiconductor to modulate (switch ON/OFF) the conduction between source and drain [7]. Upon accumulating charge carriers by applying an electric field, a conducting channel is formed and current can flow. However when the field is reversed, the conducting channel is depleted and becomes resistive.

The first reports of working transistors originated from Bell-labs with the invention of the *Point-Contact Transistor* in 1947, followed by the more stable *Bipolar Junction Transistor* in 1948, which has become the first widely adopted transistor manufactured by the semiconductor industry [8]. In 1956, John Bardeen, Walter Houser and William B. Shockley were honored for their discovery and pioneering work and received the Nobel prize in Physics ‘*for their researches on semiconductors and their discovery of the transistor effect*’ [9], [10].

Subsequently, transistors were quickly implemented in electronics in the form of integrated circuits. The number of transistors in integrated circuits started to increase rapidly due to advances in fabrication. Gordon Moore (co-founder of Intel) described this growth in 1965 as a doubling of the number of components per integrated circuit for every year [11]. In 1975, this was revised to a doubling every 2 years, which has become known as *Moore’s law* [12]. This empirical law describes the incredible speed at which technology advances and emphasizes the importance of downscaling electrical components.

Technological advances in semiconductor manufacturing enables continuous downscaling, increasing processor speed, reducing switching energy and increasing overall capabilities of electronics [13]. However, further improvement becomes increasingly difficult, because of fundamental limits to the length scales at which conventional semiconductors can operate [13]. Therefore, there is increasing interest in new materials to host next generation electronics.

In traditional semiconductor devices solely charge degrees of freedom are exploited. Therefore, materials that additionally offer the ability to use spin,

orbital and lattice degrees of freedom have large potential [7], [14]. Having these materials that provide more functionality could enable further improvement of performance. This prospect of using additional degrees of freedom is what makes Transition Metal Oxides (TMOs) a promising class of materials [7], [14]–[18]. Common denominator of transition metals is the electronic configuration, which incorporates a partially filled d-shell and the ability to adopt multiple valence states.

Moreover, the possibility to accommodate multiple valence states, makes TMOs also appealing to other (research-) fields. For instance, TMOs are expected to be important enablers in the transition towards sustainable and clean energy, via battery applications as lithium-ion [19], [20] or sodium-ion [21] batteries (a valence change is required to compensate the charge when ions are inserted or extracted). The development of these batteries focusses mostly on non-toxic and earth-abundant first-row transition metals and has resulted in commercially available materials as LiMn_2O_4 , LiCoO_2 and LiFePO_4 [20].

Another aspect of TMOs encompasses the work on Mott insulators. These particular insulators are expected to be conducting according to band-theory, but the insulating nature of these materials is governed by electron-electron interactions [22]. The balance between conducting and insulating offers the prospect of inducing a metal-insulator transition. A highly sought after application of Mott insulators therefore lies in the development of Mott-transistors (and other Mottronics); the metal-insulator transition controls the current between source and drain [22]–[24]. This type of transistor is supposed to be superior to field effect transistors and suitable to high power applications [22].

Perovskite (formula ABO_3) TMOs with first row transition metals on B-site, are also seen as promising candidates in (electro)catalysis for water splitting and CO_2 reduction. Here, the ability to take on multiple valence states is crucial for catalytic activity [4]. Research has identified perovskite TMOs such as SrMO_3 and LaMO_3 (with $\text{M} = \text{Co}, \text{Ni}, \text{Fe}$ and Fe) as promising catalysts [25]. Note that a major impact on society can be expected when the process of hydrogen production is improved: i) hydrogen has the potential to be used as a clean alternative for fossil fuels, and ii) hydrogen can be converted into electricity using fuel cells (e.g. making it possible to replace batteries by a hydrogen system) [5].

Charge transfer at the interface between transition metal oxides

The TMOs class of materials has the potential to impact society in many ways, but challenges remain. Despite significant progress that has been made in the field of TMOs, it still remains in its infancy compared to conventional semiconductors [14]. Therefore, apart from potential applications, TMOs are studied to answer fundamental questions. Moreover, the coupling between spin, orbital, lattice and charge generally requires elaborate theory to explain observations. For instance, the magnetic properties in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ are explained using specific orbital occupations, combined with a mixed valence, resulting in a ferromagnetic double-exchange coupling between Mn^{3+} and Mn^{4+} [26], [27].

One of the challenges is to understand processes that occur at the interface between two different TMOs [28]. Typically, research on perovskite TMOs focuses on bulk or thin films (few tens of nm), but when decreasing the layer thickness to below 5nm, material properties can change dramatically. Not only structural changes, as octahedral rotations imposed by the substrate [29], but also valence changing effects at the interface become more important [30], [31]. Especially with the resolution of state-of-the-art lithography being around 7nm (predicted to be replaced by 5nm in a few years, as plant building has started as announced by TSMC [32]) and thickness of high-k dielectric layers already below 1nm [14]. Since the dimensions of novel devices need to approach current industry standards in order to be compatible, this means that properties of TMOs need to be investigated at these small length-scales for TMOs to be used in next-generation electronics. Therefore, it is crucial to understand what happens at the interface between different transition metal oxides.

The band alignment at the interface between conventional semiconductors is well understood: the energy levels of the two semiconductors need to be aligned at the vacuum-level according to Anderson's rule. After this initial alignment, the resulting offsets between Fermi-levels, conduction and valence bands can be deduced and the band-bending at the interface can be extracted. However, where Anderson's rules work for conventional semiconductors, these cannot be applied to TMOs, since the work functions are not well-defined [33]–[35].

To solve the problem of band alignment, Zhong and Hansmann [33] adopted a strategy in which the initial alignment is performed by aligning the oxygen-2p (O-2p) bands of the TMOs (resulting in a band offset between the transition metal bands). This approach is based on the continuous oxygen octahedral network at

the interface between the two TMOs. Using density functional theory (DFT) calculations, it was shown that the transition metal offset can lead to a charge transfer across the interface (**see chapter 2**). Experimental verification of this model can be a vital step in obtaining a fundamental understanding of TMO interface effects.

Moreover, fully exploiting the connection between spin, charge, orbital and structural degrees of freedom in TMOs, requires ways to manipulate these. Experimentally, the valence can be altered via chemical substitution doping to (passively) donate or remove electrons. However, chemical substitution has the downside that it introduces defects in the lattice, which can negatively affect the device performance. Another option is to use an electric field to (dynamically) accumulate or deplete electrons to locally change the charge carrier concentration and valence, but this may not always be possible or practical [7]. Moreover, when the material needs extensive carrier modification, the high electric fields required can lead to breakdown. Especially when using ultra-thin layers, a large tunneling- or leakage-current can become an issue. Therefore, the understanding of interfacial charge transfer can also provide opportunities to dope a material by locally altering the valence. Although limited to ultra-thin layers, this process does not introduce defects into the lattice as associated with chemical substitution doping (similar to modulation doping in semiconductors). Moreover, a suitable combination of materials can result in a large modification of the valence, thereby creating novel materials that otherwise do not exist.

Motivation

Although observations of interfacial charge transfer already exist, a general theoretical understanding has long been missing. Now that a model has been proposed, more experiments on different material systems are required to further improve and verify this model. Additionally, DFT calculations have limitations and can become less trustworthy in certain materials, for instance in charge transfer insulators [33].

Therefore this research is aimed to systematically investigate the charge transfer in the technologically relevant charge transfer insulator LaCoO_3 [36], by interfacing this with LaTiO_3 . Apart from testing the validity of the model for a charge transfer insulator, LaCoO_3 has the largest band offset with LaTiO_3 and therefore the largest potential to accept electrons (among first row transition metals), which explores the limits of the charge transfer effect. To gain full

control on interfacial charge transfer, a LaAlO_3 layer is tested as a way to block the charge transfer.

Additional interest in LaCoO_3 stems from the debate about the magnetic properties of LaCoO_3 in relation to spin-transitions and strain [37], [38]. Little information is known about ultra-thin LaCoO_3 , making this in itself an interesting system to investigate. Especially when charge transfer can be used as a probe to gain more insight in the electron configuration (i.e. spin states) without disrupting the structure.

Goal

Obtaining a fundamental understanding about interfaces between TMOs by investigating interfacial charge transfer mechanisms, since these can prove beneficial in the creation of new emergent properties and possible future applications. (summarized in **figure 1.1**)

Figure 1.1 Illustration to summarize the goal of this thesis: Ultra-thin layers of transition metal oxides (TMOs) are combined to induce interfacial charge transfer. This charge transfer alters the valence at the interface, possibly leading to novel properties for possible applications.

1.2 Thesis outline

Chapter 2 – Theory of transition metal oxide interfaces

First, the model of band alignment at oxide interfaces is introduced in more detail, explaining the driving force behind interfacial charge transfer and several relevant predictions. Subsequently, this model is used to explain why LaTiO_3 and LaCoO_3 have been chosen as candidates to evaluate interfacial charge transfer throughout this thesis. Furthermore, this chapter elaborates on other interface effects, such as the polar-catastrophe, which should be avoided when conceptualizing the sample layout.

Chapter 3 – Fabrication of LaCoO_3 – LaTiO_3 heterostructures

In computer calculations, LaTiO_3 and LaCoO_3 can be combined. In practice however, this is less straightforward. Therefore, the main question addressed in this chapter is whether ultra-thin layers of these materials can be experimentally fabricated into samples of sufficient quality. Pulsed Laser Deposition was used for fabrication and combined with *in-situ* Reflection High-Energy Electron Diffraction to monitor the growth. Several steps had to be taken to optimize the sample quality and ex-situ Atomic Force Microscopy measurements were used to minimize the surface roughness to yield sharp, well-defined interfaces. After fabrication, Scanning Transmission Electron Microscopy and X-ray Diffraction measurements were used to evaluate the structural quality.

Chapter 4 – Charge transfer at the LaCoO_3 – LaTiO_3 interface

A systematic X-ray Absorption Spectroscopy study is presented, using reference samples, samples with a single LaTiO_3 | LaCoO_3 interface and double interface samples with LaTiO_3 | LaCoO_3 | LaTiO_3 . The spectra of titanium and cobalt are used to extract the valence changes. By varying the thickness of LaCoO_3 , the interfacial character of the charge transfer is illustrated. This is further established using Scanning Transmission Electron Microscopy combined with Electron Energy Loss Spectroscopy measurements, which shows the valence change close to the interface. Reducing the LaCoO_3 thickness to 2 unit cells in a double interface sample, the cobalt valence can be modified from nominally Co^{3+} to a 100% Co^{2+} valence. By introducing a 2 unit cell thick LaAlO_3 between LaCoO_3 and LaTiO_3 the charge transfer could be significantly suppressed.

Chapter 5 – Magnetism in ultra-thin LaCoO_3

The spin states and spin transitions of bulk LaCoO_3 and the relation to the magnetic properties has been heavily debated. In thin film LaCoO_3 , the discussion is even more complicated due to the additional effect of strain and the

arising ferromagnetic order at low temperature. Various strain relaxation mechanisms have been observed in LaCoO_3 , which can only be avoided in ultra-thin layers. Little is known in literature about these ultra-thin LaCoO_3 films, motivating our investigations into the magnetic properties of such ultra-thin LaCoO_3 layers. Experimentally, these layers are difficult to probe using conventional magnetometers, therefore element specific X-ray Magnetic Circular Dichroism was used to find the magnetic properties and extract the orbital and spin moments. Additionally, interfacial charge transfer was used to investigate the magnetism of LaCoO_3 with 100% Co^{2+} and gain further insight in the magnetic behavior and spin states upon electron-doping.

Chapter 6 – Outlook

This final chapter describes some ideas for future research to improve and extend upon the work presented in the other chapters. The relevance of conductivity in LaCoO_3 - LaTiO_3 heterostructures is explained, together with several preliminary results. Moreover, since LaCoO_3 is used in catalysis, the possibilities are explained of using charge transfer to manipulate the catalytic activity.

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Chapter 2

Theory of transition metal oxide interfaces

In this chapter, the model of band alignment at oxide interfaces is introduced to explain the driving force for interfacial charge transfer. Subsequently, this model is used to explain why LaTiO_3 and LaCoO_3 have been chosen as the materials of interest in this thesis. Additionally, this chapter elaborates on other theoretical aspects that might play a role, such as the polar-catastrophe model, and how this has been taken into consideration when conceptualizing the sample layout.

2.1 Band alignment at the interface

In the field of semiconductors, the theory of band alignment at interfaces in heterojunctions is well established: Anderson's rule states that the vacuum energy levels of two semiconductors need to be aligned [1]. After this initial alignment, the offsets between Fermi-levels, conduction and valence bands can be extracted. When aligning the Fermi-levels, these offsets can be used to predict the resulting band-bending at the interface and possible electron accumulation, as depicted in **figure 2.1**.

The procedure, described using Anderson's rule, relies on well-defined work functions. However, the work function in perovskite Transition Metal Oxides (TMOs) relies on multiple factors, such as surface termination (e.g. for SrTiO_3 : TiO_2 terminated 2.5eV, SrO terminated 4.2eV [2]), which makes this procedure inapplicable [3]–[5].

Figure 2.1 Illustration of band alignment as dictated by the Anderson's rule, based on alignment of vacuum energy-levels (E_{vac}). When both materials come into contact, band-bending can result in electron accumulation.

Figure 2.2 Interface between 2 perovskite oxides with the same A-site elements. Since the oxygen-octahedral network is continuous at the interface, the interface-plane can either be the top of $AB'O_3$ or the bottom of ABO_3 .

Recently, a procedure has been proposed to evaluate band alignment at the interface between two perovskite TMOs, by aligning the oxygen 2p bands ($O-2p$) of the two materials, instead of the vacuum levels [4]. This originates from the observation that the oxygen octahedral backbone continues across the oxide interface, as depicted in **figure 2.2**. This image depicts an interface between two perovskite oxides (formula ABO_3) with the same element on A-site (red spheres) and two different transition metal ions at the B-site (B and B' illustrated by green and blue spheres). When both materials have the same element on the A-site, the oxygen (black spheres) at the interface can belong to either material. This illustrates that the oxygen 2p bands can indeed form a suitable reference for alignment [4].

Figure 2.3 Schematic illustration of band alignment at the interface between two perovskite transition metal oxides. **a)** displays the initial alignment using the O-2p bands. The difference between the O-2p and the Fermi-level (E_F) of the TM-3d bands of both materials is indicated using orange arrows. The difference between the two orange arrows is depicted by the green arrow, which depicts the potential for charge transfer. **b)** After the materials come into contact, electrons are transferred from B to B' (in blue) to compensate the offset in E_F , accompanied rigid band shifts. Image adapted from [4].

The proposed band-alignment procedure is schematically depicted in **figure 2.3**. The green arrow in **figure 2.3a** illustrates the band offset between two different TMOs after alignment of the O-2p bands. Since the Fermi-level (E_F) cannot be discontinuous, this offset needs to be compensated when these materials come into contact, illustrated in **figure 2.3b**. Density Functional Theory (DFT) calculations show that electrons will move across the interface from transition metal B to B' (indicated in blue) to resolve this offset [4]. This required a (partial) valence change in both B and B'. Additionally, the band offset results in a rigid band shift ($\Delta\Phi$) between both O-2p bands (**figure 2.3b**).

This model naturally explains the band alignment and predicts interfacial charge transfer between the transition metal ions as mechanism to correct band offsets. According to the model, the charge transfer can be easily predicted by investigating the energy difference between oxygen 2p bands (ϵ_p) and the Fermi level E_F (electronegativity/electron affinity), as depicted by the two orange arrows in **figure 2.3a**. By investigating $\epsilon_p - E_F$, this model can be easily generalized to a large variety of TMO compounds. **Figure 2.4** displays this energy difference for various 3d, 4d and 5d transition metals. Here, the solid lines depict compounds with strontium on A-site, which gives a transition metal valence of 4+ (i.e. B^{4+}). The open symbols depict the corresponding energy of the d-bands

(ϵ_d). The black dashed line represents compounds with lanthanum on A-site, resulting in a transition metal valence of 3+ (i.e. B^{3+}).

Two general rules can be extracted from **figure 2.4**: i) within a rows of 3d, 4d or 5d transition metals, the lighter elements will donate electrons to the heavier elements, and ii) within one group, the heavier elements will donate to the lighter elements.

Further DFT calculations showed that replacing the cation by a different cation with the same oxidation state (e.g replacing La by Y or replacing Sr by Ca or Ba) leaves the result basically unchanged [4]. Moreover, when the oxidation state of the A-site cation is changed from 2+ to 3+, this leads to a decrease of ϵ_p of up to 2 eV (see black dashed line and solid line in **figure 2.4**), but the overall trends remain valid. Note that this figure only provides band offsets, but does not take into account whether electrons are available to donate (i.e. according to the figure, titanium in $SrTiO_3$ should donate to manganese in $SrMnO_3$ even though titanium has d^0/Ti^{4+} valence .)

Intermixing and surface roughness is always a concern in studying interface effects, therefore a scenario with 25% mixing was also evaluated by Zhong and Hansmann [4]. However, they conclude that the main findings remain unchanged.

In conclusion, a model to evaluate band alignment between TMOs has been proposed by Z. Zhong and P. Hansmann [4]. This procedure is based on the initial alignment of O-2p bands, since the oxygen network is continuous at the interface. This alignment results in a discontinuity at the Fermi level, which is resolved by a rigid band shift combined with a transfer of electrons. This charge transfer can be easily predicted using the difference $\epsilon_p - E_F$ (depicted in **figure 2.4**). However, this does not take into account the specific material properties.

According to the authors, the value of ϵ_p can become less reliable when the materials become more correlated (for instance when evaluating charge transfer insulators) [4]. Therefore, experimental evidence is required to verify and further improve this model, which contributed to the motivation for the work presented in this thesis.

Figure 2.4 This figure illustrates the band-offsets for perovskites with various 3d, 4d and 5d transition metals on B-site. Empty symbols depict ϵ_d and the filled symbols ϵ_p with respect to E_F for SrBO_3 perovskites. The dashed line is for LaBO_3 oxides. For interfacial charge transfer, electrons are donated from more negative $\epsilon_p - E_F$ to compounds with less negative $\epsilon_p - E_F$. From all the 3d compounds, the largest offset can be found between LaTiO_3 and LaCoO_3 leading to the largest potential for charge transfer. Image taken from [4].

LaTiO_3 and LaCoO_3

The choice was made to investigate the charge transfer among non-toxic and earth-abundant first-row (i.e. 3d) transition metal oxides. Therefore, using **figure 2.4**, it can be seen that the largest potential for charge transfer is found between Ti and Co. The band offset between Ti and Co is similar with both strontium or lanthanum on A-site. However, Ti^{4+} in SrTiO_3 cannot donate electrons, therefore lanthanum is preferred on A-site (dashed line in **figure 2.4**). With lanthanum on A-site, this combination would result in the valence change: $\text{Co}^{3+} + \text{Ti}^{3+} \rightarrow \text{Co}^{2+} + \text{Ti}^{4+}$.

Correlation effects in charge transfer insulators can affect ϵ_p and can therefore make the calculations less accurate, as pointed out by Z. Zhong and P. Hansmann [4]. This makes the LaTiO_3 - LaCoO_3 combination especially relevant, since LaTiO_3 (LTO) is a Mott insulator and LaCoO_3 (LCO) a charge transfer insulator [6]. Moreover, charge transfer was successfully shown in a heterostructure of LaTiO_3 and LaFeO_3 [7], making LTO and LCO a promising combination. Additionally, both

materials are prime candidates for future applications (e.g. LTO is of interest in Mottronics [8], LCO in spintronics [9] and catalysis [10]–[12]).

The difference between charge-transfer insulators (i.e. LaMnO_3 , LaFeO_3 and LaCoO_3) and Mott insulators (i.e. LaTiO_3 and LaVO_3) was first recognized by Zaanen, Sawatzky and Allen, who showed that transition metal oxides must be distinguished by comparing the size of both Coulomb potential (U) and charge-transfer gap (Δ) [6], [13]. When $U < \Delta$, this gives a band gap proportional to U , whereas $U > \Delta$ gives a gap proportional to Δ . Where U can be seen as a potential for hopping between transition metal ions in different unit cells and Δ can be explained as the potential for electrons to move between transition metal ions and anions. Therefore the case where $U < \Delta$, shows the classical Mott-Hubbard gap dictated by electron-electron (i.e. Coulomb) interactions, whereas for $U > \Delta$ the gap is determined by charge-transfer effects: hence the distinction.

LaTiO_3

Bulk LaTiO_3 has an orthorhombic crystal structure with pseudocubic lattice parameters $a = 3.98 \text{ \AA}$, $b = 3.97 \text{ \AA}$ and $c = 3.96 \text{ \AA}$ at room temperature [14]. Furthermore, LaTiO_3 shows G-type antiferromagnetic order with a Néel temperature of around 140K and a Mott-Hubbard gap of $\sim 0.1 \text{ eV}$ [6], [14].

The conduction in LaTiO_3 can be changed by tuning oxygen stoichiometry and epitaxial strain, invoking a metal-insulator transition [8], [15], [16]. These findings sparked recent interest in LaTiO_3 with prospects of creating a Mott-transistor. However, a practical way of switching between both states has not (yet) been found.

Using LaTiO_3 as an electron donor to LaCoO_3 , would result in a different electron-occupation of LaTiO_3 . This makes the electronic properties of LaTiO_3 after charge transfer of additional interest.

LaCoO_3

At room temperature, bulk LaCoO_3 displays a rhombohedrally distorted perovskite structure with lattice constant $a = 5.38 \text{ \AA}$ (pseudocubic $3.80 \text{ \AA}$) and α around 60° [17]–[20]. Furthermore, LaCoO_3 is a charge-transfer insulator with a gap of around 0.6 eV [6].

Moreover, spin transitions makes LaCoO_3 an intriguing material; bulk LaCoO_3 is paramagnetic from room temperature down to a transition temperature around 100K where it becomes diamagnetic, originating from a Low Spin ground state

[21]. On the other hand, thin film LaCoO_3 exhibits ferromagnetism appearing below $\sim 85\text{K}$ indicating alternative spin states [22]. The ferromagnetism has been linked to strain, although the exact origin is still under debate (as explained in **chapter 5**, where a more detailed description will be presented regarding the magnetic properties of LaCoO_3). Interfacial charge transfer will change the valence of cobalt with minimal structural changes and can therefore be used as a probe, to gain insight in the different spin states.

Apart from a fundamental understanding and insight in the magnetic properties and spin states of LaCoO_3 , other properties are also of interest. For instance in research on catalysts, in which LaCoO_3 is a material of interest [10]–[12]. Moreover, catalytic activity has been linked to electron occupation (e.g. in aiding the Oxygen Evolution Reaction [10], [23]). Therefore, it is interesting to investigate if the catalytic properties can be changed when interfacial charge transfer is employed to alter the cobalt valence (see **chapter 6**).

2.2 Polar catastrophe model

In LaTiO_3 and LaCoO_3 , lanthanum is trivalent with a positive charge and oxygen is divalent with a negative charge, resulting in a 3+ valence for both transition metal ions to ensure charge neutrality, as depicted in **figure 2.5a**. When evaluating the individual layers that make up the pseudo-cubic unit cell in the (100)-direction; these materials consist of alternating layers of LaO and TiO_2 or CoO_2 for LaTiO_3 and LaCoO_3 respectively. The $\text{La}^{3+}\text{O}^{2-}$ layers have a net charge of 1+, whereas the $\text{Ti}^{3+}\text{O}_2^{2-}$ or $\text{Co}^{3+}\text{O}_2^{2-}$ layers have a charge of 1-, which makes LaTiO_3 and LaCoO_3 polar, see **figure 2.5a**. Whenever these polar materials are grown on a non-polar substrate, such as SrTiO_3 (consisting of $\text{Sr}^{2+}\text{O}^{2-}$ and $\text{Ti}^{4+}\text{O}_2^{2-}$), this leads to a potential buildup [24]. Since an unlimited increase in potential is impossible, this needs to be compensated at a certain thickness. To resolve this potential buildup, charge (or other charged defects) need to be transferred, as illustrated in **figure 2.5b** and **2.5c**. By effectively introducing (or removing) 0.5 electron per unit cell close to the interface, the electric field is shifted and the potential buildup resolved [24].

