Structural, electronic and magnetic properties of infinite-layer nickelate heterostructures and polycrystals

Von der Fakultät Mathematik und Physik der Universität Stuttgart zur Erlangung der Würde eines Doktors der Naturwissenschaften (Dr.rer. nat.) genehmigte Abhandlung

Vorgelegt von

Roberto Antonio Ortiz

aus Tegucigalpa, Honduras

Hauptberichter:	Prof. Dr. Bernhard Keimer
Mitberichter:	Prof. Dr. Harald Giessen
Prüfungsvorsitzende:	Prof. Dr. Maria Daghofer

Tag der Einreichung:	27.06.2022
Tag der mündlichen Prüfung:	27.07.2022

Max-Planck-Institut für Festkörperforschung Universität Stuttgart

Stuttgart, 2022

Contents

Al	bstract	v			
Ζu	Zusammenfassung ix				
Al	Abbreviations xiii				
In	troduction: Transition Metal Oxides	1			
1	The Rare-Earth Nickelates 1.1 Bulk properties of perovskite nickelates 1.2 Perovskite nickelate heterostructures 1.3 Superconductivity in infinite-layer nickelates	7 7 15 24			
2	Synthesis: growth and chemical treatment2.1Pulsed Laser Deposition (PLD)2.2Topochemical reactions in oxides	35 35 39			
3	Characterization Techniques3.1Elastic x-ray scattering.3.2X-ray sources.3.3Transport Measurements: Resistivity.	43 43 60 64			
4	$ \begin{array}{llllllllllllllllllllllllllllllllllll$	67 67 71 80 88 94 103			
5	Polycrystalline infinite-layer nickelates 5.1 LaNiO _{2+δ} and NdNiO _{2+δ} samples 5.2 Magnetic correlations in bulk infinite-layer nickelates	109 110 112			
6	Summary and outlook	119			
A	ppendices	125			
A	A Crystal structure factors 12:				
В	XAS of pristine nickelate superlattices	127			

C XAS at the Gd, Dy, Sc and Ti absorption edges	129
${f D}~~{f LaNiO}_{2+\delta}/{f SrTiO}_3~{f superlattices}$	131
E Structural model and fittings from reflectivity	133
F Reflectivity preliminary data	135
G Reflectivity homogeneous charge fits	137
H Reflectivity uniqueness test results	139
Bibliography	141
Acknowledgements	167
List of Publications	169

Abstract

Materials composed of transition metal oxides possess various properties that arise from the correlated interplay between their elements. The interaction between the components of these materials results from the synergy involving the spin, charge, orbital, and structural degrees of freedom. Therefore, tuning and controlling these degrees of freedom by fabrication processes or external stimuli like temperature, pressure, or chemical doping becomes a central topic in current condensed matter research. Nowadays, modern technological developments and synthesis routes enable the combination of compounds to achieve modifications of one or more of their individual properties in the resultant composite. This procedure can also trigger different electronic, magnetic, and lattice correlations that allow the emergence of complex phases like multiferroicity, ferroelectricity, and spin glassiness and the observation of exciting quantum phenomena such as superfluidity and unconventional superconductivity. In particular, an oxide heterostructure is a material created by depositing several layers of one or more compounds on top of a single crystal substrate, which is usually orders of magnitude larger in size. One particular region of interest is the interface between these oxides, where additional effects like spatial confinement, charge transfer, structural distortions, and exchange interactions play an essential role. However, the correct mixture of parameters used to achieve new fascinating phenomena requires a deep understanding of the complex physics that governs these systems individually. In addition to heterostructuting, another way to obtain new properties in as-grown materials is by altering their stoichiometry. This modification can be achieved by producing a chemical reaction ignited by a reactant compound. In the case of oxide materials, removing oxygen atoms leads to significant changes in the electronic and structural properties and the occurrence of phase transitions.

In this doctoral thesis, we focus on the study of a prominent group of transition metal oxides, the infinite-layer rare earth nickelates with composition $RENiO_2$. At present, these materials can only be obtained by the synthesis of the perovskite $RENiO_3$ and their subsequent topotactic transformation. Much research on these materials has been devoted to bulk crystalline samples; however, the investigations have also been focused on the thin film form in the last decades. The perovskite rare-earth nickelates, which are the precursor of the infinite-layer phase, are materials that present a robust metal-to-insulator transition and an exotic antiferromagnetic order. These properties and their correlation have been studied for many years, and the results from the analysis have been portrayed in a rich phase diagram. On the other hand, the infinite-layer nickelates, relatively unexplored in comparison to their parent compounds, have been regarded as paramagnetic metals with no long-range magnetic order in their thin-film form. Recent scientific studies on chemically doped infinite-layer nickelates films found unconventional superconductivity, an exotic state of matter with potential applications to new technologies. Contrastingly, the polycrystalline counterparts of the infinite-layer films show a paramagnetic and semiconducting trend with no signs of magnetic ordering. This difference is also translated to the chemically doped nickelates, where up to date, no signs of superconductivity have been found in bulk. The discrepancy between heterostructures and bulk indicates that much work needs to be done to understand the intrinsic properties of the infinite-layer materials.