The fabrication of polar $\text{LaCoO}_3 - \text{LaTiO}_3$ heterostructures on non-polar SrTiO_3 can lead to a polar catastrophe and associated charge transfer. This polarity-induced charge transfer makes it hard to disentangle the charge transfer resulting from band alignment. Therefore, polar catastrophe effect needs to be avoided in this research.

In order to prevent polar catastrophe effects, a buffer layer of a polar material needs to be grown on SrTiO_3 before depositing the functional layers of LaCoO_3 and LaTiO_3 . By growing the buffer layer thicker than the critical thickness to resolve the polar built-up [24], [25], the polar catastrophe is compensated and would therefore no longer influence the iso-polar LCO and LTO heterostructure. Additionally, a polar capping layer will need to be introduced to prevent the removal of electrons from the surface layer, as indicated by **figure 2.5c**.

LaAlO_3 buffer layer

Since LTO and LCO both have lanthanum on the A-site, this is also preferred for the buffer layer (i.e. to eliminate A-site intermixing). Moreover, the buffer layer material needs to be inactive in the charge transfer process and well-matched to the structure of substrate, LCO and LTO. Therefore, the choice was made to use LaAlO_3 .

The buffer layer thickness was determined as 30 unit cells ($\sim 11.4\text{nm}$) for spectroscopic reasons. This thickness allows determination of the titanium valence of LaTiO_3 without interference from the titanium signal of SrTiO_3 , by exploiting the surface sensitivity of X-ray Photoelectron Spectroscopy and X-ray Absorption Spectroscopy (i.e. utilizing Total Electron Yield mode), see **chapter 4**. Since the probing depth of these techniques is limited to about 10nm [26], the titanium signal of the substrate will not contribute to the total titanium signal.

Introducing a buffer layer for LaAlO_3 substrates is not required since the substrate is polar. Nevertheless, a LaAlO_3 buffer layer with a thickness of 2-4 unit cells was used for consistency. Moreover, this buffer layer can be used to evaluate the growth-rate and performance of the deposition system, before fabricating other functional layers.

Related to a polarity difference, also a difference in transition metal d-occupancy or bond hybridization-effects can act as a driving force for a charge transfer [27]–[29]. This can occur at interfaces between TMOs with the same transition metal at the B-site, but with different valence. In these samples, this can potentially lead to a charge transfer at the interface between SrTiO_3 and LaTiO_3 [30]. However, this is also avoided by use of the LaAlO_3 buffer.

Figure 2.5 Figure adapted from [24] **a**) Although each unit cell is charge neutral, each individual plane can have a net charge. For SrTiO_3 , both TiO_2 and SrO planes are charge-neutral, but for LaXO_3 (with $\text{X} = \text{Co}, \text{Ti}, \dots$) alternating +1 and -1 is found for LaO and XO_2 planes respectively, categorizing the material as polar **b**) The alternating charge leads to an electric field and a potential buildup that rises as the thickness of the polar material increases **c**) The polar catastrophe can be resolved when electrons are transferred to the interface, either by introducing 0.5 electron/u.c. into TiO_2 or LaO . These charges are expected to originate from the surface of the LaXO_3 or by introducing charged defects such as oxygen vacancies [24].

LaNiO₃ capping layer

In an effort to reduce charging effects in photoemission measurements, the conducting LaNiO₃ (LNO) was selected as a capping layer for most of the samples (again preferring lanthanum on A-site). The limited probing depth in spectroscopy, results in a capping layer thickness that was kept around 4-5 unit cells thick. Note that it was found that charge can also be transferred from LaTiO₃ to LaNiO₃ [31]–[33], resulting in a more complex data interpretation, making this choice of material less fortunate in hindsight, as described in more detail in **chapter 4**.

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Chapter 3

Fabrication of LaCoO_3 – LaTiO_3 heterostructures

Abstract

This chapter describes optimization of the Pulsed Laser Deposition process to fabricate combinations of ultra-thin LaCoO_3 and LaTiO_3 . Normally, a low O_2 background pressure is key in avoiding $\text{La}_2\text{Ti}_2\text{O}_7$ phase formation in LaTiO_3 . Since these pressures likely result in oxygen vacancy formation in LaCoO_3 , a strategy was adopted to grow both materials in an intermediate pressure of $2\text{e-}3$ mbar. Assisted by the use of a LaAlO_3 buffer layer and by keeping the thickness of LaTiO_3 fixed at 4 unit cells. With fixed pressure, the other deposition parameters were optimized to yield a low surface roughness and the correct perovskite structure. The samples were monitored during growth by Reflection High-Energy Electron Diffraction and characterized ex-situ using Atomic Force Microscopy, Scanning Transmission Electron Microscopy and X-Ray Diffraction.

3.1 Introduction

Artificially combining several materials on a computer can be relatively straightforward, whereas experimentally fabricating the same samples can be challenging. Therefore, the question addressed in this chapter is whether suitable samples can be fabricated to investigate the prediction of charge transfer at the LaCoO_3 (LCO) and LaTiO_3 (LTO) interface (as introduced in **chapter 2**).

Moreover, since the charge transfer can only affect a region close to the interface, ultra-thin layers have to be used to increase the effect of the interfaces on the overall properties. This requires the fabrication of LaCoO_3 and LaTiO_3 combinations with a thickness of a few unit cells (u.c.) to help determine the charge transfer. Therefore, a technique is required that is not only capable of fabricating combinations of oxides, but to do this with unit cell accuracy. Pulsed Laser Deposition (PLD) is a technique that is frequently used to fabricate combinations of oxides and combined with Reflection High-Energy Electron

Diffraction (RHEED)[1]–[3], this has the capability to deposit ultra-thin films with unit cell precision.

The first articles where PLD is employed to grow complex oxides comes from 1987, where cuprate high T_c superconducting YBCO films were grown [4]. After this initial report, PLD has seen a strong rise in interest over the years, since one of the main benefits of PLD is the possibility of stoichiometric transfer from target to substrate [2]. This makes the technique versatile, since targets can be easily changed to grow a multitude of different (combinations of) materials. In addition, PLD offers precise control of deposition parameters such as background pressure, laser energy, temperature, spot size, repetition rate, etc. [2]. Moreover, when PLD is combined with RHEED, the growth-rate can be monitored using intensity oscillations and the RHEED pattern can be used to assess the structural quality and surface roughness (step-density) [1]–[3]. Therefore, RHEED-assisted PLD is regarded as a suitable fabrication technique to create the ultra-thin LaCoO_3 and LaTiO_3 combinations in this thesis.

Even though most fundamental processes involved in PLD are relatively well understood, finding the optimal growth conditions within the plethora of deposition parameters remains challenging [2], especially when combining multiple materials, since this often involves compromising on deposition conditions. For instance; materials with volatile elements limit the maximum temperature that can be used, whereas materials that are sensitive to oxidation determine the maximum/minimum oxygen background pressure. Moreover, differences in chemistry can also play an important role when combining materials, since reactive species arrive at a hot surface during deposition. All these factors play a role and can influence (and even prohibit) the fabrication of material combinations.

Goal

Use Pulsed Laser Deposition to fabricate high quality samples that combine ultra-thin layers of LaCoO_3 and LaTiO_3 .

3.2 Methods

Substrate selection

The charge transfer model is based on the difference between oxygen 2p-bands and transition metal 3d-bands, and relies on the continuous oxygen lattice across the interface [5] (as discussed in **section 2.1**). Therefore, in theory, the charge transfer should be independent of crystal orientation, as long as the oxygen

backbone is continuous across the interface, making the orientation of the substrate arbitrary. However, since the band offsets in **figure 2.3** were calculated using the (001)-direction [5], also (001)-orientated substrates have been selected.

In the DFT calculations, epitaxial strain was not taken into consideration. In practice however, there is a mismatch between the in-plane lattice constants of the substrate, the LCO and the LTO. Moreover, differences in symmetry between substrate and thin films can also play a role, since octahedral rotations from the substrate can be transmitted to thin films and vice versa [6]–[8]. To evaluate these effects, both SrTiO_3 and LaAlO_3 have been selected as suitable substrates.

At room temperature SrTiO_3 has a cubic structure with a lattice constant of 3.905 Å [9]–[11], whereas LaAlO_3 has a rhombohedral structure with a pseudocubic lattice constant around 3.79 Å [9], [12], [13]. In comparison, LaTiO_3 has an orthorhombic crystal structure with a pseudocubic lattice constant around 3.98 Å [14] and LaCoO_3 has a rhombohedral structure with a pseudocubic lattice constant around 3.80 Å [15]–[18]. This results in LCO being tensile strained on STO and slightly compressively strained on LAO. For the LTO, both substrates exert a compressive strain.

Typical PLD conditions for the growth of epitaxial oxides rely on elevated temperatures (i.e. around 750°C), to increase surface diffusion and assist crystallization [2]. Therefore, it is insightful to also evaluate the lattice constants around deposition temperature when evaluating the strain (i.e. these are the actual values that are combined during growth). **Figure 3.1** depicts the relevant bulk pseudocubic lattice constants of over a large temperature range, as obtained from literature [10]–[12], [14], [16], [18]. This shows that the mismatch between STO, LAO and LTO remains relatively constant over the temperature range, whereas LCO shows a larger variation, resulting in epitaxial strain that varies with temperature. At room temperature, the LCO and LAO are closely matched, but at deposition conditions (i.e. around 750°C), the mismatch with the LAO substrate is almost equal to the STO substrate, although opposite in sign. Since the mismatch reduces with temperature, no issues are expected upon cooling down after deposition on LAO substrates. However, for depositions on STO, the cooling can be problematic since the mismatch increases when cooling down. It has been reported that this difference in thermal expansion can lead to crack formation in thicker layers (exceeding roughly 100 nm) when the forces become too large [19].

Figure 3.1 The lattice constants of bulk LaAlO_3 [12], LaCoO_3 [16], [18], LaTiO_3 [14] and SrTiO_3 [10], [11] at various temperatures, as obtained from literature. The mismatch between LTO, STO and LAO remains almost constant with temperature, whereas the mismatch changes with temperature for LCO. At room temperature, LAO and LCO are well matched, but at deposition temperatures (i.e. around 1000K) the mismatch is roughly equal to the STO-LCO mismatch, although opposite in sign.

One of the advantages of using SrTiO_3 substrates is that these are available in conducting form when doped with niobium [20], [21]. This helps to reduce charging issues in spectroscopy measurements (see **chapter 4**), whereas LAO is a wide bandgap insulator [12]. Moreover, chemical etching procedures are available for SrTiO_3 to achieve atomically flat, well-defined TiO_2 -terminated surfaces [22], [23].

Surface termination of LaAlO_3 substrates is less straightforward and is reportedly dictated by thermal stability: the surface is AlO_2 terminated from room temperature to $\sim 150^\circ\text{C}$, mixed AlO_2 and LaO between 150°C and 250°C and LaO terminated at higher temperatures, as found by annealing in Ultra-High Vacuum (UHV) conditions [24]. On the other hand, substrates annealed in oxygen and heated in deposition conditions, are predominantly AlO_2 terminated [25], [26]. Note the room temperature measurements will therefore not give insight in the surface termination at deposition conditions. Although, termination can be enforced by deposition of 1 monolayer of AlO_2 or LaO [26], this extra step can

introduce additional roughness or errors. Since accurate determination of the surface termination of LAO at deposition conditions falls beyond the scope of this research, the choice was made to use oxygen annealed substrates, assuming a predominantly AlO_2 terminated surface in deposition conditions.

Pulsed Laser Deposition parameters

Oxygen pressure

Fabricating combinations of LTO and LCO is challenging, since LaTiO_3 is susceptible to incorporation of additional oxygen into a $\text{La}_2\text{Ti}_2\text{O}_7$ phase [27], [28]. The $\text{La}_2\text{Ti}_2\text{O}_7$ phase has additional oxygen on diagonal planes, which makes it distinguishable by scanning transmission electron microscopy (STEM) measurements, see **figure 3.2a**. Formation of this phase occurs since this results in a preferred Ti^{4+} (d^0) valence. Therefore, the LaTiO_3 phase with Ti^{3+} (d^1) can normally only be stabilized by growing in a low oxygen environment (typically well below 10^{-4} mbar, see **figure 3.2b**) and eliminating other sources of oxygen (such as the substrate) [27], [28]. On the other hand, a higher oxygen background pressure (typically around 0.1 mbar) is desirable for the growth of LCO [29]. This avoids oxygen vacancy formation or, in the more extreme case, formation of the Brownmillerite $\text{LaCoO}_{2.5}$ phase [30], [31], see **figure 3.3**.

Figure 3.2 a) In STEM measurements, the $\text{La}_2\text{Ti}_2\text{O}_7$ phase can be distinguished from LaTiO_3 by darker diagonal lines, caused by planes of additional oxygen. **b)** This phase diagram indicated that phase-pure LaTiO_3 can be stabilized in pressures well below $1\text{e-}4$ mbar. Images adapted from [27].

Figure 3.3 This figure illustrates the difference between the perovskite LaCoO_3 and the Brownmillerite $\text{LaCoO}_{2.5}$ phase, as imaged using STEM. Image taken from [30].

The difference in sensitivity to oxygen results in a dilemma: growing LCO in higher pressure on LTO likely over-oxidizes the underlying LTO, resulting in uncontrolled LTO quality. Similarly, growing LTO in low pressure on top of LCO, can create oxygen vacancies in the underlying LCO. Since the goal is to investigate the charge transfer $\text{Ti}^{3+} + \text{Co}^{3+} \rightarrow \text{Ti}^{4+} + \text{Co}^{2+}$ resulting from interfacial band-alignment, it is important to rule out valence changes related to variation in oxygen content. Therefore, the decision was made to fabricate LCO and LTO in the same intermediate background pressure (i.e. $2\text{e-}3$ mbar).

Although this pressure is non-ideal for the more oxygen-sensitive LTO, several strategies were combined to avoid $\text{La}_2\text{Ti}_2\text{O}_7$ formation: i) by keeping the thickness of LTO fixed at 4 unit cells, the strain imposed by the substrate makes it possible to stabilize the correct LaTiO_3 structure at higher oxygen pressures (as described by A. Ohtomo et al. [27]), ii) a 30 unit cell thick LAO buffer layer is grown on STO to reduce oxygen diffusion from the substrate to LTO [28], and iii) charge transfer will help stabilize the correct LTO phase, by providing titanium an alternative route to obtain the Ti^{4+} valence.

Moreover, other variations in pressure can also change the oxygen content of LTO and LCO, resulting from continuous oxygen-exchange with the environment. In an effort to not influence the sample quality by pressure changes during growth, the decision was made that the entire deposition process takes place at this intermediate pressure (including heating/cooling and deposition of other layers). For consistency, this pressure was also used in reference samples without LTO. Since the pressure has been fixed, the remaining goal is to find the optimal settings for the other PLD parameters.

Temperature

The deposition temperature is an important parameter in optimizing the growth, since this influences surface diffusion and promotes crystallization [2]. The general effect of temperature can be assessed by evaluating the surface morphology; it typically costs more energy to induce a kink compared to a straight step edge, since atoms can have more bonds in a straight step edge, as illustrated in **figure 3.4**. Whenever rough step-edges appear after deposition, this can be an indication that diffusion on the surface is insufficient for the arriving species to find the most favorable position. This can sometimes be resolved by increasing the substrate temperature.

Island formation can also occur, which can be explained by the concept of the Ehrlich-Schwoebel barrier [32]–[35]: an atom diffusing on the surface feels a diffusion barrier since it needs to temporarily break bonds with neighboring species in order to move. However, when diffusing up or down a step, the effective bonds are reduced even further, resulting in an enlarged barrier for diffusion up and down a step, as depicted in **figure 3.4b**. Increasing the growth temperature can provide the atoms more energy to overcome this barrier, resulting in reduced island growth.

Figure 3.4 a) Comparing a rough step edge (top) with a straight edge (bottom): A straight step-edge reduces the number of open bonds, as indicated by the blue arrows, making it energetically more favorable. **b)** arriving species want to find positions that are energetically favorable, which typically means a position where the most bonds can be formed. This is the case at step-edges or islands (yellow), however, it is not always possible for the ad-atoms to find such a position when the diffusion is limited (green). Increasing the temperature can increase the diffusion and ability to overcome the Ehrlich-Schwoebel barrier (orange), but too high temperature can result in desorption (red).

Since high deposition temperatures can ensure sufficient surface diffusion and crystallization, a temperature of around 750°C has been selected as initial temperature for optimization. These temperatures are known to yield good results for the deposition of LaAlO₃ on SrTiO₃ [36].

Frequency

The repetition rate of the laser is another variable that can be altered to improve growth; increasing the frequency can be beneficial, since it increases the density of species at the surface and therefore the possibility for 2 species to meet and form a nucleation site [37]. Increasing the number of nucleation sites would effectively decrease the diffusion length, thereby improving growth. As a starting point for optimization, the laser frequency was set to a repetition rate of 1 Hz.

Fluence

The influence of the energy density of the laser pulses is related to the ablation of the target: low fluence can result in preferential ablation (i.e. non-stoichiometric), so the energy density should be sufficient to evenly ablate the target [2]. Too high fluence should also be avoided, since this can result in melting and droplet formation. From experience using these targets, a fluence of 1.3 J/cm² was selected for LaAlO₃ deposition and 1.9 J/cm² for deposition of LaTiO₃, LaCoO₃ and LaNiO₃.

Characterization techniques

Experimentally, *in-situ* RHEED (Staib - 30 kV acceleration, KSA 400 software) is used to monitor the growth. Intensity oscillations provide valuable information about the growth dynamics, such as growth-rates, relaxation-times, growth mechanism (layer-by-layer or step-flow growth) and surface roughness (i.e. step density) [1], [2], [37]. Additionally, RHEED patterns can be used to obtain information about the structure and in-plane lattice constants and strain relaxation. Moreover, typical 3D RHEED patterns can indicate when the surface roughness is increased due to island formation.

Further information about the crystal structure was obtained using X-ray Diffraction (XRD) measurements (Bruker, D8 Discover diffractometer, Cu rotating anode generator)¹. However, since this technique cannot be used on ultra-thin samples, these measurements were only performed on the LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c. sample. Atomic Force Microscopy (AFM) measurements (Bruker,

¹ Measurements performed by Y.A. Birkhölzer, MESA+Institute for Nanotechnology, University of Twente, Enschede, Netherlands

Icon) were performed to obtain information about the surface morphology. These measurements were conducted using non-contact TappingMode™.

On a few selected samples, Scanning Transmission Electron Microscopy (STEM) measurements were performed to investigate the sample quality¹. These measurements were performed at room temperature, using High Angle Annular Dark Field (HAADF) imaging on a FEI Titan 80-300 microscope operated at 120kV. 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. The atomic resolution of this technique enables the visualization of columns of atoms and can therefore provide information about the structure of the ultra-thin layers. Additionally, defects in the structure can be observed and the quality of the interfaces and possible intermixing can be assessed.

Optimization

The thickness of LTO, LAO and LNO are set to 4 unit cells, 30 unit cells and 5 unit cells respectively, oxygen pressure during deposition has been fixed to 2×10^{-3} mbar for all materials and the laser fluence has been chosen from experience. However, the other deposition parameters need to be optimized. Normally, optimization is performed to obtain the best structure or properties (highest conduction, best magnetic properties, etc.). However, in optimizing the deposition of these ultra-thin layers, such criteria cannot be used. Instead, the focus lies on obtaining low surface roughness (i.e. sharp interfaces).

3.3 Experimental details

Substrate preparation

The (001)-orientated (0.5w% Nb-doped) SrTiO₃ substrates (CrysTec GmbH) with a miscut-angle of 0.1° - 0.2° (i.e. terrace width around 150nm) were chemically treated to obtain atomically smooth surfaces with TiO₂ termination (as described by [22], [23]). This procedure starts by ultrasonically cleaning the substrates for 5 minutes in acetone and ethanol. Subsequently, the substrates were immersed in demi-water and sonicated for ~30 minutes to hydrolyze strontium-oxide on the surface into strontium-hydroxide, which was then etched away by a short ~30 second dip in an ultrasonically agitated solution of Buffered Hydrofluoric acid

¹ Measurements performed by N. Gauquelin, Electron Microscopy for Materials Science, University of Antwerp, Antwerpen, Belgium.

(Technic BOE 7-1, NH_4F 87.5% – HF 12.5%). After thorough rinsing with demineralized water, the substrates were dipped in ethanol and blown dry by nitrogen-gun.

After chemical treatment, the SrTiO_3 substrates were annealed for 1.5 hours at 950°C under oxygen flow of 150ml/h to end up with well-defined step-edges, as shown by AFM in **figure 3.5a**. For the Nb-doped STO substrates, the annealing sometimes resulted in significant step-bunching as depicted in **figure 3.5b**. Therefore the annealing procedure for these substrates was slightly altered by reducing the temperature to 930°C , which proved successful in preventing the step-bunching.

Similarly, the LaAlO_3 substrates (CrysTec GmbH, 0.1° - 0.2° miscut-angle), were ultrasonically cleaned for 5 minutes in both acetone and ethanol, followed by an annealing step. Annealing took place for 1 hour under oxygen flow of 150ml/h at a temperature of 950°C [38]. This procedure yields surfaces with well-defined terraces, see **figure 3.5c**. Although, as described in **section 3.2**, the surface termination is not well defined.

Target preparation

The samples were grown using stoichiometric targets that were commercially obtained. For LaAlO_3 , the target consisted of a single crystal, whereas for LaCoO_3 , LaNiO_3 and LaTiO_3 high-density sintered targets were used.

To prepare the targets for deposition, the target were sanded to remove any visible marks from previous depositions to start with a clean surface. After course grinding, the targets are lightly polished using finer grain sand paper and any remaining loose particles are removed using a nitrogen-gun.

Figure 3.5 Atomic Force Microscopy images of SrTiO_3 substrates: **a)** after treatment the surface shown smooth step-edges and steps of $\sim 4\text{\AA}$ height, indicative of single terminated SrTiO_3 , **b)** Nb-doped SrTiO_3 after annealing at 950°C , showing severe step-bunching, **c)** the surface of a LaAlO_3 substrate after cleaning and annealing.

General procedure

A KrF excimer laser (248 nm wavelength, Coherent LPXpro) is used with a mask inserted in the beam-path, selecting only the homogeneous center part of the laser pulses. By creating an image of the mask onto the surface of the target, the spot size is defined by the size of the mask, combined with the magnification, as dictated by the optical path. In order to set the correct laser fluence, the energy of the laser is measured before the entrance window of the PLD chamber (Twente Solid State Technology) and adjusted to the correct value by means of an attenuator.

Background pressure of the system is typically below 5×10^{-8} mbar before starting the deposition. After aligning sample and electron gun to obtain a clear RHEED diffraction pattern, oxygen is introduced into the system up to the desired deposition pressure of 2×10^{-3} mbar. At this pressure, the shutter will be closed to protect the substrate and the targets are pre-ablated to remove any remaining contamination from the surface. After pre-ablation the shutter is removed and the laser heating (Coherent) is started with a typical ramp-rate of 50°C per minute. When the desired temperature is reached, typically the RHEED needs to be slightly adjusted due to thermal expansion. At this point the deposition can start by growing the LaAlO_3 buffer layer. Since this buffer layer shows pronounced intensity oscillations in RHEED, the performance of the system can be evaluated. When the growth rate (and quality) of the buffer layer is not as expected, small alterations can be made before continuing the deposition of the more crucial LaCoO_3 and LaTiO_3 layers. Finally, after deposition, the samples were cooled down to room temperature at 25°C per minute in deposition pressure.

3.4 Results

This section first describes the growth and optimization of each individual material, based on RHEED intensity oscillations during growth and *ex-situ* AFM measurements. After the deposition conditions were optimized on surface morphology, the crystal structure and strain is evaluated on selected samples using STEM, RHEED patterns and XRD measurements.