Here we propose new routes, which pursue the stabilization of superconductivity in superlattices composed of nickelates and band gap insulators, and the analysis of the infinitelayer nickelate bulk compound by multiple methods. Our results allowed us to identify a robust spin glass behavior in the polycrystalline samples, which was not previously studied in detail. Furthermore, we synthesized a new type of superlattice with a large orbital polarization, a property that is relevant in many correlated oxides. In addition, we present a collection of solid state techniques designed to monitor changes in the physical properties of the specimens throughout the transformation process. These techniques include experiments designed to characterize the structural and transport properties. Additionally, other complex methods comprise measurements performed at large-scale facilities where light is absorbed or scattered by the atoms in the material. Such advanced techniques allow the tuning of photon energies, which are in resonance with specific electronic transitions of the constituent elements. These experiments allowed us to subtract and quantify microscopic parameters, such as the orbital polarization, which gives information about the electronic configuration in transition metal oxides. We divide our analysis into two main parts associated with the study of infinite-layer nickelates. The first part is related to the design of a new material by a two-step process of heterostructuring and chemical treatment of the parent perovskite form. To this end, we tested superlattice combinations where the first compound was a nickelate material and the second was a band gap insulator called the blocking material. In addition, the blocking (buffer) materials were divided into three groups: the scandates, the La-based compounds, and the titanates.

We start our study by performing a detailed characterization of superlattices combining nickelates and scandates. Our x-ray diffraction measurements show that reducing superlattices is possible and that a system with mainly infinite-layer phase is consistently achieved. Electrical transport measurements on the reduced samples show a metallic trend with a non-Fermi liquid temperature dependence, similar to the one found in the normal state of chemically doped nickelate superconductors, although no signs of superconductivity were found in our samples. X-ray absorption measurements performed on resonance suggest that the reduction process is layer selective, given that there is no change in the valence state of the elements in the buffer layers. Our spectroscopic experiments also suggest the presence of a transition from a dominant $3d^9$ electronic configuration to a mixed $3d^8 + 3d^9$ -like orbital polarization in the Ni ions when the buffer layers approach to the two-dimensional limit (i.e., two unit cells). Furthermore, the same measurements show that a change of the A-cation element in the buffer layers yields no significant alterations to the superlattices' structural, electronic, and transport properties. On the other hand, changing the A-cation element in the nickelate layers leads to substantially different reducing conditions for the superlattice, suggesting that the composition of the nickelate slabs mainly drives the treatment process.

Next, we move to the study of nickelate superlattices where both constituent materials have Lanthanum as A-cation element. Fit models of the diffraction measurements indicate that each nickelate slab is divided into two regions, one with a pyramidal configuration at the interfaces and the other with an infinite-layer phase in the center. Moreover, the pyramidal structure accounts for approximately one unit cell at each interface, whereas the rest of the layers within the nickelate slab have a square planar configuration. In addition, we found that the reduction process is reversible, which means that the treated superlattices can go back to their unreduced state. This reversibility of the process points towards the preservation of the structural frame and makes the nickelate superlattices a good candidate for applications such as gas sensing. Furthermore, our x-ray absorption measurements indicate that the superlattices are more susceptible to a B-cation substitution than to an A-cation change in the buffer layers. In particular, substituting Gallium with Aluminium brings the orbital polarization of Ni from $3d^9$ to a mixed electronic configuration, which resembles more a $3d^8$ state.

The third group of superlattices analyzed in this thesis includes the combination of a nickelate together with SrTiO₃. A systematic increase in the number of unit cells in the nickelate slabs is consistent with a transition from an insulating to a metallic state. This result is reproduced in both Neodymium and Lanthanum based nickelates. Our experimental results yield slight differences between the two types of superlattices except for minor variations in the preferential orbital occupation in favor of the $3d_{x^2-y^2}$ orbitals. Despite achieving unit cells with the infinite-layer phase and a $3d^9$ electronic configuration, in analogy to cuprates and the newly discovered nickelate superconductors, our superlattices do not show a superconducting transition. Comparing the normalized linear dichroism produced by cuprates superconductors and our nickelates superlattices yields similar lineshapes with substantially less intensity for the nickelates. This result suggests a lower orbital polarization in Ni¹⁺ compared to Cu²⁺, which is probably related to effects originating at the interfaces and during the reduction process.