Growth of LaAlO_3 buffer layers

Deposition of the LaAlO_3 buffer layer was performed at a deposition temperature of 750°C and with a background pressure of 2×10^{-3} mbar. The laser frequency was set to 1Hz with an energy density of $1.3\text{J}/\text{cm}^2$. Growth was monitored by recording RHEED intensity oscillations and diffraction patterns, as shown in **figure**

3.6. For the first few LAO layers the RHEED intensity drops, after which it stabilizes and continues to oscillates for every unit cell, indicating layer-by-layer growth. After 30 unit cells (or 3 unit cells for LAO substrates) the deposition was stopped. AFM measurements showed the expected step-and-terrace structure (not shown), indicating atomically smooth surface and a good starting point for the deposition of LCO and LTO.

Figure 3.6 RHEED intensity oscillations during the deposition of LaAlO_3 , LaCoO_3 , LaTiO_3 and LaNiO_3 after optimizing the deposition conditions. For the 30 u.c. LAO layer, the intensity first drops before stabilizing and continuing to oscillate indicating layer-by-layer growth. The layer-by-layer growth and oscillations were also observed for LNO and LTO. However, for LCO, the oscillations were more irregular and less pronounced, probably related to the increased temperature and frequency resulting in a combination of layer-by-layer and step-flow growth.

Figure 3.7 AFM measurements on 4 u.c. films of LaTiO_3 grown at 750°C using 1Hz. The surface displays the step-and-terrace structure of the underlying substrates, indicating a desired low surface roughness **a)** sample on SrTiO_3 substrate **b)** sample on LaAlO_3 substrate.

Growth of LaTiO_3 and LaNiO_3

The depositions of LaTiO_3 were performed at the same initial deposition conditions as selected for LAO: temperature of 750°C , frequency of 1Hz, combined with a fixed pressure of $2\text{e-}3$ mbar (Note that the LTO thickness will be limited to 4 unit cells, as described in **section 3.2.**). **Figure 3.6** shows the clear RHEED intensity oscillations obtained for the growth of LTO, indicating layer-by-layer growth. These oscillations were used to ensure the correct layer thickness of 4 unit cells LaTiO_3 .

AFM measurements are depicted in **figure 3.7** and show the surface of 4 unit cell thick LTO deposited on SrTiO_3 and LaAlO_3 substrates. The surface morphology on both substrates shows the step-and-terrace structure of the substrate, indicating the desired smooth surface.

The purpose of LaNiO_3 is to serve as a protective capping layer, which makes the quality of the LNO less important. Therefore, as the growth optimization is not crucial, the same deposition parameters as LTO and LAO were selected for consistency: temperature of 750°C , repetition rate of 1Hz. The thickness was controlled using the RHEED intensity oscillations, as show in **figure 3.6**.

Growth optimization of LaCoO_3

Initially, samples of LaCoO_3 were deposited using higher pressures and temperatures of $650^\circ\text{C} - 750^\circ\text{C}$, as obtained from literature [8], [29], [39], [40], to gain insight in the deposition conditions. AFM measurements on these films displayed rough step edges, indicating that surface diffusion might be insufficient, see **figure 3.8**. Additionally, the layer has holes and islands on the

terraces indicating that the diffusion up or down a step-edge is limited, as explained in **section 3.2**. These measurements indicate that both the surface diffusion, and diffusion up/down step-edges needs to be increased to improve morphology. Note that reducing the pressure to $2\text{e-}3$ mbar can already have a positive effect, since this increases the kinetic energy of the arriving species.

Increasing the deposition temperature can help the diffusing species to overcome the Ehrlich-Schwoebel barrier, since this increases the energy of species diffusing on the surface [32]–[35]. Moreover, the diffusion can be affected by changing the repetition rate of the laser, since an increase in frequency can increase the density of nucleation sites thereby effectively reducing the distance to a nucleation site.

Figure 3.9a shows the surface morphology for a sample deposited in the intermediate oxygen pressure of $2\text{e-}3$ mbar, using increased frequency of 2Hz and a temperature of 750°C . The surface quality is improved drastically, compared to the previous samples. However, the formation of holes and islands still persist, indicating that the deposition temperature must be further increased. An increase from 750°C to 800°C hardly changes the surface (not shown), however increasing the temperature to 850°C yields the desired step-and-terrace structure indicative of a smooth surface, see **figure 3.9b**. Therefore, the optimal deposition conditions for ultra-thin LaCoO_3 at $2\text{e-}3$ mbar were determined at 2Hz and 850°C .

Figure 3.8 AFM measurements of the surface of LCO at non-optimized conditions grown in $2\text{e-}1$ mbar. Both surfaces show rough step edges and holes/islands, which could indicate a lack of surface diffusion. **a)** 10 unit cells of LCO grown on LAO using 750°C and 1Hz **b)** 10 unit cells of LCO grown on STO at 650°C and using a 1Hz repetition rate.

Figure 3.9 AFM images of 10 u.c. LaCoO_3 grown on SrTiO_3 substrates at different deposition temperatures and laser frequencies: **a)** 10 u.c. LaCoO_3 grown at 750°C using 2Hz: Islands have formed although the layer is not fully closed and step-edges are fairly rough **b)** 10 u.c. LaCoO_3 grown at 850°C using 2Hz: The desired surface with step and terrace structure and relatively smooth step edges can be observed **c)** 10 u.c. LaCoO_3 grown at 850°C with 1Hz: Upon decreasing the laser frequency to 1Hz, the step edges display increased roughness, although severe island formation is still suppressed by the increased temperature.

Another sample was produced at 850°C , but with the laser frequency reduced to 1Hz, to verify the importance of the increased repetition rate. **Figure 3.9c** shows the AFM measurement of this sample where the morphology behaves as expected: i) the holes and islands are not present, since thermal energy is still high enough to overcome the Ehrlich-Schwoebel barrier, and ii) the roughness of the step edges has returned, since the effective surface diffusion is reduced.

The RHEED intensity oscillations for the optimized LCO conditions are displayed in **figure 3.6**. These oscillations are for the growth of both 4 u.c. and 36 u.c. of LCO on a stack with LTO and 30 u.c. of LAO on a STO substrate. The fact that oscillations can still be observed after growth of the LTO and LAO indicates a low surface roughness. However, the RHEED oscillations for LCO are not well behaved (especially the initial oscillations) and indicate that the growth-mode is probably a combination of layer-by-layer growth and step-flow growth.

Scanning Transmission Electron Microscopy

Figure 3.10a displays the HAADF-STEM measurements as obtained for a sample with LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c. grown on Nb-doped SrTiO_3 with a 30 u.c. LAO buffer layer and capped with 5 u.c. LNO. The same stack, but with increased LCO thickness of 36 u.c. (for reasons explained in **chapter 4**) is displayed in **figure 3.10b**. In both images, lanthanum columns are clearly visible, since this has the largest atomic number and therefore appear brighter (approximately Z^2 proportional [41]). All materials have lanthanum on A-site, therefore only small variations in contrast can be observed, originating from the different transition metals. Due to the narrow field of view, the SrTiO_3 substrate is not visible in both images.

The entire stack appears to be fully strained and displays the expected perovskite structure in both samples. No characteristic darker diagonal lines in LaTiO_3 were observed, indicating absence of $\text{La}_2\text{Ti}_2\text{O}_7$ phases [27] (see **figure 3.2**). Similarly, no dark lines in LCO layers are observed and no Brownmillerite $\text{LaCoO}_{2.5}$ phase is present [30], [31] (see **figure 3.3**).

In-plane strain evaluation is depicted in **figure 3.10c**, where the colors indicate deviations with respect to the underlying LAO (calculated in strain values). It can be seen that the stack remains fully strained to LAO, with the LAO strained to the STO substrate (not shown).

RHEED patterns

Information regarding the structure of the layers can also be obtained using RHEED patterns, which provide information about the structure close to the surface. **Figure 3.11**, shows the RHEED patterns obtained after each layer in the deposition of the LNO 5 u.c. | LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c. | LAO 30 u.c. sample grown on a STO substrate. As shown by the dashed lines, the diffracted spots remain on the same distance throughout the stack, indicating that the in-plane lattice parameter remains constant (i.e. consistent with STEM analysis). **Figure 3.11a** shows the pattern corresponding to the atomically smooth TiO_2 -terminated $\text{STO}(001)$ surface, showing Kikuchi lines and sharp diffraction spots [1]. In the subsequent images **3.11b-f**, the diffraction pattern is hardly changed, indicating low surface roughness and no pronounced 3D-growth. Note that the RHEED intensity was adjusted after each deposited layer, whereas the geometry remained the same (although the diffraction conditions can slightly vary between the materials).

Figure 3.10 HAADF-STEM measurements on **a)** LNO 5 u.c. | LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c. | LAO 30 u.c. sample grown on a STO **b)** LNO 5 u.c. | LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c. | LAO 30 u.c. sample on STO substrate. The interfaces are indicated using dotted lines as guide to the eye. Both samples show the expected perovskite structure without pronounced defects **c)** in-plane strain mapping on the same image as in **b)**, where the colors indicate the strain with respect to the LAO that is strained to STO. It can be seen that the stack remains fully strained at 36 u.c. LCO thickness. Measurements and strain analysis performed by N. Gauquelin, Electron Microscopy for Materials Science, University of Antwerp, Antwerpen, Belgium.

Figure 3.11a-f Images of the phosphor-screen used to visualize electron intensity in RHEED measurements. These patterns were recorded at various stages in the subsequent deposition of 30 u.c. LaAlO_3 buffer | 4 u.c. LaTiO_3 | 36 u.c. LaCoO_3 | 4 u.c. LaTiO_3 | 5 u.c. LaNiO_3 capping layer on a SrTiO_3 substrate. In each picture, part of the direct beam is visible on the left (indicated by 1), the specular spot (indicated by 2) and the diffracted spots (indicated by 3). Kikuchi lines are indicated by the arrows and can be distinguished in most pictures. The dashed lines are a guide to the eye to show a constant in-plane lattice constant. **a)** Bare SrTiO_3 substrate at 750°C **b)** After 30 u.c. of LaAlO_3 **c)** After 4 u.c. LaTiO_3 **d)** After 36 u.c. LaCoO_3 **e)** After 4 u.c. LaTiO_3 **f)** After 5 u.c. LaNiO_3 capping layer.

X-Ray Diffraction measurements

As depicted in **figure 3.12**, XRD measurements have been performed to gain insight in the crystal structure of the LNO 5 u.c. | LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c. | LAO 30 u.c. sample grown on STO. Due to the different layers, the data interpretation is not straightforward, therefore the measurement in **figure 3.12a** is combined with a model obtained using *InteractiveXRDfit* [42] (offset for clarity). This calculation is not a perfect match, but nevertheless serves as reference to help interpret the data. To obtain this model, the thickness and out-

of-plane lattice constants were used as indicated in **table 3.1**. The difference between these thicknesses and the thickness extracted by STEM can be explained by noting that i) the calculation assumes a perfect sample without surface roughness, which is different in reality, and ii) STEM measurements give very local information, whereas the XRD measurement gives an average.

Figure 3.12b and **3.12c** display reciprocal space maps (RSM) obtained on the same sample to gain additional insight in the strain. The measurements have been performed around the STO (103) and (113) substrate peaks, indicated in the figure. It can be clearly seen that all the peaks have the same Qx value, indicating that the layers are fully strained to the substrate.

Table 3.1 Values used to model the XRD measurement in **figure 3.12a**. The lattice constants represent the out-of-plane lattice constants, since the stack is fully strained in-plane to the STO substrate.

	LaAlO ₃	LaTiO ₃	LaCoO ₃	LaTiO ₃	LaNiO ₃
Thickness	33 u.c.	4 u.c.	35 u.c.	3 u.c.	5 u.c.
Lattice constant	3.733Å	4.084Å	3.811Å	4.09Å	3.77Å

Figure 3.12 **a)** XRD measurement around the (002) peak of the SrTiO_3 substrate of the LNO 5 u.c. | LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c. | LAO 30 u.c. sample. Data interpretation is not straightforward due to the different layers, therefore the data is combined with a model calculation using InteractiveXRDfit [42] (offset for clarity) **b)** RSM around the (103) and (113) substrate peaks of the same sample, indicating the same Q_x value for the substrate and all layers, consistent with being fully strained. XRD and RSM measurements performed by Y.A. Birkhölzer, MESA+Institute for Nanotechnology, University of Twente, Enschede, Netherlands.

3.5 Discussion

Since the AFM measurements of the individual optimized layers indicate a smooth surface of LTO and LCO, this gives reason to believe that this will result in smooth interfaces between them. STEM measurements show a continuous perovskite structure at the interface without obvious defects, ruling out A-site to B-site intermixing. Although these STEM measurements cannot rule out B-site intermixing, STEM-EELS measurements (provided in **Chapter 4**) show no clear signs of Co-Ti intermixing.

Although the deposition conditions for these ultra-thin layers were optimized and yielded flat surfaces, this does not mean that these conditions are optimal for thicker layers. It is important to realize that these ultra-thin layers strongly influence each other (charge transfer at the interface, oxygen diffusion, strain etc.). Combining these ultra-thin layers severely limits the growth conditions and resulted in a tradeoff in order to find conditions that are reasonable for each individual layer. In this light, a distinction has to be made between ultra-thin layers and thicker layers, since these are fundamentally different. Therefore, the conditions reported in this chapter are specific to these samples.

Effort has been made to grow superlattices with alternating LCO and LTO layers using these conditions. Starting from the STO substrate, 30 u.c. LAO was grown, followed by multiple repetitions of [LTO - LCO], where the LCO and LTO thickness is kept the same. Samples were produced for 2 u.c., 3 u.c., 4 u.c. and 5 u.c. thickness with 15, 10, 8 and 6 repetitions respectively, keeping the total amount of LCO and LTO roughly the same. Unfortunately, the surface roughness strongly increased after a few repetitions. **Figure 3.13**, shows a AFM image of the surface of such a superlattice. In this image, islands can be seen with a height up to 6nm, combined with an increased surface roughness and small holes. Looking at this surface, the shape of the islands seems to indicate screw-like dislocations [43], since the holes appear to be mostly in the center of such a defect. The exact reason for this behavior is unknown, but it is likely to be caused by the large lattice mismatch between LCO (around 3.8Å) and LTO (3.95Å). Unfortunately, these samples are of insufficient quality to further investigate the properties

The epitaxial strain needs to remain throughout the stack to influence the strain in LaCoO_3 by using different substrates. This was confirmed by RHEED pattern analysis, indicating that the in-plane lattice parameters remain constant during deposition. On some selected samples, this could be additionally verified using strain analysis on HAADF-STEM measurements. Moreover, for a double

interface sample with 36 u.c. of LCO, this was verified by in-plane XRD measurements. Combining these results makes it is safe to assume that thinner films also remain fully strained.

3.6 Conclusion

In conclusion, it was possible to use RHEED assisted PLD to fabricate samples with high-enough quality to enable the investigation of charge transfer at the LaCoO_3 - LaTiO_3 interface. Combinations of ultra-thin LaCoO_3 , LaTiO_3 , LaAlO_3 and LaNiO_3 have been fabricated on both LaAlO_3 and SrTiO_3 substrates. By adopting a strategy that uses intermediate background pressure of $2\text{e-}3$ mbar, the other parameters could be optimized as summarized in **table 3.2**.

Moreover, STEM measurements indicate a lack of pronounced structural defects and a perovskite structure without secondary crystal structures that indicate oxygen off-stoichiometry. Additional strain analysis on STEM images revealed that the layers are fully strained to the substrate, which was further confirmed by RHEED and XRD measurements on a 36 u.c. double interface sample. Combining STEM results and the smooth surface found in AFM measurements indicates sharp interfaces between the various layers.

Figure 3.14 AFM measurement of the surface of a [2u.c. LTO – 2 u.c. LCO]x15 superlattice, where increased surface roughness, holes and screw-like islands can be observed.

Table 3.2 The deposition conditions after optimization to obtain low surface roughness in an intermediate oxygen pressure.

	LaCoO ₃	LaTiO ₃	LaNiO ₃	LaAlO ₃
Background pressure O ₂ [mbar]	2e-3	2e-3	2e-3	2e-3
Fluence [J/cm ²]	1.9	1.9	1.9	1.3
Temperature [°C]	850	750	750	750
Frequency [Hz]	2	1	1	1
Spot size [mm ²]	1.76	1.76	1.76	1.76

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Chapter 4

Charge transfer at the LaCoO_3 – LaTiO_3 interface

Abstract

In ultra-thin transition metal oxides, interfacial charge transfer has the possibility to control the properties, making it vital to understand these effects. Moreover, charge transfer provides opportunities to explore new functionalities, by changing the valence state without using chemical doping (and associated lattice disorder) or electric fields. In this research, the charge transfer between LaCoO_3 and LaTiO_3 was investigated experimentally by combining X-ray Absorption Spectroscopy, X-ray Photoelectron Spectroscopy and Electron Energy Loss Spectroscopy measurements on samples with various combinations of ultra-thin LaCoO_3 and LaTiO_3 . For ultra-thin LaCoO_3 sandwiched between LaTiO_3 , the valence shows a significant Co^{2+} contribution, which can be increased up to 100% Co^{2+} upon reducing the LaCoO_3 thickness to 2 unit cells. Moreover, electron microscopy measurements show that the Co^{2+} is localized to a region up to about 3 unit cells from the interface. Systematically varying the thickness of LaCoO_3 further established the interfacial nature. Samples have been made on both compressively- and tensile-strain inducing substrates, but both strain states show similar behavior. Additional experiments with LaAlO_3 spacers proved successful in blocking the charge transfer, providing additional control on cobalt valence.

4.1 Introduction

Perovskite Transition Metal Oxides (TMOs) and interfaces between two TMOs are of great importance and interest, both from fundamental science as well as technological point of view [1]. The interplay between electron correlations and band behavior, combined with a rich repertoire of spin- and orbital-ordering phenomena makes complex oxides an enduring focus of both theoretical and experimental investigation [2]–[4]. Moreover, particular oxide families have become established research fields in their own right, such as the cuprate high-temperature superconductors [5] and the colossal magnetoresistance found in manganites [6].

Possible applications of TMOs include the development of novel electronics, where charge, spin and orbital degrees of freedom provide opportunities to improve upon traditional CMOS-based components [2]. In this industry, there is a strong focus on downscaling components to increase performance. To exploit all benefits of TMOs, these materials need to be compatible with industry dimensions, demanding ultra-thin layers. However, ultra-thin layers behave differently compared to bulk, since strain, octahedral rotations and interface effects affect the properties.

Interface effects and band alignment at interfaces are well understood in silicon-based electronics, but the same concepts cannot be applied to the field of TMOs [1], [7]–[9]. This indicates the importance for a fundamental understanding about interfaces between different TMOs, which can lead to new functionalities and possibly to the ultimate downscaling, in which the interface becomes the device [10].

Interest in interfaces between perovskite oxides increased rapidly after the discovery of “*A high-mobility electron gas at the LaAlO_3 - SrTiO_3 heterointerface*” and the eponymous article published by A. Ohtomo and H.Y. Hwang in 2004 [11]. This article describes how the interface between the two insulating oxides LaAlO_3 (LAO) and SrTiO_3 (STO) can become conducting. After this initial discovery, a plethora of publications followed in order to explain and understand this interface conduction, but even after 15 years, the exact origin is continuing to be under debate. The originally hypothesized (but still debated) model used to

explain the conducting interface is the so-called “polar-catastrophe” model (**as explained in chapter 2**), which explains the transfer of charges to the SrTiO_3 at the interface to cancel the polar buildup [12]. These charges may originate from the LaAlO_3 surface, but also defects as cation off-stoichiometry and oxygen vacancy formation have been held responsible [11], [13]–[19]. Many other conducting interfaces have been discovered since [20], but the LaAlO_3 - SrTiO_3 interface can still be regarded as the model-system for an oxide interface.

These conducting oxide interfaces illustrate that the transfer of charges between TMOs can lead to remarkable effects (whatever the origin). This charge transfer effect has been seen in several material combinations [1], [8], [20]–[22] (see **table 4.1**). However, a theoretical understanding was missing. Recently, Zhicheng Zhong and Phillipp Hansmann [8] studied the band alignment at oxide interfaces by Density Functional Theory (DFT) calculations (**see chapter 2**). Using these calculations, the charge transfer between two TMOs can now be explained and predicted, which is an important next step towards understanding TMO-interfaces and the development of devices.

Table 4.1 Some examples of interfaces between transition metal oxides, where interfacial charge transfer has been observed experimentally. The various types of interfaces range from a basic interface between 2 perovskites, to interfaces between a polar and non-polar perovskite and even interfaces between oxides with different structures.

Interface type	Examples
Basic perovskite	$\text{LaTiO}_3 - \text{LaNiO}_3$ [23], $\text{LaTiO}_3 - \text{LaFeO}_3$ [24], $\text{SrIrO}_3 - \text{SrMnO}_3$ [25], $\text{LaMnO}_3 - \text{LaNiO}_3$ [26]
Polar/non-polar	$\text{LaTiO}_3 - \text{SrTiO}_3$ [27], $\text{LaMnO}_3 - \text{SrMnO}_3$ [28], $\text{LaVO}_3 - \text{SrVO}_3$ [29], $\text{GdTiO}_3 - \text{SrTiO}_3$ [30], $\text{LaCrO}_3 - \text{SrTiO}_3$ [31], $\text{SrTiO}_3 - \text{La}_{(1-x)}\text{Sr}_x\text{MnO}_3$ [32]
Other	$\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3 - \text{YBa}_2\text{Cu}_3\text{O}_7$ [33], $\text{Sr}_2\text{IrO}_4 - \text{LaNiO}_3$ [34]

The ongoing debate about the $\text{LaAlO}_3\text{-SrTiO}_3$ interface can serve as an example to emphasize the complexity of oxide interfaces. Several reasons can be identified: firstly, these interfaces are buried (by definition), which makes them harder to access experimentally. Secondly, samples with sharp interfaces (i.e. low intermixing and interface roughness) and high crystalline quality are required in order to distinguish charge transfer related to interfacial band alignment from other effects that can alter the valence. Especially, since off-stoichiometry is one of the main issues in investigating interfacial charge transfer (in particular oxygen off-stoichiometry). Oxygen vacancies can introduce additional electrons into the system, whereas excess oxygen can accept electrons from the transition metal ions. Similarly, cation off-stoichiometry can also result additional valence changes in the system. These off-stoichiometry effects are difficult to probe with great accuracy. However, in order to draw reliable conclusions, all other possible valence altering effects need to be investigated or minimized by careful design of the experiment. This requires a systematic study with multiple samples and detailed analysis, making the study of interfacial charge transfer difficult. This results in limited experimental work and corresponding literature, motivating our efforts to add to existing knowledge by devising a way to accurately determine interfacial charge transfer between two different TMOs.

In this research, the LaCoO_3 (LCO) – LaTiO_3 (LTO) interface was selected, since the calculations have shown that this specific combination yields the highest potential for charge transfer among the 3d-TMOs [8] (see chapter 2). The expected charge transfer would be: $\text{Ti}^{3+} + \text{Co}^{3+} \rightarrow \text{Ti}^{4+} + \text{Co}^{2+}$ and can prove to be a method of doping LaCoO_3 without disrupting the structure. Moreover, to achieve full control of the valence, a procedure to block the charge transfer is required. In this research, a way to stop the charge transfer was pioneered, by introducing an ultra-thin LaAlO_3 spacer between the LaCoO_3 and LaTiO_3 .

4.2 Methods

Ultra-thin layers are required, such that the influence of the interface is enhanced compared to the bulk, hereby increasing the probability to accurately determine the charge transfer. However, it is not straightforward to controllably fabricate samples with combinations of ultra-thin layers of LaCoO_3 and LaTiO_3 with atomic

precision. In this research, Pulsed Laser Deposition (PLD) combined with Reflection High-Energy Electron Diffraction (RHEED) was used (see **chapter 3**).