We employ resonant reflectivity to obtain the orbital occupation and valence state deep profiles in our superlattices. The results indicate that the major contribution to the total linear dichroism at the Ni- $L_{2,3}$ edges originates from the inner layers within the nickelate slabs. The same linear dichroism is obtained in a fitting model with interfacial Ni²⁺ and inner Ni¹⁺ layers. These results are in good agreement with theoretical calculations, which suggest that added holes will situate at the interface layers, whereas additional electrons will distribute evenly in the nickelate block. In addition, using spectroscopic measurements, we were able to quantify the orbital polarization in our superlattices and the ratio of holes in the Ni e_g orbitals. Substituting the buffer layer yields different values of the orbital polarization, modifications in the transport properties and a change in the number of interfacial nickelate layers. Comparing the O-K edge of all superlattices allowed us to find common features associated with the different Ni valence states and their hybridization with oxygen.

The second part of the thesis focuses on studying bulk LaNiO₂ samples. We performed various measurements on our samples to characterize their structural and magnetic properties. Specific heat, muon spin rotation, and susceptibility measurements confirm that there is no long-range magnetic order at any measurable temperature, as was established in previous scientific studies. Susceptibility measurements found a spin glass behavior with a temperature onset obtained around 15 K. A close observation of the intrinsic susceptibility shows a non-Curie-Weiss behavior similar to that observed in superconducting cuprates. Moreover, further comparison between cuprates and nickelates indicates that both materials present a spin glass behavior in the underdoped region, with no doping for nickelates and small doping for cuprates.

The procedures we describe in this thesis manifest the viability of designing novel materials by heterostructuring and the stabilization of exotic phases through topotactic reactions. In addition, we demonstrate an example of how theoretical methods, in combination with experiments and spectroscopic techniques, allow us to predict and describe the structural and electronic configuration in newly fabricated compounds. Our analysis gives quantitative results on essential parameters that enable the comparison between our materials and similar oxide compounds. One of such microscopic parameters is the orbital polarization, which we have fine-tuned to produce changes in the macroscopic properties. Therefore, this thesis opens a new route to modify the variety of physical properties in transition metal oxides by combining synthesis methods to obtain next-generation compounds.

Zusammenfassung

Materialien aus Übergangsmetalloxiden besitzen verschiedene Eigenschaften, die sich aus dem Zusammenspiel ihrer Elemente ergeben. Die Wechselwirkung zwischen den Komponenten dieser Materialien ergibt sich aus der Synergie von Spin-, Ladungs-, Orbital- und strukturellen Freiheitsgraden. Daher wird die Kontrolle dieser Freiheitsgrade durch Herstellungsprozesse oder externe Stimuli wie Temperatur, Druck oder chemische Dotierung zu einem zentralen Thema in der aktuellen Forschung der kondensierten Materie. Heutzutage ermöglichen moderne technologische Entwicklungen und Synthesewege die Kombination von Materialien, um Modifikationen einer oder mehrerer ihrer individuellen Eigenschaften im resultierenden Verbundstoff zu erreichen. Diese Verfahren kann auch verschiedene elektronische, magnetische und Gitterkorrelationen auslösen, die die Entstehung komplexer Phasen wie Multiferroizität, Ferroelektrizität und Spinglasigkeit sowie die Beobachtung spannender Quantenphänomene wie Suprafluidität und unkonventionelle Supraleitung ermöglichen. Im Besonderen ist eine Oxid-Heterostruktur ein Material, das durch Abscheiden mehrerer Schichten aus einer oder mehreren Verbindungen auf einem Einkristallsubstrat erzeugt wird, das normalerweise um Größenordnungen größer ist. Ein besonders interessanter Bereich ist die Grenzfläche zwischen diesen Oxiden, in welchem zusätzliche Effekte wie räumliche Begrenzung, Ladungstransfer, strukturelle Verzerrungen und Austauschwechselwirkungen eine wesentliche Rolle spielen. Die richtige Mischung von Parametern, die verwendet werden, um neue faszinierende Phänomene zu erzielen, erfordert jedoch ein tiefes Verständnis der komplexen Physik, die diese Systeme individuell steuert. Neben der Heterostrukturierung besteht ein weiterer Weg, um neue Eigenschaften in gewachsenen Materialien zu erhalten, darin, ihre Stöchiometrie zu ändern. Diese Modifikation kann erreicht werden, indem eine chemische Reaktion erzeugt wird, die durch eine Reaktantenverbindung gezündet wird. Bei oxidischen Materialien führt die Entfernung von Sauerstoffatomen zu signifikanten Änderungen der elektronischen und strukturellen Eigenschaften und dem Auftreten von Phasenübergängen.