4.2.1 Samples

Apart from ultra-thin layers, investigation of charge transfer requires a systematic approach that compares LaTiO_3 and LaCoO_3 reference samples (without interface) to samples with one and multiple interfaces. The samples without active interface serve as reference measurement for the properties of the ultrathin LaCoO_3 and LaTiO_3 films (i.e. these might differ from bulk). In the samples with active interface, the number of interfaces and the thickness of the LaCoO_3 films was systematically varied, to enable quantification. Changing the thickness of the cobaltate and the number of interfaces, provides insight in whether the charge transfer really occurs at the interface: if the $\text{Co}^{2+}/\text{Co}^{3+}$ ratio changes when altering the LaCoO_3 thickness, this indicates an interface effect (assuming the band bending is fully compensated after a certain LaCoO_3 thickness and therefore the amount of Co^{2+} will remain constant upon further increasing the LaCoO_3 thickness, reducing $\text{Co}^{2+}/\text{Co}^{3+}$ ratio). **Figure 4.1** provides an overview of the different samples that were used and shows the corresponding thickness of each layer. Note that the thickness of LaTiO_3 was fixed at 4 unit cells (u.c.), to avoid the formation of $\text{La}_2\text{Ti}_2\text{O}_7$ phases [38](as explained in **chapter 3**).

The predicted charge transfer depends on the band offset between the LaCoO_3 and LaTiO_3 , but does not consider the crystal structure [8]. However, the charge transfer can be influenced by the crystal structure, since different oxidation states of Co and Ti have a different ionic radius (e.g. there might be an additional energy cost associated with charge transfer when this involves structural changes). Therefore, both LaAlO_3 and SrTiO_3 substrates were used to induce compressive and tensile strain respectively, to investigate the influence of epitaxial strain. Note that to reduce charging effects in spectroscopy, mostly 0.5w% Nb-doped SrTiO_3 substrates were used for spectroscopy measurements instead of regular SrTiO_3 .

Additional samples were tested, where LaTiO_3 and LaCoO_3 are separated by ultra-thin LaAlO_3 spacer-layers to see if this can be used to block the charge transfer. LaAlO_3 was selected as a spacer, since this wide bandgap insulating material is

assumed to be inactive in the charge transfer process due to the trivalent aluminum that is supposed to have a fixed valence. Additionally, the lanthanum prevents A-site intermixing effects. The effectiveness can be assessed by comparing samples with various spacer thickness, to reference samples with and without charge transfer.

As described in **chapter 3**, the growth of LaCoO_3 in low background pressures can result in the formation of oxygen vacancies. These vacancies would donate electrons to the system and can therefore also result in a valence change from Co^{3+} to Co^{2+} . To test this, two samples of 10 unit cells of LCO on SrTiO_3 were fabricated in the same low pressure conditions as all other samples. However, one of these samples was annealed in higher oxygen background pressure in an effort to reduce oxygen vacancies. Comparing the Co^{2+} in the annealed sample with the non-annealed sample, the effect of oxygen vacancies can be determined.

Figure 4.1 Sample configuration: The LCO and LTO films were grown on (001)-orientated Nb-SrTiO_3 substrates with a 30 u.c. LaAlO_3 buffer layer and a 5 u.c. capping layer of LaNiO_3 . The deposition pressure for all the layers and samples was fixed at $2\text{e-}3 \text{ mbar}$. The “No interface” reference samples consist of single LaCoO_3 films while the other samples involve one or two active LTO | LCO interfaces, indicated in red. Additional samples were produced were a LAO spacer layer was introduced between LCO and LTO, to test whether this can be used to suppress the charge transfer. Variation in thickness is indicated by x , with values reported below each sample type.

LaAlO₃ buffer layers

Fabricating LaCoO₃ – LaTiO₃ heterostructures directly on SrTiO₃, can lead to charge transfer between titanium in SrTiO₃ and LaTiO₃ [27] due to i) oxygen band alignment [8], ii) polar catastrophe [12], and iii) occupation difference [21] (see **chapter 2**). Additionally, oxygen can migrate from SrTiO₃ to LaTiO₃ to form La₂Ti₂O₇ [39]. All these effects need to be prevented since this will influence the charge transfer between LaTiO₃ and LaCoO₃. Therefore, a polar buffer layer was grown on SrTiO₃ before growing the functional layers of LaCoO₃ and LaTiO₃. Additionally, a polar capping layer was introduced to prevent the removal of electrons from the surface layer [12].

Since LaTiO₃ and LaCoO₃ both have lanthanum on the A-site, this is also preferred for the buffer layer material. Moreover, the materials needs to be inactive in the charge transfer process and well matched to the lattice constants of LaCoO₃, LaTiO₃ and both SrTiO₃ and LaAlO₃ substrates. The choice was made to use LaAlO₃ since this is already used as substrate and fulfills all requirements: i) this material has La on A-site to avoid intermixing, ii) LaAlO₃ is predicted to be inactive in the charge transfer process, and iii) the lattice constants are compatible. Note that an additional benefit might come from the conducting LaAlO₃-SrTiO₃ interface [11], to reduce charging effects in spectroscopy measurements on non-doped SrTiO₃ substrates.

The thickness of the buffer layer was chosen as 30 unit cells, since this is well above the critical thickness of 4 unit cells for the polar catastrophe driven charge transfer [40]. This ensures that the functional LaTiO₃ and LaCoO₃ are well separated from the LaAlO₃- SrTiO₃ interface. Moreover, this thickness helps to distinguish of the titanium valence of the LaTiO₃ from the titanium in the SrTiO₃, by exploiting the surface sensitivity of X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS) in Total Electron Yield mode [41]. Since the probing depth of these techniques is limited, the titanium signal of the substrate will not be able to contribute to the total titanium signal. Finally, this thicker LaAlO₃ buffer layer will also help to reduce oxygen diffusion from the substrate which can affect the LaTiO₃ quality [39] (as explained in **chapter 3**).

Introduction of a buffer layer on LaAlO_3 substrates is not required, since the substrate is already polar. Nevertheless, a LaAlO_3 buffer layer with a thickness of 2-4 unit cells was used for consistency between samples fabricated on both substrates. Moreover, this buffer layer can be used to evaluate the growth-rate and thereby the performance of the deposition system, before growing the other functional layers.

LaNiO_3 capping layers

One of the ways to overcome the polar catastrophe relies on the transfer of charge from the surface of the polar material to the interface with the non-polar material [12]. To avoid this charge transfer, and possible adsorbates, from interfering with the LCO-LTO charge transfer, a polar capping layer is desired. This capping layer also avoids possible degradation of LaCoO_3 and LaTiO_3 in atmospheric conditions. Similar to the buffer layer, La is preferred on A-site and the lattice needs to match. The conducting LaNiO_3 (LNO) was selected to avoid charging effects in photoemission measurements and since probing depth of XAS and XPS is limited [41], the capping layer thickness was kept around 4-5 unit cells.

4.2.2 Structure evaluation

Measuring the valence of titanium and cobalt in reference samples without interface and comparing these to samples with interfaces is essential in the evaluation of interfacial charge transfer. However, one of the concerns is the valence of titanium in LaTiO_3 , since the titanium in ultra-thin layers is almost never found with a pure Ti^{3+} valence [27], [39]. Instead the titanium finds a way to remove electrons, resulting in a $\text{Ti}^{4+} d^0$ configuration. Two options to account for this loss of electrons in ultra-thin layers are: i) electronically, by delocalizing/transferring electrons to neighboring materials [8], [27], and ii) structurally, by oxidizing into $\text{La}_2\text{Ti}_2\text{O}_7$ (i.e. $\text{LaTiO}_{3.5}$), where the additional oxygen accounts for the Ti^{4+} valence [38], [39]. Similarly, a Co^{2+} valence in LCO could also be obtained in a Brownmillerite $\text{LaCoO}_{2.5}$ phase [42], [43]. Therefore, reliable conclusions regarding the interfacial charge transfer can only be reached, when combining structural information with valence determination.

During and after growth, RHEED images can provide some information about the structure at the top surface and the step density (roughness) at the surface [44]–

[46]. However, since the growth takes place at elevated temperatures, the buried interfaces can be affected during the fabrication of the different compounds on top (intermixing, oxidation, oxygen vacancy creation, etc.). Other methods are therefore required to evaluate the interfaces, sample quality and structure.

Scanning Transmission Electron Microscopy (STEM) measurements were used to gain information about the quality of the samples [47]. For these STEM measurements, a thin lamella is removed from the sample using a Focused Ion Beam (FIB) at a selected crystal orientation in order to obtain a thin cross-section of the sample. Additional preparation and further thinning of the lamella is required before the sample is thin enough for high-energy electrons to be transmitted through the sample. After this preparation, a high-energy electron beam (with an extremely small spot size) is scanned over the sample to enable the imaging of individual rows of atoms. By analyzing these STEM images, the crystalline quality of the deposited ultra-thin layers can be assessed.

Information about defects in the lattice, intermixing at interfaces and strain relaxation can be obtained. More specifically, the formation of $\text{La}_2\text{Ti}_2\text{O}_7$ phase can be checked, since this would show up as diagonal lines [38], as discussed in **chapter 3**. Similarly, the LaCoO_3 can be checked for Brownmillerite $\text{LaCoO}_{2.5}$ phases [42], [43] (see **chapter 3**). Other defects, such as the presence of dark stripes can also be investigated. These dark stripes have been reported in literature for STEM measurements on LaCoO_3 and have been attributed to ordering of High-Spin states, ordering of Co^{2+} or ordered oxygen vacancies [48]–[54], see **chapter 5**.

Measurements were performed at room temperature, using High Angle Annular Dark Field (HAADF) imaging on a FEI Titan 80-300 microscope operated at 120kV¹. 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.

¹STEM and EELS measurements performed by N. Gauquelin, Electron Microscopy for Materials Science, University of Antwerp, Antwerpen, Belgium.

4.2.3 Valence determination

In order to prove charge transfer at the interface, the valence close to the interface needs to be compared to bulk. For this purpose, a sample was produced with a 36 u.c. LaCoO_3 layer between LaTiO_3 , to measure the valence across the LaTiO_3 and LaCoO_3 layers using STEM measurements combined with Electron Energy Loss Spectroscopy (EELS).

The EELS measurements were performed using a monochromatic beam with a 120meV energy resolution. The Ti L-edge, Co L-edge, O K-edge and La M-edges were acquired simultaneously (the La being used for energy calibration). The acquisition parameters were 0.25s/pixel, 0.4A/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.

Other ways to access the valence of the transition metals at buried interfaces, is by using x-ray spectroscopy techniques. These techniques probe specific electron transitions, resulting in an element specific fingerprint for the average valence. In this work, samples were measured using X-ray Photoelectron Spectroscopy (XPS) in the lab, combined with synchrotron-based X-ray Absorption Spectroscopy (XAS) measurements.

The *ex-situ* X-ray Absorption Spectroscopy experiments¹ were carried out at the i10 beamline at the Diamond Light Source in both Total Electron Yield (TEY) and Fluorescence Yield (FY) detection mode. Using soft x-rays, the TEY XAS has a maximum probing depth of around 10nm at the Co L-edge energy, whereas the FY provides more bulk-sensitive information that exceeds 100nm in probing depth [41]. For both the cobalt and titanium valence the $L_{3,2}$ -edge was selected, which relies on electron transitions from the $2p_{1/2}$ and $2p_{3/2}$ to the unoccupied 3d states to obtain the XAS spectrum. For different oxidation states, the number of unoccupied 3d states changes, which alters the XAS spectrum and therefore provides a ultra-sensitive fingerprint of the valence [55].

¹ Collaboration with Mark Golden and Georgios Arazi-Kanoutas, Van der Waals-Zeeman Institute for Experimental Physics, Institute of Physics, University of Amsterdam, Amsterdam, Netherlands

Most of these XAS experiments were conducted around 6K to probe the ground state and exclude influence of spin state fluctuations (**see chapter 5**), although few spectra were also taken at other temperatures to investigate the temperature dependence of the charge transfer. The XAS spectra consist of the average of circular right and circular left polarization and care was taken to minimize any potentially time-dependent artefacts by recording and averaging multiple spectra. The incident light formed an angle of either 90° or 20° with respect to the surface of the sample to measure in Grazing Incidence (GI) and Normal Incidence (NI) respectively.

In order to quantitatively resolve the various valence contributions, the spectra were compared to literature spectra of single crystal model compounds as EuCoO_3 (Co^{3+} Low Spin), $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_3$ (Co^{3+} High Spin) and CoO (Co^{2+} High spin) [56], [57].

XPS measurements were performed in house, using an Omicron XPS system equipped with a XM1000 monochromatic Al- $\text{K}\alpha$ source (1486.6 eV). When charging occurred, charge neutralization was performed using a low energy electron source. Unless stated otherwise, an angle of 89° (Normal Incidence) was used between the detector and sample surface.

4.2.4 XPS Heating experiments

Additional heating experiments were performed to investigate whether the charge transfer occurs at high temperature during growth or if this takes place during cool down. Ideally, the valence needs to be measured in deposition conditions and during the pulsed laser deposition process, but this is impossible in this setup. Instead the samples were fabricated using standard conditions and after being cooled down to room temperature, the system was pumped down and the samples were transferred in vacuum to the XPS system to be heated. Since the XPS system can only work in low pressures (below $1\text{e-}7$ mbar), these experiments do not replicate deposition conditions. However, these measurements can still provide value insights in the charge transfer mechanism.

Since SrTiO_3 is easily reduced, the SrTiO_3 substrate could act as an oxygen supply and donate oxygen to the other layers. Therefore, the samples for the heating

experiments were produced on LaAlO_3 substrates since these substrates are more stable against reducing conditions [39]. Additionally, the LaNiO_3 capping layer was replaced by a thin LaAlO_3 layer.

Heating and cooling cycles were performed on reference samples of 4 unit cells of LaCoO_3 and LaTiO_3 and a double interface sample with 3 unit cells of LaCoO_3 sandwiched between LaTiO_3 layers of 4 unit cell thick, as depicted in **figure 4.2**.

4.3 Results

4.3.1 STEM-EELS measurements

In **Figure 4.3a**, a STEM image of a LTO 4u.c. | LCO 36 u.c. | LTO 4 u.c. sample is presented (same image as shown in **chapter 3**). The image shows good quality of the samples and absence of stripes in the LCO. Furthermore, no obvious other structural defects such $\text{La}_2\text{Ti}_2\text{O}_7$ phase or interstitials could be detected and the stack remains fully strained to the STO substrate (as shown in **chapter 3**).

Figure 4.2 Sample configurations as used for the XPS heating experiments. All samples were made on a $(100)_{\text{pc}}$ -orientated LaAlO_3 substrate with a 3 u.c. LAO buffer layer and 3 u.c. LAO capping layer. For the heating experiments, a 4 u.c. LTO and LCO reference sample were compared to a LTO 4 u.c. | LCO 3 u.c. | LTO 4 u.c. sample.

The STEM-EELS measurement¹ of the same area is depicted in **Figure 4.3b**, where Co L-edge and O K-edge close to the interface show the bending of their onset energies towards lower/higher energies respectively. This is in agreement with a valence change from Co^{3+} to Co^{2+} . More detailed analysis of the Co valence shows a region up to about 3 u.c. from the interface being affected by the charge transfer. No pronounced inter-diffusion effects were found and the small overlapping of the Co and Ti signal, visible at the interface, can be attributed to the size of the probe.

In-plane strain was already extensively evaluated in **chapter 3**, but the out-of-plane unit cell parameters can also be evaluated by comparing the distance between the lanthanum-columns of each unit cell in the direction perpendicular to the substrate. This analysis has been performed¹ for both the LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c. and the LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c. sample, displayed in **figure 4.4**. In this figure, it can be seen that for both samples, the lattice of LTO is expanded in the out-of-plane direction. However, it can also be seen that the bottom LTO is only expanded at the interface with LCO, as indicated by the white arrows. For a LTO 4u.c. | LAO 4 u.c. | LCO 4 u.c sample (with a 4 u.c. LAO spacer in between the LTO and LCO), this effect was not observed.

¹ STEM measurements and strain analysis performed by N. Gauquelin, EMAT, Antwerp

Figure 4.3 **a)** STEM measurements of (001)-SrTiO₃ substrate | LaAlO₃ 30 u.c. | LaTiO₃ 4 u.c. | LaCoO₃ 36 u.c. | LaTiO₃ 4 u.c. | LaNiO₃ capping layer. No obvious defects such as La₂Ti₂O₇ impurity phase in LaTiO₃ or formation of LaCoO_{2.5} or dark stripes in LaCoO₃ could be observed. **b)** Ti L_{3,2} edge, Co L_{3,2}-edge and O-K edge of the same area. In a region up to ~3 u.c. from the interface, the Co spectrum shifts towards lower energy indicating Co²⁺ presence, which is also confirmed by the shift of O K-edge towards higher energies. This is evidence for the interfacial nature of the charge transfer. Slightly overlapping Ti and Co signals can be attributed to the size of the probe rather than intermixing. Measurements by N. Gauquelin.

Figure 4.4 Strain analysis, where the scale-bar depicts the strain-value as calculated with respect to the LAO (strained to STO). **a)** LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c. and **b)** LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c. sample. In both, an expansion of the out-of-plane LTO lattice is seen, as indicated by the red color. Surprisingly, the expansion is only present at the bottom LTO that is in contact with LCO, as indicated by the white arrows. Analysis by N. Gauquelin.

4.3.2 XAS measurements

The Co $L_{3,2}$ -edge TEY XAS spectra of LCO 4 u.c. (no interface), LTO4 u.c. | LCO 4 u.c. (single interface) and LTO 4 u.c. | LCO x u.c. | LTO 4 u.c., $x=2, 4, 6, 36$ (double interfaces) are depicted in **Figure 4.5a**. These spectra were collected at normal incidence and at a temperature of 6K. It can be clearly seen that the Co-spectra of samples with LTO and LCO interfaces are different from the spectrum of the LCO 4 reference sample. These differences are reflected in the main L_3 -peak of the cobalt, indicated with the letter **C**, and the L_2 -edge indexed by **F**.

The smaller peaks **E₁** and **E₂** appear to indicate a small barium signal (possible contamination). Since the thickness of the two LTO layers is fixed to 4 unit cells, this peak is most pronounced in the LTO 4 u.c. | LCO 2 u.c. | LTO 4 u.c. sample, since this has the weakest cobalt signal (2 u.c. buried below LTO and LNO). When the cobalt signal is increased, in the LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c. or LTO 4 u.c. | LCO 6 u.c. | LTO 4 u.c. samples, this peak becomes weaker.

For comparison, **figure 4.5b** displays the room temperature Co-spectrum for reference compounds EuCoO_3 (Co^{3+} Low Spin), $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_3$ (Co^{3+} High Spin) and CoO (Co^{2+}) [56], [57]. The LCO 4 u.c. reference sample without interface resembles to great extent the XAS spectrum of the Low Spin Co^{3+} (d^6) EuCoO_3 , indicating a valence close to the expected Co^{3+} valence. Upon introduction of LTO, the spectrum of the single interface system LTO 4 u.c. | LCO 2 u.c. shows the appearance of a characteristic feature around 776 eV, indexed by the letter **A**, and a shoulder indicated with **B**. For samples that contain double interfaces, these features are even more pronounced and shows a monotonic increase with decreasing LCO thickness. By comparing the spectra to the reference spectra in **figure 4.5b**, it can be seen that these features are also present in CoO and can therefore be recognized as Co^{2+} signatures. For the most extreme LTO 4 u.c. | LCO 2 u.c. | LTO 4 u.c. sample, where all LCO is in contact with LTO, the XAS spectral features are almost identical to those of the CoO reference.

Figure 4.5 a) XAS spectra obtained for different samples at 6K and Ni. The features **A** and **B**, indicate the Co²⁺ features (as also present in CoO), **C** and **F** depict the main L₃ and L₂ peaks respectively. The two shoulders **B** and **D** found on LCO 4 can be linked to High Spin (HS) and Low Spin (LS) configuration respectively, as seen in EuCoO₃ and SrCo_{0.5}Ru_{0.5}O₃. **E₁** and **E₂** indicate the L₃ and L₂ peaks of a small barium contamination that was present. This peak is largest for the 4-2-4 sample, since this samples has the weakest Co-signal. The dashed lines behind 4-2-4 and LCO 4, represent fits obtained using the CoO, EuCoO₃ and SrCo_{0.5}Ru_{0.5}O₃ reference spectra. For the other samples, the fits (presented in the dashed lines) were made using a combination of the 4-2-4 and LCO 4 spectra. The amount of Co²⁺ obtained from the fitting procedure is indicated for each sample. **b)** The CoO, EuCoO₃ and SrCo_{0.5}Ru_{0.5}O₃ reference spectra at room temperature, as obtained from [56], [57]. Comparing the EuCoO₃ and SrCo_{0.5}Ru_{0.5}O₃ spectra, the different shoulders for LS and HS can be observed. For CoO, the clear Co²⁺ spectral features are seen a lower energies.

Quantification

In order to evaluate the spectra more quantitatively, each spectrum has been fitted with a combination of the three reference spectra. Comparing the different spectra in figure 4.5a with reference spectra in 4.5b, it can be seen that the 4 u.c. LaCoO_3 reference sample lacks the Co^{2+} features of CoO and resembles the EuCoO_3 in which the formal valence is Co^{3+} . However, apart from the shoulder at position **D**, as seen in the Low Spin (LS) reference, a small shoulder can also be distinguished at position **B**, as seen in the High Spin (HS) reference. Therefore, the best fitting of the 4 u.c. LCO was achieved using a combination of 30% High Spin and 70% Low Spin Co^{3+} , indicated by the dashed grey lines in figure 4.5a. This mixture of spin states is consistent with other reports of a low temperature mixed spin state in strained LaCoO_3 [58] (see chapter 5).

For the sample with the 2 unit cell LaCoO_3 layer in between LTO, the spectrum resembles the CoO , in which the formal valence is Co^{2+} . Investigating the LTO 4 u.c. | LCO 2 u.c. | LTO 4 u.c. sample using the fitting procedure, the fitting becomes worse when Co^{3+} is introduced. Therefore, this procedure gives close to 100% Co^{2+} for this sample. The agreement between the measured spectrum and fitting is reasonable and differs mostly at feature **B**. The exact origin of this difference in spectral features is unknown, but is likely to originate from differences in temperature, rather than a difference in valence (see figure 4.6).

The ratio between Co^{2+} and Co^{3+} in the other samples can be extracted by fitting the spectra with a linear combination of the CoO , EuCoO_3 and $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_3$ reference spectra. However, to further improve the fitting, the LTO 4 u.c. | LCO 2 u.c. | LCO 4 u.c. was used as a Co^{2+} reference spectrum and the LCO 4 u.c. was used as the Co^{3+} reference (i.e. since a Co^{2+} reference with the same LCO crystal structure does not exist, and other differences in for instance temperature or measurement setup are excluded). The grey dashed lines for the other samples in figure 4.5a indicate the fits obtained using this procedure. Therefore, this analysis allows us to determine the percentage of Co^{2+} with reasonably accurately (error around +/- 5%), with values as indicated in figure 4.5a.

Temperature and strain

Most measurements have been performed at 6K, to probe the ground state of the system. However, it is interesting to determine if temperature has a strong effect on the Co valence (i.e. charge transfer). **Figure 4.6**, displays XAS measurements at several temperatures obtained on a LTO 4 u.c. | LCO 6 u.c. | LTO 4 u.c. sample and collected at grazing incidence. The spectra display a mixed $\text{Co}^{2+}/\text{Co}^{3+}$ character with about 65% Co^{2+} at 6K. Upon heating the sample to 125K, the spectral features are hardly changed, apart from changes in peak **A** and **B**, as indicated. The insert shows a zoomed-in overlay of all the same spectra, which illustrates the decrease of **B** for higher temperatures. In the CoO reference spectra, measured at room temperature, the **B** feature is lower, which would be consistent with this effect of temperature observed in **figure 4.6**.

Figure 4.6 Measurements obtained for 4-6-4 at GI and different temperatures. Upon increasing the temperature, feature **A** becomes larger compared to feature **B**. The insert shows an overlay of all spectra, indicating that in fact **B** reduces in height.