In dieser Doktorarbeit konzentrieren wir uns auf die Untersuchung einer bekannten Gruppe von Übergangsmetalloxiden, den unendlich schichtigen Seltenerd-Nickelaten mit der Zusammensetzung RENiO₂. Diese Materialien können derzeit nur durch die Synthese des Perowskits RENiO₃ und deren anschließende topotaktische Umwandlung gewonnen werden. Ein Großteil der Forschung zu diesen Materialien wurde kristallinen Massenproben gewidmet; allerdings haben sich die Untersuchungen in den letzten Jahrzehnten auch auf die Dünnschichtform konzentriert. Die Perowskit-Seltenerd-Nickelate, die der Vorläufer der unendlichen Schichtphase sind, sind Materialien, die einen robusten Metall-zu-Isolator-Übergang und eine exotische antiferromagnetische Ordnung aufweisen. Diese Eigenschaften und ihre Korrelation werden seit vielen Jahren untersucht, und die Ergebnisse der Analyse wurden in einem reichhaltigen Phasendiagramm dargestellt. Andererseits wurden die im Vergleich zu ihren Ausgangsverbindungen relativ unerforschten Nickelate mit unendlichen Schichten als paramagnetische Metalle ohne magnetische Fernordnung in ihrer Dünnschichtform betrachtet. Jüngste wissenschaftliche Studien zu chemisch dotierten Nickelatfilmen mit unendlichen Schichten ergaben unkonventionelle Supraleitfähigkeit, einen exotischen Zustand der Materie mit potenziellen Anwendungen für neue Technologien. Im Gegensatz dazu zeigen die polykristallinen Gegenstücke der Schichten mit unendlichen Schichten einen paramagnetischen und halbleitenden Trend ohne Anzeichen einer magnetischen Ordnung. Dieser Unterschied überträgt sich auch auf die chemisch dotierten Nickelate, bei denen bis heute keine Anzeichen von Supraleitung in der Masse gefunden wurde. Die Diskrepanz zwischen Heterostrukturen und Volumen weist darauf hin, dass viel Arbeit erforderlich ist, um die intrinsischen Eigenschaften der Materialien mit unendlichen Schichten zu verstehen.

Hier schlagen wir neue Wege vor, die die Stabilisierung der Supraleitung in Übergittern aus Nickelaten und Bandlückenisolatoren und die Analyse der unendlichen Nickelat-Massenverbindung durch mehrere Methoden verfolgen. Unsere Ergebnisse ermöglichten es uns, ein robustes Spin-Glas-Verhalten in den polykristallinen Proben zu identifizieren, das zuvor nicht im Detail untersucht wurde. Darüber hinaus haben wir eine neue Art von Übergittern mit einer großen Orbitalpolarisation synthetisiert, eine Eigenschaft, die in vielen korrelierten Oxiden relevant ist. Desweiteren, hinaus präsentieren wir eine Sammlung von Festkörpertechniken, die entwickelt wurden, um Anderungen der physikalischen Eigenschaften der Proben während des Transformationsprozesses zu überwachen. Diese Techniken umfassen Experimente, die zur Charakterisierung der Struktur- und Transporteigenschaften entwickelt wurden. Außerdem hinaus umfassen andere komplexe Methoden Messungen an Großanlagen, bei denen Licht von den Atomen im Material absorbiert oder gestreut wird. Solche fortschrittlichen Techniken ermöglichen die Abstimmung von Photonenengien, die in Resonanz mit spezifischen elektronischen Ubergängen der konstituierenden Elemente stehen. Diese Experimente ermöglichten es uns, mikroskopische Parameter wie die Orbitalpolarisation, die Informationen über die elektronische Konfiguration in Übergangsmetalloxiden liefert, zu subtrahieren und zu quantifizieren.

Wir unterteilen unsere Analyse in zwei Hauptteile, die mit der Untersuchung von Nickelaten mit unendlichen Schichten verbunden sind. Der erste Teil bezieht sich auf das Design eines neuen Materials durch einen zweistufigen Prozess aus Heterostrukturierung und chemischer Behandlung der Ausgangsform des Perowskits. Zu diesem Zweck haben wir Übergitterkombinationen getestet, bei denen die erste Verbindung ein Nickelatmaterial und die zweite ein Bandlückenisolator war, der als Sperrmaterial bezeichnet wird. Außerdem wurden die blockierenden (Puffer-)Materialien in drei Gruppen eingeteilt: die Scandate, die La-basierten Verbindungen und die Titanate. Wir beginnen unsere Studie mit einer detaillierten Charakterisierung von Supergittern, die Nickelate und Scandate kombinieren. Unsere Röntgenbeugungsmessungen zeigen, dass die Reduktion von Übergittern möglich ist und dass durchgängig ein System mit hauptsächlich unendlich schichtiger Phase erreicht wird. Elektrische Transportmessungen an den reduzierten Proben zeigen einen metallischen Trend mit einer Nicht-Fermi-Flüssigkeits-Temperaturabhängigkeit, ähnlich derjenigen, die im Normalzustand von chemisch dotierten Nickelat-Supraleitern gefunden wird, obwohl in unseren Proben keine Anzeichen von Supraleitung gefunden wurden. Bei Resonanz durchgeführte Röntgenabsorptionsmessungen legen nahe, dass der Reduktionsprozess schichtselektiv ist, da es keine Anderung des Wertigkeitszustands der Elemente in den Pufferschichten gibt. Unsere spektroskopischen Experimente deuten auch auf das Vorhandensein eines Übergangs von einer dominanten elektronischen $3d^9$ -Konfiguration zu einer gemischten $3d^8 + 3d^9$ -ähnlichen Orbitalpolarisation in den Ni-Ionen hin, wenn sich die Pufferschichten der Grenze der Zweidimensionalität annähern (d. h. zwei Einheitszellen). Darüber hinaus zeigen dieselben Messungen, dass eine Änderung des A-Kationen-Elements in den Pufferschichten keine signifikanten Änderungen der strukturellen, elektronischen und Transporteigenschaften der Übergitter ergibt. Andererseits führt die Änderung des A-Kationen-Elements in den Nickelatschichten zu wesentlich unterschiedlichen Reduktionsbedingungen für das Übergitter, was darauf hindeutet, dass die Zusammensetzung der Nickelatplatten hauptsächlich den Behandlungsprozess antreibt.

Als nächstes gehen wir zur Untersuchung von Nickelat-Übergittern über, bei denen beide konstituierenden Materialien Lanthan als A-Kationenelement aufweisen. Angepasste Modelle der Beugungsmessungen zeigen, dass jede Nickelatplatte in zwei Bereiche unterteilt ist, einen mit einer pyramidenförmigen Konfiguration an den Grenzflächen und den anderen mit einer unendlichen Schichtphase in der Mitte. Darüber hinaus macht die Pyramidenstruktur etwa eine Einheitszelle an jeder Grenzfläche aus, während der Rest der Schichten innerhalb der Nickelatplatte eine quadratische planare Konfiguration hat. Außerdem fanden wir heraus, dass der Reduktionsprozess reversibel ist, was bedeutet, dass die behandelten Übergitter in ihren nicht reduzierten Zustand zurückkehren können. Diese Reversibilität des Prozesses weist auf die Erhaltung des strukturellen Rahmens hin und macht die Nickelat-Übergitter zu einem guten Kandidaten für Anwendungen wie Gassensorik. Dass die Übergitter anfälliger für eine B-Kationen-Substitution als für eine A-Kationen-Anderung in den Pufferschichten sind, zeigen uns darüber hinaus die Röntgenabsorptionsmessungen. Insbesondere das Ersetzen von Gallium durch Aluminium bringt die Orbitalpolarisation von Ni von $3d^9$ zu einer gemischten elektronischen Konfiguration, die eher einem $3d^8$ -Zustand ähnelt.

Die dritte Gruppe von Übergittern, die in dieser Arbeit analysiert wird, beinhaltet die Kombination eines Nickelats zusammen mit SrTiO₃. Eine systematische Erhöhung der Anzahl von Einheitszellen in den Nickelatplatten steht im Einklang mit einem Übergang von einem isolierenden in einen metallischen Zustand. Dieses Ergebnis wird sowohl bei Nickelaten auf Neodym- als auch Lanthanbasis reproduziert. Unsere experimentellen Ergebnisse zeigen geringfügige Unterschiede zwischen den beiden Arten von Ubergittern, abgesehen von geringfügigen Abweichungen in der bevorzugten Orbitalbesetzung zugunsten der $3d_{x^2-y^2}$ -Orbitale. Obwohl Einheitszellen mit der unendlichen Schichtphase und einer elektronischen Konfiguration von $3d^9$ erreicht werden, zeigen unsere Übergitter in Analogie zu Cupraten und den neu entdeckten Nickelat-Supraleitern keinen supraleitenden Übergang. Ein Vergleich des normalisierten linearen Dichroismus, der von Cuprat-Supraleitern und unseren Nickelat-Übergittern erzeugt wird, ergibt ähnliche Linienformen mit wesentlich geringerer Intensität für die Nickelate. Dieses Ergebnis deutet auf eine niedrigere Orbitalpolarisation in Ni¹⁺ im Vergleich zu Cu²⁺ hin, was wahrscheinlich mit Effekten zusammenhängt, die an den Grenzflächen und während des Reduktionsprozesses entstehen.

Wir verwenden resonante Reflektivität, um die tiefen Profile der Orbitalbesetzung und des Valenzzustands in unseren Übergittern zu erhalten. Die Ergebnisse zeigen, dass der Hauptbeitrag zum gesamten linearen Dichroismus an den Ni- $L_{2,3}$ -Kanten von den inneren Schichten innerhalb der Nickelatplatten stammt. Derselbe lineare Dichroismus wird in einem Anpassungsmodell mit Ni²⁺-Grenzflächen und inneren Ni¹⁺-Schichten erhalten. Diese Ergebnisse stimmen gut mit theoretischen Berechnungen überein, was darauf hindeutet, dass sich zusätzliche Löcher an den Grenzflächenschichten befinden, während sich zusätzliche Elektronen gleichmäßig im Nickelatblock verteilen. Außerdem können wir durch spektroskopische Messungen die Orbitalpolarisation in unseren Übergittern und das Verhältnis der Löcher in den Ni e_g-Orbitalen quantifizieren. Der Austausch der Pufferschicht führt zu anderen Werten der Orbitalpolarisation, zu Modifikationen der Transporteigenschaften und zu einer Änderung der Anzahl der Nickelat-Grenzflächenschichten. Der Vergleich der O-K-Kante aller Übergitter ermöglichte es uns, gemeinsame Merkmale zu finden, die mit den verschiedenen Ni-Valenzzuständen und ihrer Hybridisierung mit Sauerstoff verbunden sind.