The influence of epitaxial strain was investigated by measuring certain LTO-LCO combinations on LaAlO_3 substrates, changing the epitaxial strain from tensile to compressive. Due to the insulating nature of the LAO substrates, only a few spectra could be obtained (as expected, several measurements suffered from charging effects). Some of the successful measurements at grazing incidence are depicted in **figure 4.7**. The measurements of LTO 4u.c. | LCO 6 u.c. and LTO 4 u.c. | LCO 2 u.c. | LTO 4 u.c. on LAO were obtained at 100K, whereas the two measurements on STO substrates were conducted at 6K. The difference between feature **A** and **B** in both 4-2-4 spectra is consistent with this temperature difference, as seen in **figure 4.6**. For the LTO 4 u.c. | LCO 6 u.c. | LTO 4 u.c. samples, both measurements were performed around 20K.

Figure 4.7 Measurements obtained at GI for samples fabricated on LAO and STO substrates. Due to the insulating nature of LAO, only few spectra could be obtained. For this reason, the only available spectrum for the 4-2-4 and 4-6 samples on LAO were measured at a temperature of 100K, whereas the corresponding spectra on STO were measured at 6K. The difference between feature **A** and **B** in both 4-2-4 spectra is consistent with this temperature difference, as also seen in figure 4.5. Both 4-6-4 spectra were obtained around 20K.

Although, the spectra show small differences between samples grown on LAO and STO, the valence change seems to occur independently of these two different substrates, illustrating the robustness of the valence change.

Spacer layers

In **Figure 4.8**, the grazing incidence Co $L_{3,2}$ -edge TEY XAS spectra of samples with a LAO spacer are depicted: LTO 4 u.c. | LAO x u.c. | LCO 4 u.c., $x=0,1,2,8$ u.c.. For reference, the spectrum of a 10u.c. LCO (without LTO) is included. It can be seen that the introduction of a LAO spacer layer alters the spectra, by strongly suppressing the lower-energy Co^{2+} features. This suppression already occurs for a thickness of 1 unit cell, and increases with a 2 u.c. LAO layer, which start to resemble the LCO reference. Upon further increasing the spacer to 8 u.c., the Co^{2+} features are fully suppressed, apart from a small Co^{2+} contribution (few %) that is also present in the LCO reference, which can probably be related to oxygen vacancies in the LCO.

Figure 4.8 XAS spectra obtained at GI and 6K, for samples with and without spacer layers. Comparing the sample without spacer to the sample with 1 u.c. LAO spacer, it can be seen that the Co^{2+} features are suppressed. Increasing the spacer thickness to 2 u.c. (or 8 u.c.) further suppresses these features and the spectrum resembles the LCO reference.

Annealing experiments

In some reference samples of LCO (i.e. without LTO interface), a small contribution of Co^{2+} can be observed. This can be related to oxygen vacancies in LCO, resulting from the low oxygen background pressure during fabrication. To test this, annealing experiments were performed in which two LCO samples were fabricated in standard conditions, but with one of these samples being annealed in higher oxygen background pressure after deposition. **Figure 4.9**, shows the grazing incidence Co-spectra of two samples of 10 u.c. LCO grown on SrTiO_3 substrates. It can be seen that the spectral features associated with Co^{2+} were somewhat suppressed in the sample that was annealed.

Figure 4.9 XAS measurements obtained at 6K and GI for two samples fabricated on STO substrates in identical conditions. One of these samples underwent an annealing procedure in order to suppress possible oxygen vacancies. Comparing the two spectra, indeed a reduction in Co^{2+} can be observed.

Titanium-edge

Certain Ti-spectra have also been acquired at grazing incidence, as shown in **figure 4.10a**. Comparing these spectra to literature reports on Ti^{3+} and Ti^{4+} , provided in **figure 4.10b** (taken from [39]), predominantly $4+$ features are observed. From the reference spectra it can be seen that Ti^{4+} features are stronger in intensity and more pronounced. Therefore, a contribution of Ti^{3+} would only modulate the intensities, but not directly alter the shape, making it difficult to extract exact values. Upon further investigation, some differences with respect to the Ti^{4+} reference can be observed. For instance, the peak heights of the L_3 - e_g and $-t_{2g}$ peaks in **4.10a** differ from a Ti^{4+} system like SrTiO_3 , where the L_3 - t_{2g} is higher [39].

Analyzing the peak separation between the t_{2g} and e_g peaks for both L_3 and L_2 -edges can provide insight in the Ti^{3+} content [59]. For pure Ti^{4+} systems like STO, these peaks are separated by roughly 2.4 eV. Upon introduction of Ti^{3+} , this separation is reduced.

Figure 4.10 **a)** XAS measurements of the titanium L-edge, obtained at 6K and GI for several samples fabricated on STO substrates. The features resemble mostly Ti^{4+} character, but subtle differences were observed for the samples without LaNiO_3 capping layer when calculating the L_3 and L_2 differences (as indicated with dotted lines). **b)** Reference spectra to illustrate the difference between Ti^{3+} and Ti^{4+} (figure taken from literature [39]).

Calculating this difference for all the spectra provided in **figure 4.10a**, gives values of 2.45 eV and 2.4 eV for L_3 and L_2 edge respectively. However, for the LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c. sample without LaNiO_3 capping layer, this separation is 2.3 eV for L_3 and 2.25 eV for the L_2 edge. This could indicate a larger Ti^{3+} contribution, although it requires a more thorough analysis to draw such conclusions.

Comparing the cobalt spectra of this LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c. sample without capping layer, to a similar sample with capping layer, yields only minor differences, as displayed in **figure 4.11**. The amount of Co^{2+} is somewhat increased from 75% to 80%, which can possibly be related to the absence of LaNiO_3 (see **Discussion**).

Figure 4.11 Comparison between LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c. samples with and without LaNiO_3 capping layer. The amount of Co^{2+} is higher without LaNiO_3 (80% compared to 75%) .

4.3.3 XPS heating experiments

This section describes the heating experiments performed using *in-situ* X-ray Photoelectron Spectroscopy (XPS). For these measurements, samples were produced in standard conditions, cooled down and in vacuum transferred to the XPS setup. In this setup, XPS measurements were performed at elevated temperatures in low pressure (below 10^{-7} mbar). Several heating/cooling cycles were performed to check reproducibility.

Figure 4.12a show the Ti spectrum for the LTO reference sample as illustrated in **4.12c**. Spectra were obtained using a step size of 0.05 eV, pass energy of 20 eV, dwell time of 0.2s and using an average of 10 spectra. The bottom curve, is obtained directly after growth and indicates a Ti^{4+} valence. After heating to roughly 500°C , the spectrum changed and a small Ti^{3+} contribution can be seen on the right side of the main peak, as indicated by the dotted line. Upon further increasing of the temperature to about 700°C (closer to the deposition temperature), a larger Ti^{3+} signature becomes apparent. Remarkably, after cooling down, this Ti^{3+} feature increases dramatically up to an area of about 75% of the main Ti^{4+} peak.

After this first observation, the heating/cooling cycles were repeated, as seen in **figure 4.12b**. The first measurement is performed directly after cooling down in **figure 4.12a**, but now with 0.1 eV step size, 50 eV pass energy, 0.2s dwell time and no averaging to severely reduce measurement times. Now, measurements are performed at 1.5-minute intervals while heating the sample to 700°C . The difference in the two spectra is due to the loss in energy resolution and reduced signal-to-noise ratio, but the large Ti^{3+} contribution is still evident **Figure 4.12b** clearly shows that upon increasing the temperature, the amount of Ti^{3+} decreases. After cooling down, the amount of Ti^{3+} increases again. This heating/cooling cycle has been repeated several times, with similar outcomes indicating a reversible process.

Similar heating/cooling experiments were performed on a LTO 4 u.c. | LCO 3 u.c. | LTO 4 u.c. sample grown on LAO and capped with 3u.c. of LAO. Instead of increasing the temperature to 700°C , the temperature was increased in smaller steps. **Figure 4.13**, shows the resulting spectra for both the titanium (in **4.13b**)

and the cobalt (in 4.13a) and all the temperature steps are indicated in the legend in figure 4.13c (not all spectra are included in the figure). Both cobalt and titanium spectra were taken subsequently at each temperature. The spectra depicted in red are taken at high temperature and the blue spectra after cooling down. When comparing the spectra of the first two temperature steps (50°C and 100°C) to the spectrum of the sample after being deposited, no obvious changes can be observed in both titanium and cobalt. In the first red curves taken at 150°C, a small amount of Ti^{3+} can be distinguished, whereas changes in the cobalt spectrum are less obvious. The Ti^{3+} persists after cooling down, but in cobalt a small peak appears at the position of the dotted line, which can be attributed to cobalt metal [60]. Repeating the experiment for 150°C results in an increase in Ti^{3+} and an increase in the cobalt metal peak. Continuing the heating/cooling cycles, with increasingly higher temperatures, the amount of Ti^{3+} and cobalt metal further increases and remains present both at high temperature and after cooling down, indicating an irreversible process.

Figure 4.12 a) XPS measurements taken at room temperature after growth, where the as-grown spectrum resembles Ti^{4+} valence. Upon heating, a small Ti^{3+} contribution appears, which increases with temperature. After cooling down, the amount of Ti^{3+} is strongly increased and remain stable over time. b) Taking faster measurements at 1.5-minute intervals while heating and cooling shows the reversible appearance of a Ti^{3+} contribution at low temperature, which reduces upon heating. c) Schematic depiction of the sample.

Figure 4.13 *In-situ* XPS heating experiments where the blue curves are measured at room temperature, and the red curves at increasingly higher temperatures. **a)** Co-peaks at different temperatures, where a Co-metal peak appears when heated to above 150°C as indicated by the dotted line. **b)** Ti-peaks, where a Ti^{3+} peak becomes visible and increases, similarly to the Co metal. **c)** The different temperatures as experienced by the sample. **d)** Schematic depiction of the sample.

Figure 4.14 *In-situ* XPS measurements where **a)** depicts the Co-peaks before, during and after heating to 375°C. An increase in Co^{2+} features can be observed, whereas a Co metal signature does not appear, **b)** schematic depiction of the sample as used.

Since the behaviour of the LTO 4 u.c. | LCO 3 u.c. | LTO 4 u.c. sample differs from the LaTiO_3 reference sample, a LaCoO_3 reference sample has also been measured. These results are summarized in **figure 4.14**, where the spectra of the as grown sample, the sample at 375°C and after cooling down, are displayed. Comparing the spectrum for the as grown sample, to the spectrum at 375°C, a small increase in Co^{2+} can be detected. No cobalt metal peak could be distinguished, even though this temperature is significantly higher than the 150°C at which this peak first appeared in **figure 4.13a**. After cooling down down, the cobalt spectrum has hardly changed and the Co^{2+} persists.

4.4 Discussion

XAS measurements have shown that the average valence approached Co^{2+} in the LTO-LCO-LTO double layers, when the amount of LCO is decreased. This behavior is evidence that charge is indeed transferred at the interface. This is further established by the STEM-EELS observation that a region of Co^{2+} can be found at the interface with LTO. However, since both the exact probing depth in XAS and the charge distribution in the sample are unknown, it is difficult to quantify the charge transferred per interface. Especially, since a 100% Co^{2+} reference with the same strained LCO structure does not exist. However, the amount can be

approximated using the reasonable agreement achieved between the spectra and fitting: the close to 100% Co^{2+} in the LTO 4 u.c. | LCO 2 u.c. | LTO 4 u.c sample indicates a minimal charge transfer of 1 electron per unit cell of interface area. Since the spectra of the LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c sample indicates 75% Co^{2+} , this could indicate a charge transfer that is possibly as large as 1.5 electron per unit cell.

The reported XAS measurements have been performed in several beam-times. Similar results were obtained when measurements were repeated up to half a year apart, indicating excellent sample stability for samples with and without capping layers. The robustness of the charge transfer is further established by the weak dependence on temperature and strain.

Structurally, the samples need to be in the right phase and of good quality to draw reliable conclusions regarding interfacial charge transfer. Using only spectroscopy data, it is not possible to rule out defect formation or alternative phases as a cause for a change in valence. As shown by STEM measurements, both for a LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c sample and a LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c sample (see also **chapter 3**), all layers are in the perovskite phase. Apart from the somewhat irregular contrast in the bottom LTO layer in the LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c sample, no obvious defects could be observed. The exact origin of the different bottom LTO layer remains unknown, but this defect concentration alone would not be sufficient to explain the large valence change (up to 100% Co^{2+}) observed in LaCoO_3 when inserted in between LaTiO_3 . Especially, since these defects do not seem to be present in the LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c sample and are only observed in the bottom LTO, with the top LTO unaffected.

Similarly, the small barium contamination that was found in XAS measurements on the Co-edge (see **figure 4.5a**), cannot be used to explain the large Co^{2+} content close to the interface. When the thickness of LCO is increased, the relative height of these peaks is decreased (as if the Ba-signal were constant), indicating that the origin cannot be the LCO. This was confirmed by measuring a LTO reference sample (without LCO) on the Co-edge, when this spectrum indeed showed these two peaks. This can point towards a contamination in the LTO, however, when X-

ray Fluorescence (XRF) measurements were performed on the LTO target to verify this, no sign of barium was found. Moreover, XPS measurements did also not show barium peaks. Therefore, the exact origin of these peaks remains unknown.

In addition, if we would assume that some barium would be present in the sample, this would not alter the conclusions: the perovskite structure is seen in STEM, so the Ba^{2+} would replace La in LTO. Resulting in a $\text{Ba}^{2+}\text{Ti}^{4+}\text{O}^{2-}_3$ contribution, which will manifest itself in a larger Ti^{4+} contribution and slightly reduces the number of electrons available for charge transfer. Therefore, this small barium signal will not affect our findings.

Spectroscopy measurements illustrate the presence of a Co^{2+} valence, but do not explain the origin of these charges. A valence change can be related to interfacial charge transfer, but can also be obtained by the creation of oxygen vacancies or off-stoichiometry in LCO, originating from growing LCO in non-ideal conditions. In reference samples, indeed a small (~5%) amount of Co^{2+} could be observed. The annealing experiments on 10 u.c. LCO, show that the amount of Co^{2+} is reduced after annealing in higher background pressure, indicating that oxygen vacancies are indeed responsible for the small amount of Co^{2+} in LCO reference samples. Since all samples were produced under identical conditions, the small amount of oxygen vacancies in reference samples clearly indicate that there is a big difference between samples with LCO in contact to LTO, compared to samples with LCO in contact to LNO and LAO. Oxygen vacancies originating from too low deposition pressure would be equally present in all samples and can therefore not explain the high amount of Co^{2+} observed in the double interface samples.

Another possible way to explain the Co^{2+} at the interface is the creation of oxygen vacancies induced by contact with LaTiO_3 . This mechanism is harder to prove or disprove, since the band offset (or electronegativity) used in the charge transfer model, also relates to the tendency to reduce or oxidize. For LTO, it is known that thicker layers can only be grown in low oxygen background pressures. In higher pressures the $\text{La}_2\text{Ti}_2\text{O}_7$ phase (or $\text{LaTiO}_{3.5}$) can be formed, since titanium prefers the Ti^{4+} valence [38], [39]. One could argue that this tendency for LTO to incorporate oxygen, leads to a situation where LTO removes oxygen from the

adjacent LCO layers. This could then result in a Co^{2+} valence that can be observed at the interface. However, this is highly unlikely since

- i) The LTO is already grown in a pressure that normally would result in the $\text{La}_2\text{Ti}_2\text{O}_7$ phase [38], [39]. Stabilizing strain from the substrate prevent this 227-phase formation [38], therefore (in terms of oxygen) it should not matter if LCO is present, since the stack remains fully strained.
- ii) No evidence for the $\text{La}_2\text{Ti}_2\text{O}_7$ phase was found in STEM measurements. Certainly not enough to explain the large amount of Co^{2+} . Similarly, for LCO, the loss of oxygen would alter the structure. In the case of 100% Co^{2+} , this would result in the formation of $\text{LaCoO}_{2.5}$ with Brownmillerite structure [42], [43], but no evidence supporting a high content of such Brownmillerite phases was found in STEM.
- iii) In the LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c sample, EELS has shown Co^{2+} close to the interface. If oxygen is removed from LCO, there would be no reason (apart from band bending at the interface) why these vacancies should occupy a region close to the interface, instead of distributing homogeneously throughout the sample. Especially, since the diffusion-lengths of oxygen vacancies at elevated growth temperatures far exceed a few u.c. [61].
- iv) Finally, introducing a thin layer of LAO in between the LTO and LCO strongly reduced the Co^{2+} content. However, it is unlikely that 1 or 2 unit cells of LAO are enough to severely block the oxygen diffusion at elevated temperatures [62].

Doping caused by intermixing can also be ruled out, since all materials have lanthanum on the A-site position, which results in a formal 3+ valence for La, Co and Ti. Therefore, replacing Co with Ti or La (or even La with Ti or Co for that matter) would not alter their valence. Only when the intermixing occurs at interstitial sites, can the valence change. However, this has not been observed in STEM measurements, certainly not at the scale required to explain the amount of Co^{2+} observed.

Measurements on the Ti valence using XAS and EELS indicate predominantly Ti^{4+} valence, in agreement with the electrons being transferred into the LCO. However, judging by the Co valence, a significant amount of Ti^{3+} should remain in LTO, but is not observed in XAS or EELS. This can be attributed to a combination of factors i) the spectral features of Ti^{4+} are much stronger compared to the more

subtle Ti^{3+} features. In mixtures of Ti^{4+} and Ti^{3+} , the Ti^{4+} features would dominate the spectrum, whereas the Ti^{3+} contribution would only result in a small intensity modulation. This makes it hard to clearly distinguish low Ti^{3+} contributions in predominantly Ti^{4+} spectra in XAS and EELS measurements without proper reference, and ii) Unfortunately, at the time the samples were conceptualized, it was not known that charge transfer can also take place from LTO to LNO (since the band offset calculations did not include Ni [8]). Since the Ni-edge has significant overlap with the La-edge, the Ni valence was not measured in this research. Although, several literature reports claim charge being transferred from Ti to Ni via $\text{Ti}^{3+} + \text{Ni}^{3+} \rightarrow \text{Ti}^{4+} + \text{Ni}^{2+}$ [23], [63]–[66]. Moreover, at the LNO-LTO interface, an out-of-plane lattice expansion has been observed, with lanthanum positions displaced in the direction of the charge transfer [66]. Therefore, the displacements observed in **figure 4.4**, would be consistent with charge transfer at both LTO-LCO interfaces and the LTO-LNO interface. The LAO-LTO interface does not exhibit charge transfer, which effectively reduced the out-of-plane lattice constant.

Speculating that the trend in band offsets continues beyond Co [8](see **chapter 2**), the LNO could potentially be a stronger acceptor than LCO. This can account for a significant additional removal of electrons, which would be consistent with the differences in titanium spectra, as observed in **figure 4.10**. Moreover, since the LNO capping layer was also used on the 4 u.c. LTO reference sample (but not on the samples used in the XPS heating experiment), this can explain the Ti^{4+} valence. Although more extensive research would be required to support such claims.

Quantitatively, if the 5 u.c. of LNO can act as additional electron acceptor, for a LTO 4 u.c. | LCO 4 u.c. | LTO 4 u.c sample this means: the combined 8 u.c. of LTO can donate electrons to 9u.c. of acceptor, resulting in a predominantly Ti^{4+} spectrum. Whereas, in samples without capping layer, the electrons from LTO can only be transferred to the 4 u.c. of LCO, leaving more Ti^{3+} in the LTO. In **figure 4.11**, the Co-spectra valence of these 2 samples is displayed and a small increase in Co^{2+} signal from 75% to 80% can be seen for the sample without capping layer. Although, this can possibly be related to the LNO, the effect is minimal.

Moreover, since most samples have this 5 u.c. LNO capping layer, this does not affect our main trends and conclusions.

In theory, the small band offset between LCO and LNO can also lead to charge transfer in the samples where LCO is in contact with LNO. This charge transfer would manifest itself as $\text{Co}^{3+} + \text{Ni}^{3+} \rightarrow \text{Co}^{4+} + \text{Ni}^{2+}$, however this has been ruled out since the expected Co^{3+} valence (only a minimal Co^{2+} contribution) is observed in LCO reference samples with and without LNO capping layers. However, the potentially larger band offset for LTO-LNO, compared to LTO-LCO can result in a situation where LCO receives electrons from LTO and transfers part of those electrons to LNO, even though the band offset between LCO and LNO is small. This can explain the reduced Co^{2+} content in samples with only a bottom LTO-LCO interface, see **figure 4.5**. Although, this remains speculation.

XPS heating experiments

From the STEM measurements, it is known that the correct perovskite phase of LTO can be formed in non-ideal deposition conditions and with LCO present. In this case, the ultra-thin LTO is stabilized both by the strain from the STO substrate and by charge transfer to the LCO, resulting in the favored Ti^{4+} valence. The LTO reference sample on LAO as used for the heating experiments, does not show the expected Ti^{3+} valence in XPS when measuring directly after fabrication. Although, interfacial charge transfer to the LAO capping layer or substrate is impossible, leaving only acceptor-type defects or excess oxygen uptake responsible. Whether this behavior can be related to the lack of an appropriate electron acceptor (like LCO or LNO) or the difference in strain between LAO and STO remains unknown.

The reversibility of the $\text{Ti}^{3+}/\text{Ti}^{4+}$ character in XPS heating experiments cannot be explained using oxygen diffusion alone. Regarding oxygen, one would expect to reduce the LTO by heating in UHV conditions, resulting in Ti^{3+} [39]. Once reduced, there are two options i) there is little oxygen available, so oxygen will not be incorporated again and this Ti^{3+} can be stable, and ii) oxygen will be incorporated in the LTO and the Ti^{4+} will return. The appearance of the Ti^{3+} after the first heating cycle can be explained by the former mechanism, but the reversibility in the following heating/cooling cycles cannot. Therefore, it is more likely that this reversibility originates from a delocalization of electrons at high temperatures:

At elevated temperatures, the electrons have enough energy to be delocalized and support the favored Ti^{4+} valence, upon cooling the electrons 'condense' into a suitable potential-well (e.g. $LaCoO_3$, $LaNiO_3$, etc. or back onto the $LaTiO_3$ to form Ti^{3+}). It remains unknown if this occurs, where the electrons are at higher temperatures, and if this process can be measured or controlled.

Similar XPS heating experiments with the LTO 4 u.c. | LCO 3 u.c. | LTO 4 u.c. sample, show something interesting. At the same time that the Co-metal signal appears, the Ti^{3+} signal becomes apparent. Since this behavior is irreversible, this is probably related to redox-type interactions in combination with interfacial charge transfer. Comparing this to the LTO reference sample, this can be explained the following way: It is expected that heating in these reducing conditions removes oxygen from the sample. Since LTO needs to be fabricated in strongly reducing conditions (removing oxygen, effectively adds electrons), it is more likely to remove oxygen from LCO. This seems to be the case, since a metallic cobalt signal appears after heating. Before heating, electrons from LTO could be transferred to LCO resulting in Ti^{4+} and Co^{2+} . However, once metallic cobalt signal appears, electrons can no longer be donated to these Co-atoms, resulting in a rise in Ti^{3+} . When more oxygen is removed, more Co-metal is formed and the Ti^{3+} signal increases. Since the loss of oxygen is irreversible, the Co-metal and Ti^{3+} signals persists upon further heating/cooling. Interestingly, at high temperature the Ti^{3+} signal is still present, whereas this was converted (reversibly) to Ti^{4+} in the LTO reference sample. Indicating that the behavior of LTO is influenced by contact with LCO.

In the LCO reference sample, a small increase in Co^{2+} signal was observed after heating to 375°C. Upon cooling, the spectrum remained the same, which can be explained by the creation of oxygen vacancies in LCO. No Co-metal peak was observed, Although, this temperature far exceeds the 150°C at which Co-metal was formed in the LTO 4 u.c. | LCO 3 u.c. | LTO 4 u.c. sample, which further proves that samples with LTO - LCO interfaces behave differently from reference samples.

In a superlattice of $SrTiO_3$ and $LaTiO_3$, it has already been shown that the electrons of LTO can be strongly delocalized [27]. Combined with the ~3 u.c.

range of interfacial charge transfer, this shows that the length scales involved in electronic reconstructions at the interface are far greater than a few unit cells. Combined with the results of the heating experiments, this leads to proposing the following model: instead of the generally assumed charge neutrality in one unit cells or few unit cells, this needs to be revised into charge neutrality over a few nm. Especially, at deposition conditions, where the electrons and ions are thermally activated and can move over large distances (i.e. be strongly delocalized). Upon cooling, the electrons (and ions) become more localized and condense in an appropriate potential-well provided by the ions, defects, build-in potentials etc., and possibly the band offsets at the various interfaces.