Der zweite Teil der Arbeit konzentriert sich auf die Untersuchung von LaNiO₂ Massenproben. Wir haben verschiedene Messungen an unseren Proben durchgeführt, um ihre strukturellen und magnetischen Eigenschaften zu charakterisieren. Spezifische Wärme, Myon-Spin-Rotation und Suszeptibilitätsmessungen bestätigen, dass es bei keiner messbaren Temperatur eine magnetische Ordnung mit großer Reichweite gibt, wie in früheren wissenschaftlichen Studien festgestellt wurde. Suszeptibilitätsmessungen ergaben ein Spin-Glas-Verhalten mit einem Temperatureinsatz von etwa 15 K. Eine genaue Beobachtung der intrinsischen Suszeptibilität zeigt ein Nicht-Curie-Weiss-Verhalten ähnlich dem, das bei supraleitenden Cupraten beobachtet wird. Darüber hinaus zeigt ein weiterer Vergleich zwischen Cupraten und Nickelaten, dass beide Materialien ein Spin-Glas-Verhalten in dem unterdotierten Bereich zeigen, ohne Dotierung für Nickelate und geringer Dotierung für Cuprate.

Die Verfahren, die wir in dieser Dissertation beschreiben, demonstrieren die Realisierbarkeit des Designs neuartiger Materialien durch Heterostrukturierung und die Stabilisierung exotischer Phasen durch topotaktische Reaktionen. Darüber hinaus geben wir ein Beispiel dafür, wie theoretische Methoden in Kombination mit Experimenten und spektroskopischen Techniken es uns ermöglichen, die strukturelle und elektronische Konfiguration in neu hergestellten Verbindungen vorherzusagen und zu beschreiben. Unsere Analyse liefert quantitative Ergebnisse zu wesentlichen Parametern, die den Vergleich zwischen unseren Werkstoffen und ähnlichen Oxidverbindungen ermöglichen. Einer dieser mikroskopischen Parameter ist die Orbitalpolarisation, die wir fein abgestimmt haben, um Änderungen in den makroskopischen Eigenschaften zu erzeugen. Daher eröffnet diese Dissertation einen neuen Weg, um die Vielzahl physikalischer Eigenschaften in Übergangsmetalloxiden zu modifizieren, indem Synthesemethoden kombiniert werden, um Verbindungen der nächsten Generation zu erhalten.

Abbreviations

AFM	Antiferromagnet/antiferromagnetic
ARPES	Angle-resolved photoemission spectroscopy
a. u.	arbitrary units
BESSY II	Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung II,
	synchrotron facility in Berlin, Germany
\mathbf{DFT}	Density-functional theory
DMFT	Dynamical mean-field theory
DSO	Dysprosium scandate, i.e., $DyScO_3$
\mathbf{E}_F	Fermi energy
\mathbf{FM}	Ferromagnet/ferromagnetic
FY	Fluorescence yield
GSO	Gadolinium scandate, i.e., $GdScO_3$
LAO	Lanthanum aluminate, i.e., $LaAlO_3$
LD	Linear dichroism
LNO	Lanthanum nickelate, i.e., $LANiO_3$
LGO	Lanthanum gallate, i.e., $LAGaO_3$
LSAT	Lanthanum aluminate strontium aluminium tantalate, i.e.,
	$(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{TaAlO}_6)_{0.7}$
MBE	Molecular-beam epitaxy
$\mu \mathbf{SR}$	muon spin rotation
MIT	Metal-to-insulator transition
MPI-FKF	Max Planck Institut fur Festkörperforschung
NLD	Normalized linear dichroism
NNO	Neodimyum nickelate, i.e., $NdNiO_3$

p. c.	pseudo-cubic
PLD	Pulsed laser deposition
PPMS	Physical properties measurement system
RXR	Resonant x-ray reflectivity
RXS	Resonant x-ray scattering
<i>RE</i> NiO	Rare-earth nickelate
\mathbf{RP}	Ruddlesden-Popper
\mathbf{SC}	Superconductor
\mathbf{SL}	Superlattice
SOC	Spin-orbit coupling
STEM	Scanning transmission electron microscopy
STO	Strontium titanate, i.e., $\rm SrTiO_3$
TEY	Total electron yield
TEM	Transmission electron microscope
\mathbf{TF}	Thin film
TMO	Transition metal oxide
u. c.	unit cell
XAS	X-ray absorption spectroscopy
XLD	X-ray linear dichroism
XRD	X-ray diffraction
XRR	X-ray reflectivity

Introduction: Transition Metal Oxides

Strongly correlated materials like the transition metal oxides (TMOs) are among the most studied functional systems in modern physics. They possess a large variety of structural, electronic, magnetic, and optical properties that can be controlled to produce cooperative effects which give rise to novel and fascinating phenomena. Among these alluring phenomena appear the metal-to-insulator transition (MIT), multiferroicity, colossal magnetoresistance, ferroelectricity, and high-temperature superconductivity. These effects emerge when there is a specific combination of the spin, charge, orbital and structural degrees of freedom, which in the TMOs are mainly governed by electrons in the *d*-orbitals. More specifically, in the case of 3d TMOs, the transition metal strongly interacts with the oxygen ligands, resulting in a distinct electronic behavior. This chapter will discuss the structural and electronic properties of TMOs. However, a broader description of the topic can be found in Refs. 1–3.

Crystal structure of the ABO₃ perovskites

TMOs of the form ABO₃ are perovskite materials composed of three elements, namely a large cation A, which is usually (but not always) a rare-earth element, a small cation B, i.e., the transition metal, and the oxygen anion O. These compounds derive from the more general Ruddlesden-Popper series $A_{n+1}B_nO_{3n+1}$, for $n = \infty$. The ideal ABO₃ perovskite structure belongs to the space group with $Pm\bar{3}m$ symmetry and consists of a cubic lattice with one A cation at the center and one BO₆ octahedron at each of the corners of the cube (see Fig. 1 a). This configuration fulfills two conditions: (i) the electrical neutrality condition, where cations A and B have a combined valence state of +6 to account for the three O^{-2} in the chemical formula and (ii) a geometrical relation $a = (r_B + r_O) = \sqrt{2} (r_A + r_O)$ that associates the ionic radii of each element (r_A, r_B, r_O) and the lattice constant a of the material, which in this case is the same for all three crystallographic directions ($a = a_x = a_y = a_z$). The latter criterion requires that the arrangement of atoms leaves the least amount of space in the unit cell, forming the most optimal ionic configuration in this way.

The ABO₃ crystal structure is very stable and allows various combinations of A and B cations, which produce an extensive collection of physical properties. However, the significant differences between the A and B cations radii cause that condition (ii) is not fully satisfied for real systems such as the TMOs perovskites. Then, in these materials, structural distortions usually occur to reduce the system to a minimum size and keep a compact ionic filling. In order to describe the degree of distortion, one can employ a term called the Goldschmidt tolerance factor [4], which is related to the cation-anion distances d_{A-O} and d_{B-O} as

$$t = \frac{(r_B + r_O)}{\sqrt{2}(r_A + r_O)} = \frac{d_{B-O}}{\sqrt{2}d_{A-O}}$$
(1)



Figure 1: a) Ideal perovskite ABO₃ structure with the cations A (yellow) and B (blue) and the anion O (red). b) Structural distortion caused by the rotation of the rigid BO₆ octahedra. c) bond disproportionation in breathing mode occurring in some TMOs. d) The angle θ serves as a parameter to describe distortions. The structures have been drawn with the program VESTA [7].

where t = 1 would correspond to the ideal perovskite structure. Thus, depending on the values of t, materials will have tendencies to adopt different non-cubic phases. For example, in the 0.9 < t < 1 region, although most compounds have the cubic perovskite phase, cases with rhombohedral symmetry start to appear. For 0.7 < t < 0.9, both rhombohedral and orthorhombic structures can be found. A threshold occurs at values of t < 0.7 where materials substantially distorted adopt other phases different from the perovskite-like structure. Finally, for t higher than 1, the material will tend to adopt a hexagonal-type structure [3].

Common distortions of the cubic structure can be characterized by modifications to the shape of the BO₆ octahedra produced by the change of the d_{B-O} distances or by the rigid rotation of the BO₆ octahedra along with translations of the A cation. For many TMOs, the d_{B-O} distances remain approximately constant as the A cation changes to one with a lower ionic radius. Then, the distortions associated with a lowering or increasing of the A cation size can be described in terms of the BO₃ octahedral rotations (see Fig. 1 b). However, there are cases of materials where a bond disproportionation scenario has been proposed to describe distortions. One of such cases are the $RENiO_3$, where a picture with octahedra having different bond lengths was suggested [5] (see Fig. 1 c). Nevertheless, up to a good approximation and in addition to the tolerance factor t, the magnitude of distortion can be described in terms of the B-O-B angle θ (see Fig. 1 d) given that both parameters are proportional [6] according to

$$\Delta \theta_{B-O-B} \approx c \,\Delta t \approx -c \,(d_{A-O} d_{B-O}^2 \sqrt{2}) \Delta d_{B-O} \tag{2}$$

where c is a constant that depends on the material (i.e., 275 for $RENiO_3$). According to the previous expression, $\theta = 180^{\circ}$ describes the perfect perovskite structure, and lower values indicate distortions of the cubic lattice.