4.5 Conclusion

The theoretically predicted charge transfer at the interface between LCO and LTO was observed experimentally in several combinations of ultra-thin LCO and LTO. STEM measurements showed the expected perovskite structure and no obvious signs of structural defects as $\text{La}_2\text{Ti}_2\text{O}_7$ formation in LTO or $\text{LaCoO}_{2.5}$ phases in LCO, indicating a good sample quality.

XAS measurements show that the average Co valence in LCO can be varied from the expected Co^{3+} (d^6) to 100% Co^{2+} (d^7), by tuning the thickness of the LCO layer and the number of interfaces with LTO. The interfacial nature of the Co^{2+} is further established by EELS measurements on a LTO 4 u.c. | LCO 36 u.c. | LTO 4 u.c. sample, showing a Co^{2+} contribution in LCO in a region of up to about 3 u.c. from the interface with LTO. Quantitatively, the results suggest an interfacial charge transfer from LTO to LCO that could be as large as 1.5 electrons per unit cell.

Moreover, samples grown on both SrTiO_3 and LaAlO_3 substrates show similar Co^{2+} content, indicating a strain-independent phenomenon. Similarly, measurements at several temperatures, show that the charge transfer seems to be independent of temperature. Additional experiments indicate that upon introduction of a LaAlO_3 spacer layer of 1 u.c. thickness, the charge transfer is already strongly suppressed. When the spacer layer thickness is increased to 2 u.c., the charge transfer can be almost completely blocked.

Heating experiments in XPS indicate that samples with LCO sandwiched between two LTO layers behave different from the individual layers in the response to a reducing environment. To explain these results, a model is proposed using a combination of redox-type interactions and interfacial charge transfer on the basis of electron delocalization at higher temperatures and subsequent condensation in available electron-sinks (which can have consequences on the fabrication of ultra-thin layers). Moreover, these observations call for spectroscopy measurements during fabrication, to further investigate what happens during growth.

In conclusion, our research has shown that interfacial charge transfer can be used as a method to strongly alter the valence of a material without using chemical substitution, thereby providing a promising new way to create (quasi 2D) materials that otherwise do not exist.

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Chapter 5

Magnetism in ultra-thin LaCoO_3

Abstract

Bulk LaCoO_3 displays a paramagnetic to diamagnetic transition when cooled down below 100K, whereas strained thin films of LaCoO_3 display ferromagnetism below 85K. The transition in bulk is attributed to spin state transitions, although the exact nature of these transitions has been under debate. For thin films, the situation is more complex since additional factors can play a role (variations in fabrication, different thickness, influence of various substrates, etc.). A relation between strain and magnetic moments has been established, but the exact origin remains unclear. Complex strain relaxation behavior and influence of oxygen vacancies have been identified in literature, therefore this work focusses on ultra-thin LaCoO_3 layers with a well-defined strain state. Moreover, charge transfer has been used to evaluate the effect of electron doping (up to 100% Co^{2+}) on the magnetic properties. X-ray Magnetic Circular Dichroism was used to investigate the magnetic properties and extract spin and orbital moments. Vibrating Sample Magnetometer measurements on thicker 55nm LaCoO_3 samples established ferromagnetic behavior, making these samples a suitable reference. The measurements established that ultra-thin LaCoO_3 layers behave paramagnetic, with an increasing effective moment upon increasing Co^{2+} content. Therefore, it was concluded that strain alone cannot be responsible for ferromagnetism in LaCoO_3 films.

5.1 Introduction

Introduction to the spin states of LaCoO_3

A free cobalt atom has 3d-orbitals that are equal in energy (degenerate), but this degeneracy can be lifted when the atom is influenced by its surroundings [1]. For instance in a perovskite crystal structure, the octahedral oxygen cage lifts the degeneracy and splits the energy levels into a t_{2g} set of degenerate d_{xy} , d_{xz} and d_{yz} orbitals with lower energy and the e_g orbitals $d_{x^2-y^2}$ and d_{z^2} with higher energy, see **figure 5.1**. This so called Crystal Field Splitting (CFS) makes the electron configuration a balance between i) the energy cost of having 2 electrons in the same orbital (due to Coulomb repulsion) and ii) the energy cost of promoting an electron into the higher e_g orbitals.

For Co^{3+} in LaCoO_3 (LCO), 6 electrons are distributed over the t_{2g} and e_g orbitals, which means there are 3 options:

- i) When the Coulomb energy is smaller than the energy costs associated with promoting an electron into the e_g orbital: the ground state has all 6 electrons in the 3 lowest t_{2g} energy levels (t_{2g}^6), whereby each energy level is occupied by both a spin-up and a spin-down electron, see **figure 5.1**. This means that there are no unpaired electrons which is called the Low Spin ($S=0$) spin state.
- ii) The Coulomb energy is larger compared to the $t_{2g} - e_g$ energy separation, making it is favorable to have the least amount of paired electrons. This results in a ground state with 2 unpaired electrons in the e_g orbitals and 2 unpaired electrons in the t_{2g} orbitals ($t_{2g}^4 e_g^2$), which is called the High Spin ($S=2$) spin state, see **figure 5.1**.
- iii) The third option can only be stabilized in special cases (as will be explained in a following section), but there is the possibility to have 1 electron in the e_g orbitals and the rest in the t_{2g} orbitals. This state has 2 unpaired electrons ($S=1$) and is therefore called the Intermediate Spin (IS) state, see **figure 5.1**.

Note that spin state transitions can occur when the $t_{2g} - e_g$ energy separation changes by a change in structure or when the temperature changes, so electrons have more energy to overcome the $t_{2g} - e_g$ energy separation.

Figure 5.1 In octahedral crystal field splitting, the d-orbitals are separated in energy into the e_g and t_{2g} orbitals, as depicted. When the energy cost of putting 2 electrons in the same orbital is lower, compared to the energy separation between e_g and t_{2g} , the 6 cobalt electrons in LaCoO_3 cobalt will arrange in a Low Spin ($S=0$) state. When the energy cost associated with two electrons in the same orbital is high, this results in a High Spin ($S=2$) state. It has been debated whether the Intermediate Spin ($S=1$) state can be formed (e.g. for certain distortions).

Not only do these 3 spin states illustrate the distribution of electrons within the Co^{3+} in LaCoO_3 , they also affect the magnetic properties: in the LS ($S=0$) state, there are no unpaired spins that can be aligned between adjacent unit cells and therefore, by definition, this spin state can only result in diamagnetic (DM) behavior. For both the IS and HS state, the unpaired spins can be aligned between unit cells: aligned parallel, this gives rise to Ferromagnetism (FM), whereas anti-parallel alignments results in Anti-Ferromagnetism (AFM). Moreover, the IS and HS states can also result in Paramagnetic (PM) behavior if the spins can be aligned using an external field, but will return to a random state when the field is removed (e.g. when the interaction between the unit cells is too weak, or if the temperature is too high, which results in thermal fluctuations of the spin direction).

5.1.1 Literature review

Magnetism in bulk LaCoO_3

Bulk LaCoO_3 is a material that has been widely studied, for its interesting magnetic properties. In bulk form, LCO is a charge transfer insulator that shows an interesting magnetic transition around 100K, where the material goes from diamagnetic at low temperatures to paramagnetic above this transition temperature [2]. The diamagnetic behavior can only be explained by having a LS state at low temperature without unpaired electrons. When the temperature is increased, the energy of the electrons is increased and the unit cell expands. Combined, this makes it possible for electrons to overcome the energy difference between the lowest t_{2g} energy levels and the higher e_g levels, effectively resulting in a spin transition from Low Spin ($S=0$) to High Spin ($S=2$) (or Intermediate Spin) [3]. A similar transition can be triggered solely by using pressure [4], since

compression/expansion of the unit cell alters the CFS and therefore the energy balance.

The Low Spin (LS) state at low temperature is well-accepted, since there is no alternative possibility to explain the diamagnetic response. However, the paramagnetic state has been under debate, since the measured effective paramagnetic moment (μ_{eff}) of bulk LCO is much lower as expected for a pure High Spin ($S=2$) system. Theoretically, using the spin-only formula $\mu_{\text{eff}} = g_e \sqrt{S(S+1)}$ with $g_e \approx 2$, the $S=2$ for HS would results in $\mu_{\text{eff}} = 4.90 \mu_B/\text{Co}$. However, in magnetic susceptibility measurements, the effective paramagnetic moment (extracted using a Curie-Weiss fitting) has been reported in 1964 to be $3.07 \mu_B/\text{Co}$ ($S=1.12$) [5]. More recent measurements in a temperature ranging from 150K to 350K, resulted in $\mu_{\text{eff}} = 3.4 \mu_B/\text{Co}$ ($S=1.27$) [6].

Naturally, this discrepancy is a reason for debate: originally the reduced moment was explained by mixing LS ($S=0$) and HS ($S=2$), but another option is to introduce an Intermediate Spin ($S=1$) state. The existence of a IS state in LaCoO_3 , in combination with a possible orbital ordering, was first proposed by M.A. Korotin et al. in 1996 based on calculations using the Local Density Approximation + Hubbard U (LDA+U) approach [3]. This IS state was not considered before, since the existence of this IS state is not trivial in a octahedral crystal field splitting, when only the energy costs of Coulomb repulsion and the energy cost of promoting an electron into the e_g orbitals are taken into account. However, when additional energy terms are included in the energy balance, the formation of the IS state can be favorable. For instance in the case of charge-transfer materials (like SrCoO_3 or LaCoO_3), where a ligand hole can hybridize with the IS state which can result in an overall energy gain [7]. Moreover, since the IS state has a strong double degeneracy (e_g^1 configuration) this can lead to orbital/magnetic ordering or Jahn-Teller distortions, which further complicates the discussion [3].

Experimentally, the underlying problem is that the exact electron configuration is not easily accessible; therefore, only indirect evidence can be used in the discussion. Some articles may therefore focus on explaining susceptibility measurements, whereas other publications may rely on x-ray spectroscopy data, Electron Spin Resonance (ESR) or Inelastic Neutron Scattering (INS) data for validation. Moreover, since most measurements only concern average properties, the discussion is further hampered by the possibility of inhomogeneous samples or magnetic dead-layers. Additionally, inhomogeneities can manifest themselves in ordering (i.e. a mixture of ferromagnetic,

paramagnetic, diamagnetic and anti-ferromagnetic regions), but also in the spin states (i.e. a mixture of LS, IS and HS) or even in stoichiometry variations (i.e. oxygen vacancies or Co^{2+}) and structural domains (i.e. twinning).

The debate on the spin transition in bulk LaCoO_3 has been largely resolved when X-ray Magnetic Circular Dichroism (XMCD) was used by Haverkort et al in 2006 [8]. This technique exploits the difference in absorption between left-hand and right-hand circular polarized x-rays to extract both spin and orbital contributions to the magnetic moments using the XMCD sum-rules. This technique is very suitable to investigate the spin states of cobalt in LCO, since it is highly sensitive, chemically specific and does not require modeling to extract the spin and orbital moments. Additionally, it can be used to simultaneously extract the valence, which helps to correctly interpret the data. From the measurements, a surprisingly large orbital moment was found with a ratio $L_z/S_z \approx 0.5$ indication that spin-orbit coupling needs to be considered, instead of the generally assumed quenching of orbital moments and spin-only calculations [8]. The combination of spin and orbital momentum is taken into account in cluster calculations, in which the $J=1$ triplet was found to be lowest in energy and with $L_z = 0.6$ and $S_z = 1.3$ (in good agreement with the experimental result for L_z/S_z). Moreover, they state: *“Realizing that this state is a triplet with a spin momentum (S_z) so close to 1, it is no wonder that many studies incorrectly interpreted this state as an IS state”* [8].

Although, the combination of spin and orbital moments is quite convincing and explains why previous results seem to indicate IS, the debate has not completely ended. Recently, a model based on excitons has been proposed based on Resonant Inelastic X-ray Spectroscopy (RIXS) data [9], which combines mobile bosonic IS excitations with immobile HS excitons on a LS background. This goes to show that the magnetic behavior of bulk LCO is not easily explained and continues to be under debate even after more than 50 years of research.

Ferromagnetism in thin film LaCoO_3

The initial reports on ferromagnetism in thin film LaCoO_3 renewed interest into this material, and many publications followed. Similar to bulk LaCoO_3 , the various spin states and transitions are under debate in thin films (and existence of a strain-induced IS state). However, the discussion in thin films is even more complex as in bulk: substrates impose epitaxial strain and related strain relaxation effects, but can also affect the symmetry and induce octahedral rotations [10]–[12]. Additionally, the specific growth conditions (temperature, pressure etc.) can result in off-stoichiometry. Other reports are focused around

the origin of dark stripes, observed in Scanning Transmission Electron Microscopy measurements, and their relation to strain and magnetism [13]–[19].

The next section reviews existing literature and highlights certain discrepancies between reports and indicates main conclusions, in order to highlight the importance of our work on ultra-thin LaCoO_3 layers. The section is divided in the following parts: First observations, Strain, Scanning Transmission Electron Microscopy, Valence, Octahedral rotations, and Size effects.

First observations

For bulk LaCoO_3 , the diamagnetic-paramagnetic transition clearly indicates an absence of long-range order, however, this is different for strained thin films of LaCoO_3 . In 2007, D. Fuchs *et. al.* [20] published the first observation of ferromagnetic behavior in thin films of LaCoO_3 , grown on (001) oriented $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT) substrates by Pulsed Laser Deposition (PLD). The critical temperature (T_c) was found to be around 85K, below which the ferromagnetism can be observed. Above this Curie-temperature, the system behaves paramagnetic. Moreover, it was also realized in this work, that the thickness of the LCO affects the magnetization, since the magnetic moment in saturation was decreased for films with a thickness below 50 nm [20].

In the paramagnetic regime above 100K, the effective paramagnetic moments (μ_{eff}) were determined by susceptibility measurements. For the epitaxial films an effective moment of $\mu_{\text{eff}} = 3.87 \mu_B$ was obtained, which is higher compared to bulk values (i.e. $3.07 - 3.4 \mu_B$ [5], [6]). When ignoring spin-orbit coupling and using the spin-only $\mu_{\text{eff}} = g_e \sqrt{S(S+1)}$ with $g_e \approx 2$ this results in $S=1.5$, which can be explained by mixing LS with 75% HS, or mixing IS with HS in a 1:1 ratio.

To test the origin of the discrepancy between bulk LCO and thin film LCO, polycrystalline films have also been produced by this group (by using a 20 nm polycrystalline CeO_2 buffer layer on the LSAT substrate) [20]. In these polycrystalline samples, paramagnetic behavior is observed down to 5K and the temperature dependent susceptibility behavior was claimed to be similar to bulk LCO. However, in these polycrystalline films, an effective paramagnetic moment of $2.0 \mu_B/\text{Co}$ was determined, which is lower than previously reported bulk values. Using the spin-only formula, this results in $S=0.62$ (explained by mixing LS ($S=0$) with 62% IS ($S=1$) or 31% HS ($S=2$)).

In the ferromagnetic regime, the saturated magnetic moment, M_{sat} , was determined as $0.4 \mu_{\text{B}}/\text{Co}$ at 5K, as extracted from field-dependent magnetization data after subtracting linear contribution of unsaturated moments. Since, ferromagnetism is a manifestation of long-range ordering of spins in the systems, this can only occur when i) the cobalt atoms of neighboring unit cells are interacting, and ii) the electron configuration (spin states) of the system have unpaired spins. Therefore, the FM in thin LCO films is surprising, since the ground state in bulk is LS and at higher temperature, there seems to be no ordering between HS-LS or HS-HS states.

Only a small amount of Co^{2+} is observed in these films, ruling out double-exchange as dominant exchange mechanism and leaving superexchange between e_{g} orbitals as proposed ordering mechanism [20]–[23]. According to the Goodenough-Kanamori-Anderson rules [24]–[26]; superexchange interactions are ferromagnetic when virtual hopping occurs between half-filled and empty orbitals or between filled orbitals and half-filled orbitals (i.e. hopping between half-filled orbitals favor antiferromagnetic coupling) [21]. Therefore, mixed spin states with superexchange interaction between LS and HS (or LS and IS) would result in ferromagnetic ordering (i.e. LS has only completely filled or empty orbitals, see **figure 5.1**). So superexchange explains the ferromagnetic ordering and the magnitude of the magnetic moments is explained by mixing LS with HS (or IS).

Strain

After this initial discovery, the same group published results on various LCO films grown on (001) oriented SrLaAlO_4 (SLAO), LaAlO_3 (LAO), SrLaGaO_4 (SLGO), $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT) and SrTiO_3 (STO) substrates to impose different epitaxial strains [12]. The deposited films had a thickness of around 100nm and all films showed a ferromagnetic transition with a magnetization that increases strongly with increasing strain, see **figure 5.2a**. The T_{c} increased with increasing tensile strain and saturates around 85K above $a=3.86\text{\AA}$, see **figure 5.2b**. Upon investigating the paramagnetic state with susceptibility measurements between 100K and 150K, the effective moment was found to increase almost linearly as a function of the mean LCO lattice constant: from $2.8 \mu_{\text{B}}/\text{Co}$ on SLAO, up to $4.6 \mu_{\text{B}}/\text{Co}$ for LCO on STO, see **figure 5.2c**. Moreover, the difference in magnetic properties between epitaxial LCO films and polycrystalline films further establishes the relation to strain [20].

The model used to explain the relation between strain and ferromagnetism is based on the notion that the Co-O-Co bond length appears to be unaffected by tensile strain [12]. Therefore, the bond-angle must change to account for strain-induced unit cell distortions. Increasing the bond angle toward 180° leads to enhanced hybridization between Co-3d and O-2p orbitals, increasing superexchange-interaction strength [21]. With increased exchange, the system has a stronger tendency for ferromagnetic order which increases T_c and magnetic moments.

Figure 5.2 To illustrate the effect of strain, this image has been taken from literature [12] **a)** this image shows the magnetic moments as observed for LaCoO₃ films grown on several substrates as the temperature is varied **b)** T_c as extracted from the temperature dependence, plotted against the in-plane lattice constant **c)** The effective moment in the paramagnetic regime depends linearly on the lattice constant.

Several other reports further establish the strong dependence of magnetic properties on lattice mismatch [16], [18], [27]–[30]. Although, magnetic moments can vary between reports (e.g. due to differences in film thickness, growth conditions, etc.), most reports claim highest magnetization on LSAT substrates [12], [18], [27], [28], [30]. On STO, the moments are slightly reduced, although the tensile strain is larger. The explanation is that the strain imposed by LSAT is enough to reach a 180° bond angle, which maximizes the superexchange interaction [21]. When the strain is further increased, on STO, the bond-length is increased which reduced the strength of the superexchange [28].

For other substrates with intermediate lattice mismatch, the magnetization values follow the trend that tensile (compressive) strain enhances (reduces) the magnetization [12], [28]. The unit cell volume also depends on strain, although the value seems to be larger than bulk, with a Poisson-ratio of 0.33 to 0.38 [12], [27]–[29]. Moreover, experiments using 50nm and 100nm thick LaCoO_3 films grown on a piezoelectric PMN-PT substrate, further established the effects of strain on the magnetization [29].

Regarding the absolute strain-value, an additional tensile strain of around 0.3% can be induced by the thermal expansion difference between LCO and the substrates [12] (due to the elevated growth temperatures). This thermal expansion mismatch, combined with epitaxial strain, is the assumed reason that films thicker than 80-100nm on STO can develop cracks [12], [18], [27] (400nm on LSAT [20]).

Scanning Transmission Electron Microscopy

Scanning Transmission Electron Microscopy (STEM) measurements on thin films of LCO revealed dark stripes [16], see **figure 5.3a-c**. Compressively strained to a LAO substrate, some occasional stripes were visible parallel to the substrate surface. Moreover, for tensile strain inducing LSAT or STO substrates, result in a larger amount of dark stripes perpendicular to the substrate surface. Therefore, direction and concentration of stripes appears to be linked to the strain, since the amount of stripes increases up to 1 in every 3 unit cells on STO. Additionally, these stripes are not observed in a thin region close to the substrate (see **figure 5.3d and 5.3e**), which can indicate towards a mechanism to (partially) relax the strain.

Figure 5.3 Images taken from [16] **a-e**) dark stripes as revealed by STEM measurements. On LAO the LCO is strained compressively and the stripes run parallel to the substrate, whereas the stripes run perpendicular for tensile strain-inducing LSAT and STO. Moreover, the stronger tensile strain on STO increases the stripe density. Upon close inspection, the stripes only occur a certain distance from the substrate, pointing towards a possible relation with strain relaxation **f-g**) these images display the magnetic properties of the same samples which indicate that the stripe density can be related to the magnetic properties.

Figure 5.3f-g, depict the magnetic properties of the same films: the magnetic moments in STO were slightly higher compared to the moments on LSAT (as expected, the magnetic moments were smaller on LAO substrates). These observations contributed to speculation on magnetism in LCO thin films, since magnetic properties could now be linked to strain and dark stripes, even though the STEM measurements were performed in the paramagnetic regime [16].

The main challenge is to explain the origin of these dark stripes and the causal relation (i.e. do these stripes cause ferromagnetism, or are these a result of other effects that are linked to the magnetic properties?). In the initial report on dark stripes, X-ray Absorption Spectroscopy (XAS) measurements were used to determine the valence of cobalt. Since no significant Co^{2+} signatures were found, oxygen vacancies could not be the origin [16] (especially with concentrations of stripes as high as 1 in 3 unit cells). Instead the dark stripes were attributed to strain-induced ordering of HS states (since the HS states have a larger ionic radius compared to the LS state). This explanation was consistent with the LS-HS mixture that was already proposed. Moreover, the mixture of 30% HS and 70% LS that was used to explain the paramagnetic moments in bulk LCO [12], matches the 2:1 ratio of LS to HS as extracted from the dark lines.

Following reports, claimed the origin of the dark-stripes was more likely found in strain-induced ordering of oxygen vacancies, since oxygen vacancies give rise to Co^{2+} which has a larger radius compared to Co^{3+} [19]. This report used Electron Energy Loss Spectroscopy (EELS) instead of XAS, to determine the cobalt valence and found significant amounts of Co^{2+} , although the background pressure during deposition of these samples was higher [19] (320 mTorr/0.42 mbar instead of the previous 100mTorr/0.13 mbar, both grown at 700°C). These contradictory publications were followed by several reports that held either spin states responsible [15], [16] or oxygen vacancies [13], [17]–[19]. Note that before these stripes were observed in LCO, similar dark stripes were already reported in Sr-doped LaCoO_3 , accompanied by a similar discussion [31]–[35].

What has become clear from the discussion between oxygen vacancies, valence or spin state ordering, is that the stripes appear related to strain. Therefore, another possible explanation involves the occurrence of monoclinic domains of a few u.c. wide as a mechanism to relax the strain (possibly in combination with spin state ordering [16]). More recently, these monoclinic domains have indeed been observed in thin films using X-ray Diffraction (XRD) measurements [36]. Interestingly, in non-magnetic bulk LCO, dark stripes with similar periodicity can

be observed, arguing against a causal ferromagnetic relation [37]. Furthermore, this striped superstructure in bulk was indeed found to be sensitive to strain, but can disappear over time [14]. Moreover, ferroelastic monoclinic twinning with room temperature creep can also be observed [14], [37], [38]. Time-dependent observations of stripes combined with room temperature creep indicate that STEM measurements at temperatures below 85K are required to link the structure to ferromagnetic behavior.

Valence

The valence of cobalt can be another factor affecting the magnetism through double-exchange interaction between cobalt atoms with mixed valence [21], [22], [35], [39], [40]. In LaCoO_3 , the valence can be intentionally changed by introducing dopants, but also unintentionally due to oxygen vacancies acting as electron donors. The resulting Co^{2+} is empirically almost always found in a HS ($S=3/2$) state [18], [39]–[42], whereas only in certain special cases LS Co^{2+} ($S=1/2$) is possible [43], [44], see **figure 5.4**.

Introducing HS Co^{2+} into a Co^{3+} system with mixed LS and HS states can affect the magnetism in several ways: i) ignoring interactions; replacing LS Co^{3+} by HS Co^{2+} increases the number of unpaired spins, whereas replacing HS Co^{3+} reduces the amount of unpaired spins (i.e. increasing the unpaired spins enhances the paramagnetic moment), and ii) mixed valence results in competition between superexchange and ferromagnetic double exchange interaction [35], [39], [42], with the possibility of regions being dominated by either type of exchange [45]. Experimentally, the relation between oxygen vacancies in LCO and the magnetic properties remains uncertain: oxygen vacancy ordering is claimed to enhance ferromagnetic properties [13], [17]–[19], whereas a recent study indicates a reduction of magnetic moments for vacancy concentrations above 10% [46].

Figure 5.4 This shows the Low Spin ($S=0$) and High Spin ($S=2$) states of Co^{3+} in black, with the addition of an electron due to charge transfer. This results in Low Spin ($S=1/2$) and High Spin ($S=3/2$) for Co^{2+} .

Experiments with substitutional doping of LCO provide insight into the role of valence, although at different levels of concentration. For instance, doped with 30% cerium ($\text{La}_{0.7}\text{Ce}_{0.3}\text{CoO}_3$, LCCO) or strontium ($\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$, LSCO), the LCO valence includes 30% Co^{2+} or 30% Co^{4+} respectively. For the hole-doped LCO, the T_c increases to 240K, where electron doping reduced T_c to around 22K [39]. From XMCD measurements, the conclusion is that undoped LCO consists of 36% HS and 65% LS Co^{3+} with a spin moment of around $0.8\mu_B/\text{Co}$, the LSCO gives 40% Co^{3+} HS, 30% Co^{3+} LS and 30% Co^{4+} HS with $0.9\mu_B/\text{Co}$, whereas for LCCO this changes to 30% Co^{2+} HS and 70% Co^{3+} LS with $0.2\mu_B/\text{Co}$ [39]. The discrepancy between hole-doped and electron-doped LCO is attributed to a spin-blockade phenomenon: Co^{2+} is HS, therefore hopping between Co^{2+} and Co^{3+} LS is strongly reduced since this results in a Co^{2+} LS configuration instead [39], [40], [42], [47], [48]. This spin-blockade does not occur between Co^{3+} and Co^{4+} , since these can be both LS and HS.

Octahedral rotations

Rotations of the octahedral oxygen cage in LaCoO_3 can affect the magnetic behavior by altering the Co-O-Co bond angle. These rotations can be influenced by multiple factors, such as the substrate, LaCoO_3 thickness and temperature. For example, it has also been shown that a single layer of STO can strongly reduce the rotations in $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ [10]. Therefore, thin LaCoO_3 films on SrTiO_3 substrates are also expected to have reduced rotations through octahedral coupling, however, rotations can still develop further away from the substrate as the film thickness is increased. This has been investigated in STEM measurements, by comparing epitaxial films of 5 u.c., 15 u.c. and 20nm of LCO grown on STO substrates [11], [49]. The 5 u.c. film exhibits no tilts, while the 15 u.c. sample was fully tilted, with tilts propagating into the STO and a structural distortion of the film, see **figure 5.6**.

Figure 5.6 This image displays the octahedral rotations found by STEM measurements on a 15 u.c. film of LaCoO_3 deposited on SrTiO_3 . Close to the interface the rotations are reduced but still present, with rotations that are induced in the SrTiO_3 . Further away from the interface, at about 5-6 unit cells, the rotations are fully developed. Image taken from [11].

Furthermore, the 20nm LaCoO_3 film and substrate were no longer coherent with orientational-domain-boundaries nucleating at a thickness of 15-17 unit cells [11]. Note that dark stripes were not observed in any of the samples.

Interestingly, upon measuring the magnetic moments, 15 uc of LCO on STO gives $0.74 \mu_{\text{B}}/\text{Co}$, whereas 5 u.c. of LCO on STO gives no signal. The relation between octahedral rotations and magnetism was also investigated by comparing the magnetic properties of the 5 u.c. and 15 u.c. LCO films with a superlattice of [5uc STO - 5uc LCO] $3\times$ [49]. This superlattice has the same amount of material as the 15 u.c. film, however, due to the STO interlayers, the octahedral tilts should be removed. The magnetic moment of the superlattice was determined at $0.34 \mu_{\text{B}}/\text{Co}$ and STEM measurements reveal some tilting in LCO films in the superlattice [49]. Since the severity of the tilting is in between the 5 u.c. (no tilts) and the 15 u.c. (strong tilts), their conclusion is that tilt are related to the value of the magnetic moment that also lies in between the 5 u.c. and 15 u.c. films.

Another article reports the investigation of superlattices of LCO and STO on LAO, LSAT and STO substrates [50]. Here, the superlattices consist of $[d \text{ LCO} - 4 \text{ nm STO}]_x$, where d is the LCO layer thickness and the total amount of LCO is around 50 nm. The magnetization was found to remain significant down to a LCO thickness of $d=1.5\text{nm}$ for all substrates, whereas the magnetization vanished below 6nm for a single layer of LCO on STO. The STO thickness in the multilayers was also varied, which showed that a STO interlayer thickness of 1nm results in higher saturated moments compared to 4nm STO interlayers. Surprisingly, dark stripes were observed in the superlattices, but not in the single layers (no stripes were seen in the previous report).

Comparing both reports, it can be concluded that ultra-thin LCO layers (5 u.c. /1.5 nm) can be magnetic in a superlattice with STO, even if a single ultra-thin layer of LCO of the same thickness is not magnetic. This was explained using octahedral rotations: rotations are absent in a thin single layer, but rotations can develop in the superlattices through the increased amount of LCO that transmits rotations through STO. Unfortunately, the question remains whether ultra-thin LCO can become ferromagnetic when rotations are induced, since this would definitively proof the relation between magnetism and octahedral rotations.

Size effects

Octahedral rotations in superlattices indicate a thickness effect, but thin films can also be compared to powders, nano-particles and nano-wires. These can have similar dimensions, but without the influence of substrates.

In one report, bulk single crystals were ground into powder and pressed in pellets, with magnetic measurements performed at every stage [51]. The single crystal behaved as expected, but the powder showed ferromagnetic behavior with a T_c of around 85K (i.e. similar to thin films). Moreover, the magnetism in the compressed pellet was even stronger. These observations were attributed to a change in surface/volume ratio, combined with reduced oxygen-coordination at the surface that was held responsible for higher spin states of surface cobalt [51].

Similar magnetic properties were found in sol-gel produced nano-particles with an average size of 80nm [52]. Moreover, structural analysis on these particles revealed an enlarged unit cell compared to bulk, similar to thin films. Another report compares scanning superconducting quantum interference device (SQUID) measurements on single crystals to measurements on nano-particles with different sizes [53]. Here it was found that the surface of a LCO single crystal

showed stray magnetic flux below a temperature of 85K, indicative of ferromagnetism. Upon measuring LCO particles, it was found that the magnetic properties were proportional to the particle radii. For the smallest particles (radius of 60nm), the ferromagnetic moments were highest. Using X-ray Photoemission Spectroscopy (XPS) combined with *in-situ* argon etching, it was shown that the ferromagnetism at the surface could originate from metallic conductivity at the surface induced by chemisorbed oxygen that results in Co^{4+} ions.

The magnetic properties of nanowires have also been investigated and give a similar relation between ferromagnetic moments and diameter [54]. When the diameter is decreased in steps from 104 nm down to 51 nm, the saturated moment increases, whereas T_c remains around 85K. Furthermore, XRD measurements were performed (refined using the monoclinic symmetry) and reveal that lattice constants, Co-O bond-lengths, bond-angles, and Jahn-Teller distortions change with the diameter of the nanowire. When the Co-O bond length is plotted against the spin moment (or effective moment in the paramagnetic regime), the values lie on a straight line indicating a strong relation [54].

5.1.2 Motivation and goal

Summarizing the literature overview in **section 5.1.1**, it can be concluded that many factors play a role in the magnetic properties of LaCoO_3 . Multiple publications try to relate the ferromagnetism to structure (i.e. strain, strain relaxation, octahedral rotations, bond angles, etc.), however, this relation is not straightforward since there are 3 types of strain involved: epitaxial strain, shear strain (symmetry), thermal strain. Combining the STEM results on both the octahedral rotations and dark stripes with other observations in literature on LaCoO_3 films on SrTiO_3 , this results in complex strain and strain-relaxation behavior in several different thickness regimes:

- i) **Ultra-thin:** films with a thickness up to ~ 5 unit cells. These films are fully strained (both in shear strain and epitaxial strain). No octahedral rotations or dark stripes are observed by STEM and there is no epitaxial strain relaxation, with a pure tetragonal distortion of the unit cell.
- ii) **Thin:** films with a thickness up to about 15 unit cells. In these films, the shear strain starts to relax and octahedral rotations can be seen in STEM measurements, combined with monoclinic distortions, twin formation and dark stripes.

- iii) **Intermediate:** thin films with a thickness above 15 unit cells. For these films, both shear strain and epitaxial strain start to relax. Apart from octahedral rotations, monoclinic distortions, dark stripes, and twin formation, also changes in bond lengths and presence of structural defects can be seen. This can even result in LCO films that are no longer coherent to the substrate.
- iv) **Thick:** This exact thickness varies in literature, but films with a thickness above roughly 80-100 nm can exhibit crack formation. The formation of cracks has been reported by many groups and for several substrates and can be related to the difference in thermal expansion.

Judging from these regimes, the only samples that are well-defined are LCO films with a thickness up to around 5 unit cells, since thicker films show a combination of relaxation effects that alter the CFS. Since most techniques give the average magnetic response of the sample, these cannot distinguish between strained and relaxed parts of the sample. Therefore, the only way to test the magnetism in systems without rotations and full epitaxial strain, is to measure the response of ultra-thin films.

Moreover, the role of oxygen vacancies or other electron-dopants in thin films of LCO is debated. It is always assumed that Co^{2+} is HS in LaCoO_3 , however, experimental evidence for the exact spin state of Co^{2+} in LCO is lacking. To determine this Co^{2+} spin state requires a system with 100% Co^{2+} in an undisturbed LaCoO_3 crystal, which would normally be impossible. As described in **chapter 4**, this has now become experimentally available in ultra-thin LCO by use of interfacial charge transfer. Therefore, the goal is to measure the magnetism in ultra-thin LaCoO_3 films with and without interfacial charge transfer, to determine the spin state of Co^{2+} and investigate the magnetism in ultra-thin films with different electron-doping.

In addition, Resonant Inelastic X-ray Scattering (RIXS) techniques have been used to investigate spin states in bulk LaCoO_3 [9]. Therefore, it is of interest to perform RIXS measurements on both compressively and tensile strained LCO thin films with various thickness and compare these measurements to a LaCoO_3 single crystal¹, see appendix I.

¹ Collaboration with Ru-Pan Wang and Frank de Groot, Debye Institute for Nanomaterials Science, Utrecht University, Netherlands. See [60], where part of this work has been published.

Goals

- Investigate the magnetism and spin states in ultra-thin LCO, since only these layers are well defined.
- Determine the spin state of Co^{2+} in LCO with 100% Co^{2+} , induced by interfacial charge transfer
- Measure the magnetic properties of LCO with various Co^{2+} concentrations to gain insight in the effects of a mixed valence.

5.2 Methods

5.2.1 Sample types

Several samples were made with LaCoO_3 and various combinations where LCO is interfaced with LaTiO_3 , to induce Co^{2+} via charge transfer. These samples were used to gain insight in the magnetic properties of ultra-thin LaCoO_3 with and without electron-doping. The samples can be separated in 3 types: i) ultra-thin LCO, ii) ultra-thin electron-doped LCO, and iii) thicker (55nm) LCO films, to serve as comparison for ultra-thin films and use in RIXS measurements.

All of these samples were fabricated on both LaAlO_3 and (Nb-doped) SrTiO_3 substrates to compare the effect of tensile and compressive strain. For the first 2 categories, the same samples have been used as described in **chapter 4**. The thicker 55nm LCO samples were grown directly on LAO and STO substrates without buffer layer or capping. An overview of the different samples is provided in **figure 5.7**.

Figure 5.7 This image illustrates the various samples as used in this chapter.

5.2.2 X-ray Magnetic Circular Dichroism

X-ray photons (100eV to 100keV) have a spin angular momentum that can be either left-hand or right-hand with respect to the direction of travel. This photon spin is reflected in the polarization, since an electromagnetic wave composed of photons with only one type of spin is called circular polarized, whereas linear-polarization is a superposition of circular-left and circular-right polarization. This means that circular polarized x-rays are capable of probing spin polarizations in materials. For instance, in x-ray absorption, where a core electron is excited from the $2p_{1/2}$ or $2p_{3/2}$ levels into the unoccupied 3d states, a different amount of spin-up and spin-down in the 3d orbitals leads to a difference in absorption of circular-left (σ^-) and circular-right (σ^+) polarization [55]. Therefore, this absorption difference (circular dichroism) can be used to extract information about magnetism in materials via the technique called X-ray Magnetic Circular Dichroism (XMCD).

Using this technique has several benefits; firstly, the magnetic properties and valence can be measured simultaneously, which is important in understanding the relation between valence, magnetism and spin states. Secondly, XMCD is element specific, which enables the distinction of the cobalt signal (in ultra-thin LCO layers) from other contributions such as the (much thicker) substrate, resulting in a high sensitivity [55]. Finally, this technique allows the extraction of spin moments, orbital moments, and their ratio via the sum rules [56]. The combination of these moments can provide important clues towards the electron occupation (similar to the work on bulk LCO performed by Haverkort [8]).

In **chapter 4**, the X-ray Absorption Spectroscopy (XAS) spectra were obtained by measuring σ^- and σ^+ polarization and taking the average to be independent of the spin. However, for XMCD, the difference of these measurements has to be taken instead of the average. As described in **chapter 4**, these XAS/XMCD measurements were performed at the i10 beamline of Diamond Light Source¹, with spectra measured in both Total Electron Yield (TEY) and Fluorescence Yield (FY). Although, due to self-absorption effects in FY, only TEY was used to extract the XMCD.

An external magnet, capable of fields up to 14T, was employed to magnetize the samples, with the direction of the magnetic field parallel to the incoming beam.

¹ Collaboration with Mark Golden and Georgios Arazi-Kanoutas, Van der Waals-Zeeman Institute for Experimental Physics, Institute of Physics, University of Amsterdam, Amsterdam, Netherlands.

Measurements were performed with and without magnetic fields and both in-plane and out-of-plane magnetization was investigated by changing the angle between beam and sample from grazing incidence (GI, 20°) to normal incidence (NI, 90°) respectively. Additional experiments were performed with samples magnetized in-plane and measured without field in both GI and NI to investigate the remnant magnetization.

Furthermore, most measurements were performed around 10K to probe the ground state of the system (excluding spin state fluctuations). Although, few other temperatures were used to investigate the effect of temperature.

5.2.3 Vibrating Sample Magnetometer

A Quantum Design PPMS-system equipped with a Vibrating Sample Magnetometer (VSM) insert was used to measure magnetism in magnetic fields up to 7T. For this technique, the samples are mounted on a holder that oscillates inside of a coil. The movement of the sample induces a current in the coil which is a measure of the magnetism. Since this technique is less sensitive and not element-specific, this technique could only be used for thicker films otherwise the substrate contribution would dominate the signal.

More sensitive VSM measurement were performed at Diamond Light Source, using a Quantum Design system equipped with a Superconducting Quantum Interference Device (SQUID) as pickup loop. Although, these measurements still suffer from the drawbacks mentioned above.

5.2.4 X-ray Diffraction Measurements

X-ray diffraction measurements can be used to determine the lattice constants in order to investigate the strain relaxation behavior. These measurements were only performed on the 55nm films (and 4-36-4 sample, see **chapter 3**), due to the limited thickness of the other samples.

The out-of-plane lattice constants have been measured using high resolution 2theta-omega scans around the (002) peaks, using the triple axis configuration with a parabolic X-ray mirror, four-bounce Bartels monochromator and Ge analyzer crystal on a PANalytical X'Pert Pro MRD system with a sealed tube Cu anode source in line-focus mode¹. Reciprocal Space Maps (RSM) were obtained around the (103) peaks from sets of high-resolution rocking curves collected with an EIGER2 R 500K area detector on a Bruker D8 Discover diffractometer. High

¹ XRD and RSM measurements performed by Y. Birkhölzer, MESA+Institute for Nanotechnology, University of Twente, Enschede, Netherlands.

brilliance microfocus Cu rotating anode generator, Montel optics, and a Ge (220) two-bounce monochromator were used in these measurements. The thickness of the 55nm films was measured using X-ray Reflectivity (not shown).

5.3 Results

5.3.1 XMCD measurements

Measurements can suffer from charging effects or otherwise noisy backgrounds (especially for samples on LAO substrates), making sum-rule analysis impossible. Although, these spectra can still hold information, these will not be included.

Figure 5.8a shows normalized XAS spectra consisting of $(\sigma^- + \sigma^+)/2$, which were collected at GI and 10K. The spectra are identical for both directions of magnetic field, illustrating excellent reproducibility. In **figure 5.8b**, the L_3 -spectra of the individual σ^- and σ^+ polarizations are shown for a field of 6T (offset for clarity). A clear difference between the 2 polarizations can be observed, which is the XMCD signal.

Figure 5.9a displays the XMCD intensity of 4 u.c. LCO on a Nb-doped STO substrate for different field strengths. At 0T, the XMCD signal is negligible, whereas an increased magnetic field results in a dichroism signal up to around 8% of the L_3 maximum at 14T. Importantly, the signal switches sign when the field direction is reversed, indicating a true dichroism effect. In **figure 5.9b**, this 4 u.c. LCO sample is compared to a film of 10 u.c., where it can be seen that both XMCD signals are similar in strength at -14T. Comparing the 4 u.c. LCO to the 55nm film, however, the thicker film shows a much stronger dichroism for the same field, as depicted in **figure 5.9c**. The XMCD spectra in **figure 5.9d** were obtained without external magnetic field, after magnetizing the sample in-plane at 6T (increased noise can be attributed to the small signal). For the 55nm LCO a significant XMCD intensity was observed at GI, whereas no significant XMCD was observed at NI or for the 4 u.c. LCO sample. This is indicative of an in-plane remnant magnetization in the 55nm sample, consistent with ferromagnetism (further established by VSM, see 5.3.2).

Figure 5.8a Normalized XAS spectra consisting of the average of circular left and circular right polarization as collected at 10K and under grazing incidence. The spectra overlap for both field directions, illustrating excellent reproducibility **b)** here both the σ^- and σ^+ polarizations are shown for a field of 6T, where the difference gives the XMCD signal.

Figure 5.9a The XMCD signal for 4 uc of LaCoO₃ as obtained in different magnetic fields **b)** a comparison between 4 uc and 10 uc LaCoO₃ films, where the XMCD signal is similar **c)** comparing the XMCD signal of 4 uc with 55nm LaCoO₃ where a clear difference is observed **d)** the 55nm LaCoO₃ samples shows a clear in-plane remnant magnetization, whereas this is absent in the 4uc film.

Figure 5.10 Comparing the XMCD signal between samples, it can be seen that the signal increases in intensity with increasing Co^{2+} content.

The effect of Co^{2+} in LCO was investigated by interfacing the LCO with LTO to induce interfacial charge transfer, as described in **chapter 4**. The GI XMCD signal at 14T for double interface samples (i.e. LCO between LTO, see **figure 5.7**) with 2, 4, 6 and 36 u.c. of LCO, is plotted in **figure 5.10**. Only the L_3 -edge is shown for clarity and 4 u.c. LCO without interface is included as a reference. As described in **chapter 4**, the valence in these samples ranges from close to 100% Co^{3+} in the 4 u.c. LCO to 30%, 65%, 75% and 100% Co^{2+} in the 4|36|4, 4|6|4, 4|4|4 and 4|2|4 samples respectively. When the amount of Co^{2+} is larger, the intensity of the XMCD signal is increased. The shape of the XMCD signal changes since Co^{2+} features become more pronounced in the XAS spectrum. Measurements on these samples were also conducted or in low fields or without magnetic field, but the XMCD signal vanishes without field (i.e. no clear remnant magnetization).

On the 4|6|4 double interface sample with 6 u.c. of LCO, measurements were performed at several temperatures and under different field strengths. Using the sum-rule analysis, the total magnetic moment was extracted and plotted in **figure 5.11**. It can be seen that the moments increase with decreasing temperature, but no obvious change was found around 85K and no saturation or ferromagnetic hysteresis was observed.

The sum rule analysis has also been used to find the spin and orbital contributions for various other samples. **Table 5.1** gives an overview of these values as obtained at 10K, GI and -14T.

Table 5.1 Spin and orbital moments as extracted using the sum-rule analysis performed by M. Golden and G. Arazi-Kanoutas, Van der Waals-Zeeman Institute for Experimental Physics, Institute of Physics, University of Amsterdam, Amsterdam, Netherlands. These values have been published in [57].

System	Orbital moment, m_l (μ_B/Co)	Spin moment, m_s (μ_B/Co)	Total moment, m_{tot} (μ_B/Co)	m_l/m_s
LCO4	0.15	0.33	0.48	0.45
LTO4 LCO4	0.2	0.38	0.58	0.55
LTO4 LCO6 LTO4	0.26	0.5	0.76	0.52
LTO4 LCO4 LTO4	0.26	0.47	0.73	0.54
LTO4 LCO2 LTO4	0.37	0.75	1.13	0.50
LCO55nm (-6T)	0.18	0.57	0.75	0.32

Figure 5.11a) The total moments per Co atom for various temperatures, as obtained on a LTO4|LCO6|LTO4 sample at -14T and grazing incidence **b)** the moments as the magnetic field is varied at a temperature around 10K. Images adapted from [57].

5.3.2 VSM measurements

In-plane Vibrating Sample Magnetometer measurements were performed on various samples, however, for most of the samples the signal was too weak and could not be distinguished from the substrate. Therefore, only the 55nm samples on STO and LAO substrate yield reliable VSM measurements. These results are depicted in **figure 5.12a-b**, where a paramagnetic background was subtracted using a linear fit of the high field data. The total magnetic moment was divided by the amount of cobalt to extract the magnetic moment per Co-atom. Hysteretic behavior and remnant magnetization were observed for both samples. As the temperature is decreased, the saturated magnetic moment and the coercive fields increase. Furthermore, the magnetization loops seem to consist of several contributions with different coercive field. Moreover, for both samples, the ferromagnetism appears when the temperature is below 90K. This can be more clearly seen when the magnetic moment is measured while cooling down in 0.05T, as show in **figure 5.12c**. From this measurement, the T_c can be estimated to be around 75K. Note that the magnetic moments in this measurement are lower, probably because the samples are not fully saturated by the lower field.

Figure 5.12a) In-plane VSM measurements performed at several temperatures for 55nm LaCoO₃ on LaAlO₃ **b)** on SrTiO₃ **c)** moment as the samples are cooled down in a field of 0.05T.

Figure 5.13a) XRD measurements to find the out-of-plane lattice constants of the 55nm LaCoO_3 films on LaAlO_3 and SrTiO_3 substrates, with a single crystal included for reference¹. Strained (S) and relaxed (R) parts of the films can be seen and are indicated using arrows **b)** reciprocal space maps on the same samples, illustrating significant relaxation. Measurements performed by Y. Birkhölzer, MESA+Institute for Nanotechnology, University of Twente, Enschede, Netherlands.

5.3.3 XRD measurements

X-ray diffraction measurements, including reciprocal space maps, were made on the 55nm films to determine the strain state and relaxation behavior, as depicted in **figure 5.13a-b**. The tensile strain (on STO) compresses the out-of-plane lattice constant, making the film peak appear on the right of the single crystal in **figure 5.13a**. The opposite occurs for the film on LAO, although the LAO is much more closely matched. Moreover, part of the intensity of the thin films peaks (both on STO and LAO) can be found close to the peak for a LCO single crystal¹ (included for reference), due to partial relaxation. Therefore, the black arrows (marked S), indicate the strained portions, whereas the grey arrows (marked R) show the partially relaxed parts. This relaxation can be more clearly seen in reciprocal space maps in **figure 5.13b**, where part of the film adopts the Q_x value of the substrate, whereas other parts deviate.

5.4 Discussion

The absence of remnant magnetization in the ultra-thin films and the Brillouin-like behavior indicate that the ultra-thin films are paramagnetic. No clear change in paramagnetic behavior was observed with temperature or the amount of Co^{2+} , although the effective moment changed, indicating a different amount of

¹ Single crystal provided by Ru-Pan Wang, Debye Institute for Nanomaterials Science, Utrecht University, Netherlands, see also [60].

unpaired spins. The most obvious explanation is to attribute this behavior to a magnetic-dead-layer, similar to the 3 u.c. critical thickness in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [58], however, even the thicker sample with 36 u.c. of LCO showed no signs of ferromagnetic behavior or hysteresis. It remains unclear if this can also be related to the absence of dark stripes in STEM measurements, see **chapter 4**.

Sum rule analysis on various samples revealed a ratio of around 0.5 between spin and orbital moments in ultra-thin films, independent of Co^{2+} content. This ratio is in agreement with the work on bulk LCO in the paramagnetic regime [8]. For the 55nm film on SrTiO_3 , this ratio was different and lies around 0.32, which roughly agrees with work from Merz *et al* [39], where a ratio of 0.2 was found for 50nm films of LCO. The spin moments of ultra-thin LCO are increased from 0.33 to 0.75 upon increasing Co^{2+} content from <5% to close to 100% by interfacial charge transfer. These values are inconsistent with values on 50nm thick films reported by Merz *et al*, that found m_{spin} of 0.77 for undoped LCO and a decrease of spin moments to 0.24 for electron-doped $\text{La}_{0.7}\text{Ce}_{0.3}\text{CoO}_3$ (30% Co^{2+}) [39], although this can be caused by the different thickness and doping mechanism.

As described in **chapter 4**, the XAS measurements on 4 u.c. LCO film without LTO showed only a small contribution of Co^{2+} and the spectrum could be fitted with a combination of reference spectra: 30% HS $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_3$ and 70% LS EuCoO_3 . However, using the spin-only formula given by $\mu_{\text{eff}} = \sqrt{4S(S+1)}$ and the $S=2$ for HS, this would result in an effective moment $\mu_{\text{eff}} = 0.3 \cdot 4.90 = 1.47$ which is inconsistent with the total moment of 0.48 obtained using XMCD. Moreover, for the LTO4|LCO2|LTO4 sample with 100% Co^{2+} , the total moment that was extracted from XMCD was around $1.13 \mu_{\text{B}}/\text{Co}$. Assuming a HS state ($S=3/2$) for Co^{2+} , this would result in a magnetic moment of $3.87 \mu_{\text{B}}/\text{Co}$, whereas LS state ($S=1/2$) results in $1.73 \mu_{\text{B}}/\text{Co}$. Combined with the significant orbital moment observed in XMCD, this indicates that the spin-only formula is not valid (similar to bulk LaCoO_3 [8] and CoO_2 [41]). Therefore, no conclusions can be drawn from these values without further analysis and resorting to cluster calculations and more elaborate modeling.

The thicker 55nm films on both LAO and STO showed ferromagnetism in the VSM measurements with magnetic moments and T_{c} consistent with literature observations. For the sample on STO, the ferromagnetic behavior was further confirmed by a persistent in-plane XMCD signal, after first magnetizing the sample and measuring without external magnetic field. Comparing the values for spin and orbital moment between the ferromagnetic and paramagnetic samples

reveals a difference in ratio between spin and orbital moments: the samples with charge transfer have a ratio of 0.5-0.55, whereas the 55nm sample has 0.32 (0.45 for 4u.c. LCO). This difference might help in linking strain and strain relaxation to ferromagnetism, although further research and theoretical modeling is required.

Recent reports on a $[2\text{uc LTO} - 2\text{uc LCO}]_{10x}$ superlattice of LTO and LCO also found charge transfer an absence of ferromagnetic behavior [59]. This report proposes a G-type antiferromagnetic order of HS Co^{2+} in LCO [59]. Although, a superexchange interaction between half-filled HS Co^{2+} orbitals would generally result in an antiferromagnetic arrangement, antiferromagnetic order would not show any XMCD signal since the amount of spin-up and spin-down electrons would be identical. Therefore, antiferromagnetic order cannot explain our observations. Furthermore, this would only apply to the LTO4|LCO2|LTO4 sample of 100% Co^{2+} . (Note: although bulk LaTiO_3 is a G-type antiferromagnetic material with a T_N around 125K, after charge transfer the Ti^{4+} has no (unpaired) electrons that can order, making exchange bias effects unlikely.)

5.5 Conclusions

In summary, XMCD measurements on various samples of LCO with up to 100% Co^{2+} have been performed. Spin and orbital moments were determined using the sum rules. The spin state of Co^{2+} could not be determined and further investigation and more elaborate modeling and cluster calculations are required. The magnetic properties of ultra-thin films with various Co^{2+} concentrations were investigated and a paramagnetic response was found up to a thickness of 36 u.c. LaCoO_3 . Transport measurements on a LTO4|LCO2|LTO4 sample with 100% Co^{2+} yielded insulating behavior down to 400mK. Furthermore, for the 55nm LCO layers on STO and LAO, ferromagnetic properties were found using XMCD and VSM with a T_c around 75K and low temperature saturated magnetic moments of $0.2 \mu_B/\text{Co}$ on LAO and $0.6 \mu_B/\text{Co}$ on STO.

In conclusion

- Fully strained and well-defined LaCoO_3 layers lead to paramagnetic behavior. Therefore, it can be concluded that strain alone is not enough to yield ferromagnetic LaCoO_3 .
- The spin state of 100% Co^{2+} in LaCoO_3 could not be determined without more extensive modeling.
- Increasing the Co^{2+} content increases the spin moment, but the samples remain paramagnetic.

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Appendix I Resonant Inelastic X-ray Scattering

On the 55nm samples, *2p3d* Resonant Inelastic X-ray Scattering (RIXS) measurements have been performed¹. This technique is based on a photon-in-photon-out process, which can be described by $2p^63d^n \rightarrow 2p^53d^{n+1} \rightarrow 2p^63d^n$ transitions. Therefore, these transitions depend on the specific electronic occupation within the d-orbitals and can be used to extract information the spin states [9]. Note that this information can only be extracted from the measurements by extensive modeling/calculation, which falls beyond the scope of this thesis.

The goal of the experiments was to investigate the different behavior of the two ferromagnetic samples with 55nm LCO on STO and LAO substrates to measurements on a single crystal of LCO. Measurements were performed in the ferromagnetic regime at low temperature (20K) and at the paramagnetic regime at higher temperatures (150K-300K).

As shown by the XRD measurements, these films are partially relaxed which cannot be easily incorporated into the calculations. This makes data analysis less straightforward, although reasonable agreement was achieved between measurements and calculations. No clear spin state transitions were found around 70K, indicating that a sudden spin transition cannot be the trigger for ferromagnetism in these films.

Additional RIXS measurements were performed on fully strained ultra-thin films, to further evaluate the effect of strain and to complete the dataset (bulk, thin films and ultra-thin films). For this purpose, two ultra-thin samples of 10 u.c. LCO have been fabricated on STO and LAO substrates. For these 10 u.c. samples, the sample on STO (LAO) was capped with 2 u.c. of STO (LAO) to protect the thin LCO and have symmetrical top and bottom interfaces. However, this data needs further evaluating.

¹ RIXS measurements and data analysis were performed by Ru-Pan Wang, Debye Institute for Nanomaterials Science, Utrecht University, Netherlands.

Chapter 6

Outlook

6.1 Magnetism

The spin and orbital moments, as extracted from X-ray Magnetic Circular Dichroism (XMCD) measurements, enable the determination of the spin state of Co^{2+} in LaCoO_3 . Although this involves more extensive modeling of the sample, all the relevant inputs such as the lattice constants and valence have already been determined. Moreover, since this data was gathered for most of samples, the calculations can be extended to incorporate these to come to a consistent description of ferromagnetism in LaCoO_3 .

6.2 Conductivity

Apart from magnetic properties, the electric properties of LaCoO_3 are of interest: samples with mixed valence remain insulating due to a spin-blockade effect, but it was calculated that a metal-insulator transition can occur when approaching 100% Co^{2+} (private communication Z. Zhong).

Furthermore, superconductivity has been found in compounds containing copper or iron, but has been more rare in nickel compounds and almost absent for cobalt-based systems (even though cobalt and nickel lie in between copper and iron in the periodic table) [2]. In cuprate superconductors, holes reside in the $d_{x^2-y^2}$ orbital with the remaining orbitals fully occupied [2], [3]. In tensile strained LCO, the $d_{x^2-y^2}$ orbital is found to be lower in energy [4]. Therefore, if a 100% Co^{2+} Low Spin state can be established in LaCoO_3 , this mimics the cuprate electron configuration. In cuprates, the conducting layers are separated by insulating layers, which can be established in a superlattice, as shown by the superconductivity in a $\text{LaNiO}_3\text{-La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ superlattice [5]. For LCO, these insulating layers can be formed by the LaTiO_3 (LTO), required to induce charge transfer. Although, superconductivity in CoO_2 layers has been found in $\text{Na}_x\text{CoO}_2 - y\text{H}_2\text{O}$ [6] and LaCo_2B_2 [7] (both with superconducting temperature around 5K), compared to these compounds, the CoO planes in LaCoO_3 would better resemble the cuprate CuO_2 planes [2], making LaCoO_3 an interesting candidate.

To test this, some preliminary measurements were performed on several samples. These samples were grown on regular SrTiO_3 substrates instead of the conducting Nb-doped STO and the 30 u.c. LAO buffer layer was not used, because

of the possibly conducting LAO-STO interface. Contact was established by ultrasonic wire-bonding to the corners with aluminum wire in order to measure the 4-point resistance in Van der Pauw geometry. All samples remained insulating from room temperature down to temperatures of 2K. Since the LTO4|LCO2|LTO4 sample with 100% Co^{2+} is most interesting, this sample was measured more thoroughly in a dilution refrigerator down to 400mK. Even at these temperatures, no sign of (super)conduction was found and the sample remained insulating. To eliminate bad contacts, the corners were etched and gold contacts pads were deposited, but this made no difference.

The strongly insulating nature of the samples was not expected for several reasons: i) LTO with Ti^{4+} can become conducting [8], [9] ii) LCO with 100% Co^{2+} was predicted to become conducting iii) the LTO-STO superlattices and the LTO-STO interface have been shown to be conducting [9], [10], and iv) low pressure growth on STO can introduce oxygen vacancies in the substrate which can result in conduction. Therefore, this absence of conduction should be further investigated.

6.3 Catalysis

Hydrogen can be an important factor in the pursuit of sustainability, since hydrogen can replace fossil-fuels in cars, but can also be used in fuel cells to generate electricity [12]. This makes the electrochemical process of water splitting highly relevant. The reactions to produce hydrogen and oxygen from water can be divided into 2 parts [13]:

1. Oxygen Evolution Reaction (OER): $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
2. Hydrogen Evolution Reaction (HER): $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$

Of these two partial reactions, the HER is a relatively easy and straightforward 2-electron process [14] (i.e. this involves 2 electrons per H_2). Since the OER reaction involves 4 electrons, this is seen as the more limiting reaction that would benefit from suitable catalysts [14].

Transition metal oxides are seen as promising candidates in catalysis for water splitting ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$), where the ability to take on multiple valence states is crucial for catalytic activity [14]. The exact mechanisms responsible for catalytic activity remain under debate, but it is clear that the activity is linked to (temporarily) donating/accepting electrons at the surface between catalyst and reactant. Therefore, the absorption energy, crystal orientation, orbital

occupation (e_g filling) and valence are seen as important factors [15]–[19]. One of the materials of interest as an OER-catalyst is LaCoO_3 [15]–[19]. Similar to the magnetic properties, it can therefore be interesting to investigate how well-defined ultra-thin LaCoO_3 layers behave, compared to thicker films or bulk. Moreover, interfacial charge transfer can be used to change the valence and orbital occupation.

Some preliminary measurements were performed¹ to test the effect of charge transfer. Three samples have been fabricated as illustrated in **figure 6.1**. All samples were produced on Nb-SrTiO_3 substrates to act as electrode and had a total of 6 unit cells to exclude differences in tunneling currents or polar-catastrophe (see **chapter 2**). The two samples with 2 unit cells of LaCoO_3 can be compared to see the effect of charge transfer and exclude differences due to the different amount of LaCoO_3 . All samples had Pt contacts sputtered on the backside *ex-situ* after fabrication.

The catalytic performance of these samples was measured using standard 3 electrode electrochemical cell with rotating working electrode and oxygen gas inlet (similar to **figure 2b** in [13]). Characterization was performed in 0.1 M KOH solution.

Figure 6.1 Three samples used to test interfacial charge transfer as a way to manipulate catalytic activity in LaCoO_3 .

¹ Collaboration with Christoph Baeumer, Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA.

The results of the electrochemical characterization are given in **figure 6.2**, where clear differences in activity can be observed in these ultra-thin heterostructures. Electrochemical impedance spectroscopy measurements (not shown) indicate that these differences are mostly related to variations in resistance between the different complex oxide interfaces. This indicates that more systematic studies are required to investigate interfacial charge transfer as a way to tune the catalytic activity.

Figure 6.2 Preliminary results on catalytic performance. Clear differences between the samples can be observed, although mostly related to variations in resistance. Measurements performed by Christoph Baeumer, Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA.

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List of publications

Co valence transformation in isopolar LaCoO₃/LaTiO₃ perovskite heterostructures via interfacial engineering

Georgios Araizi-Kanoutas*, Jaap Geessinck*, Nicolas Gauquelin, Steef Smit, Xanthe H. Verbeeck, Shrawan K. Mishra, Peter Bencok, Christoph Schlueter, Tien-Lin Lee, Dileep Krishnan, Jarmo Fatermans, Jo Verbeeck, Guus Rijnders, Gertjan Koster, and Mark S. Golden

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Low-energy orbital excitations in strained LaCoO₃ films

Ru-Pan Wang, Jaap Geessinck, Hebatalla Elnaggar, Yorick A. Birkhölzer, Keisuke Tomiyasu, Jun Okamoto, Boyang Liu, Chao-Hung Du, Di-Jing Huang, Gertjan Koster, and Frank M. F. de Groot

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Saturation and self-absorption effects in the angle-dependent 2p3d resonant inelastic X-ray scattering spectra of Co³⁺

Ru-Pan Wang, Hebatalla Elnaggar, Charles J. Titus, Keisuke Tomiyasu, Jaap Geessinck, Gertjan Koster, Federica Frati, Jun Okamoto, Di-Jing Huang and Frank M. F. de Groot

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Two-dimensional electron systems in perovskite oxide heterostructures: Role of the polarity-induced substitutional defects

Shih-Chieh Lin, Cheng-Tai Kuo, Yu-Cheng Shao, Yi-De Chuang, Jaap Geessinck, Mark Huijben, Jean-Pascal Rueff, Ismael L. Graff, Giuseppina Conti, Yingying Peng, Aaron Bostwick, Eli Rotenberg, Eric Gullikson, Slavomír Nemšák, Arturas Vailionis, Nicolas Gauquelin, Johan Verbeeck, Giacomo Ghiringhelli, Claus M. Schneider, Charles S. Fadley

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Summary

The demand for computational power in electronics is ever rising, resulting in an increasing amount of transistors and other components being used in electronics, which drives a continuous downscaling of electronic components. However, conventional semiconductors are reaching the fundamental limits of downscaling, resulting in a search for alternative materials. In devices based upon conventional semiconductors, the properties originate from the movement of electrons. However, when alternative degrees of freedom can be manipulated, next to electrons, this can lead to increased functionality. A promising alternative can be found in transition metal oxides, because the combination of orbitals, crystal lattice and spin dictates the properties of these materials.

In combining semiconductors or transition metal oxides, the understanding of possible interface effects is vital in optimizing the properties, especially since the influence of the interface becomes larger as device dimensions are decreased. Band-bending at the interface between semiconductors is well established due to the work-function that acts as a reference between materials, but these principles cannot be applied for transition metal oxides, due to the lack of a suitable reference. Moreover, this is further complicated by the shorter length scales on which screening operates and the lack of a well-defined work function for transition metal oxides.

A proposed solution lies in using the oxygen bands as a reference, because of the continuous oxygen octahedral network across the interface. Charge transfer between two different transition metal oxides predicted by this method is investigated experimentally in this thesis. The interface between LaCoO_3 and LaTiO_3 was selected, since the combination of these materials is calculated to result in a large potential for charge transfer among the 3-d transition metal oxides. Moreover, LaCoO_3 exhibits interesting magnetic properties and is investigated as catalyst. Additionally, LaCoO_3 is expected to transition from paramagnetic and insulating to ferromagnetic and conducting upon electron doping (possibly even superconducting).

In computer simulations, perfect materials can be made and combined, whereas this is not always possible in a real system. Therefore, sample layout, fabrication of the samples, and optimization of the deposition conditions have been subjected to careful scrutiny. A low background pressure is desired during deposition of LaTiO_3 , whereas a higher background pressure is required for the

fabrication of LaCoO_3 . Therefore, the decision was made to use an intermediate pressure of 2×10^{-3} mbar during the deposition and optimize the other parameters accordingly. Care has been taken to verify the ABO_3 perovskite structure, since other phases can result in a different valence. Therefore, the crystal structure has been evaluated using a combination of Scanning Transmission Electron Microscopy, X-ray Diffraction and Reflection High-Energy Electron Diffraction measurements. The adopted fabrication strategy proved to be successful for the various combinations of ultra-thin layers as used in this research.

Several electron and x-ray spectroscopy techniques have been used to determine the valence of the various transition metals in order to investigate the interfacial charge transfer. It is difficult to distinguish between interfacial charge transfer and valence changes related to oxygen vacancies. However, by varying the combinations of materials and the thickness of LaCoO_3 , it has become clear that interfacial charge transfer is indeed occurring. Importantly, this charge transfer was found to be severely reduced by separating the LaCoO_3 and LaTiO_3 by a layer of LaAlO_3 with a thickness of two or more unit cells.

After establishing the charge transfer towards LaCoO_3 , the resulting properties were investigated. The ultra-thin LaCoO_3 layers are paramagnetic and non-conducting without charge transfer, and remain so with charge transfer, although the additional electrons result in a larger amount of spins that can be polarized. The paramagnetic behavior does indicate that only strain induced by the substrate is not enough to result in ferromagnetic behavior (contrary to what is generally believed). Finally, preliminary measurements were performed regarding the influence of charge transfer on the catalytic performance of LaCoO_3 .

In conclusion, this thesis indicates that charge transfer takes place at the interface between LaCoO_3 and LaTiO_3 (as predicted). These results bring us closer to understanding interfaces between transition metal oxides.

Samenvatting

De vraag naar computerkracht in elektronica neemt continue toe, waardoor steeds meer transistoren en andere componenten in elektronica verwerkt worden. Om die reden dienen deze componenten voortdurend verkleind te worden. Echter zitten de conventionele halfgeleiders steeds dichterbij hun fundamentele limiet aan voor verdere verkleining, waardoor de zoektocht naar alternatieve materialen toe neemt. In componenten gebaseerd op conventionele halfgeleiders komt de werking uitsluitend middels de manipulatie van elektronen. Echter, als naast elektronen ook andere vrijheidsgraden gemanipuleerd kunnen worden, kan dit leiden tot een verhoogde functionaliteit. Een veelbelovend alternatief kan worden gevonden in de transitietetraoxides, doordat in deze materialen de combinatie van orbitalen, kristalrooster en spin de eigenschappen dicteert.

Bij het combineren van halfgeleiders of transitietetraoxides is het van belang om mogelijke effecten op het grensvlak te begrijpen om zo de eigenschappen te optimaliseren. Helemaal omdat de rol van het grensvlak groter wordt naarmate componenten kleiner worden. De verbuiging van elektronenbanden op grensvlakken tussen halfgeleiders wordt beschreven door de werkfuncties van de materialen die als referentie fungeert. Deze methodiek kan echter niet gebruikt worden bij transitietetraoxides, omdat hier een geschikte referentie ontbreekt. Daarnaast wordt de situatie in transitietetraoxides verder bemoeilijkt door kortere lengteschalen waarop lading zich vereffend en het ontbreken van een eenduidige werkfunctie.

Een voorgestelde oplossing gaat uit van zuurstofbanden als referentie, door het continue rooster van zuurstof-octaëders op het grensvlak. De ladingsoverdracht op het grensvlak tussen transitietetraoxides, voorspeld met deze methode, is experimenteel getest in dit proefschrift. Het grensvlak tussen LaTiO_3 en LaCoO_3 is hiervoor geselecteerd aangezien er berekend is dat deze combinatie onder de 3d-transitietetraoxides groot potentieel heeft voor ladingsoverdracht. Daarnaast kent LaCoO_3 interessante magnetische eigenschappen en wordt dit materiaal als katalysator onderzocht. Ook wordt er verwacht dat LaCoO_3 van isolerend en niet-magnetisch kan veranderen naar geleidend en magnetisch wanneer er extra elektronen toegevoegd worden (mogelijk zelfs supergeleidend).

In computersimulaties kunnen perfecte materialen gemaakt en gecombineerd worden, terwijl dat niet altijd mogelijk is in een echt materiaalsysteem. Vandaar dat er in dit proefschrift aandacht besteed is aan sample-ontwerp, het fabriceren van de samples en het optimaliseren van de depositie-condities. Waar LaTiO_3 eigenlijk gegroeid dient te worden in de zuurstofarme omgeving, heeft LaCoO_3 een zuurstofrijke depositie-omgeving nodig. Uiteindelijk is er gekozen voor een zuurstofdruk van 2×10^{-3} mbar tijdens de depositie en zijn de andere parameters hierop geoptimaliseerd. Er is kritisch gekeken naar de juiste ABO_3 perovskiet-structuur, aangezien afwijkende fases kunnen resulteren in een verandering van valentie-toestand. De kristalstructuur is daarom onderzocht met Scanning Transmission Electron Microscopy, X-ray Diffraction en Reflection High-Energy Electron Diffraction metingen. Voor de verschillende combinaties van ultradunne lagen die gebruikt zijn in dit onderzoek, bleek deze fabricage strategie succesvol.

Om de ladingsoverdracht te meten is er gebruik gemaakt van verschillende röntgen- en elektronenspectroscopie technieken om de valentie van de verschillende transitie-metalen te meten. Het is lastig onderscheid te maken tussen ladingsoverdracht op het grensvlak en valentie verandering door zuurstof deficiëntie. Echter, door de combinaties van materialen en de diktes van LaCoO_3 te variëren is duidelijk geworden dat er inderdaad ladingsoverdracht plaats vindt aan het grensvlak. Verder is een belangrijke vinding dat deze ladingsoverdracht sterk verminderd kan worden door LaTiO_3 van LaCoO_3 te scheiden door er twee of meer eenheidscellen LaAlO_3 tussen te plaatsen.

Na aantoning van ladingsoverdracht in LaCoO_3 zijn hiervan de eigenschappen onderzocht. De ultradunne LaCoO_3 lagen zijn en blijven paramagnetisch en isolerend na ladingsoverdracht, hoewel de extra elektronen zorgen voor een groter aantal spins dat gepolariseerd kan worden. Het paramagnetische gedrag in deze ultradunne lagen toont echter wel aan dat alleen de spanning vanuit het substraat niet genoeg is om LaCoO_3 magnetisch te maken (in tegenstelling tot wat vaak aangenomen wordt). Als laatste zijn inleidende metingen verricht naar het effect van ladingsoverdracht op de katalyserende werking van LaCoO_3 .

In conclusie, dit proefschrift toont aan dat ladingsoverdracht plaats vindt tussen LaCoO_3 en LaTiO_3 (zoals voorspeld). Met deze resultaten zijn we een stap dichterbij het begrijpen van grensvlakken tussen transitie-metaaloxides.

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