Electronic Structure of TMOs

The electronic properties of the TMOs are determined mainly by effects happening in their *d*-orbitals. Therefore, a consistent description of these systems in terms of electronic



Figure 2: Schematic representation of the 3d wave functions and the oxygen ligands. The dark gray points indicate the six oxygen atoms surrounding the transition metal ion located in the center of the octahedron. The blue and yellow colors represent different signs of the wave functions. Figure was adapted from Ref. 8.

interactions implicates understanding the behavior of the *d*-electrons. In a 3*d* transition metal, the orbitals have five different wave functions associated with the spherical harmonics $Y_l^m(\theta, \phi)$ for l = 2 and $-2 \le m \le 2$ (see Fig. 2). For the ABO₃ structures, the six oxygen anions surrounding the metal ion produce a crystal field that removes the initial degeneracy in the isolated ion and make some orbitals more energetically favorable than others. More specifically, when the degeneracy is lifted, the orbitals divide into two groups, i.e., the e_g and t_{2g} levels. The overlap between the p ($Y_l^m(\theta, \phi)$), l = 1, $-1 \le m \le 1$) and d wave functions corresponding to the oxygen and transition metal governs the electronic and magnetic interactions between charges and spins. Then, deformations associated with the BO₆ octahedra can increase or decrease the orbital overlap and lead to modified properties such as localization. The following paragraphs describe the scientific efforts made in the last decades to understand the localization effects in TMOs and to classify these materials according to their electronic properties.

One of the first approaches to characterize the electronic response of TMOs involved band structure calculations. In this picture, a metallic or insulating ground state is expected depending on whether the transition metal of the material has an odd or even number of electrons [9]. However, in reality, many TMO perovskites with partially filled d-orbitals are insulating despite being predicted to be metallic. Therefore, conventional band structure theory alone cannot describe the electronic properties of TMOs. One of the earliest works to give a step further in solving the problem was done by N. Mott. In his study, Mott suggested that an insulating state will arise in TMOs with partially filled *d*-orbitals due to strong electronic correlations [10, 11]. These correlation effects can be described in terms of the electron-electron interaction, which was not included in early band theory calculations. J. Hubbard used Mott's results together with the tightbinding approximation to explain transitions between metallic and insulating states in partially occupied orbital systems in terms of the on-site Coulomb interaction U [12, 13]. The Hubbard model describes interactions between moving charges in a periodic lattice constituting a single electronic band. In this model, the Hamiltonian is composed of a kinetic and a potential term, which describe the hopping of particles between lattice sites and that account for the on-site interaction as

$$\mathcal{H} = -t \sum_{i,j,\sigma} c_{i,\sigma}^{\dagger} c_{j,\sigma} + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$
(3)



Figure 3: Schematic representation of the energy versus density of states (DOS) diagram for two types of materials a) Mott-Hubbard insulator and b) charge-transfer insulator. The occupied and unoccupied *d*-bands are equivalent to the LHB and UHB respectively. Figures have been reproduced from Ref. 14. c) Modified Zaanen-Sawatzky-Allen phase diagram reproduced from Ref. 2.

where t is the hopping integral, U is the on-site interaction strength, $c_{(i,j),\sigma}$ are the spinonly density operators and $n_{(i,j),(\uparrow,\downarrow)}$ are the density operators. For the TMOs case, the Coulomb interaction U is defined as the energy required to produce charge fluctuations of the form

$$d_i^n + d_j^n \longrightarrow d_i^{n-1} + d_j^{n+1}, \qquad \Delta E = U \tag{4}$$

where *n* represent the *d*-orbital occupation and *i* and *j* correspond to the *d* TM sites. Moreover, according to the Hubbard model, when the on-site interaction increases, the band structure splits into two regions above and below the Fermi surface called the upper Hubbard band (UHB) and lower Hubbard band (LHB). These two bands correspond to the electron-addition and electron-removal spectrum which in a non-interacting system coincide with the unoccupied and occupied density of states respectively (see Figs. 3 a, b). Therefore, localized systems characterized by the d-d excitations are called Mott-Hubbard insulators, and their band gap is mainly controlled by the interaction term U.

The Mott-Hubbard model (and its extensions) succeeds in describing the electronic properties of various TMOs in the early 3*d*-series, such as the titanates and vanadates. However, for later 3*d*-transition metals such as Ni and Cu, the insulating state cannot be described only in terms of the Coulomb interaction and the hopping term. In this regard, A. Fujimori and F. Minami proposed the incorporation of interactions between the oxygen 2p and the transition metal 3*d* states [15]. This incorporation can be accomplished by introducing a new energy parameter Δ that account for the transfer of electrons from the filled oxygen 2p levels to the unoccupied TM 3*d* orbitals. Then, the charge excitation process leaves a ligand hole *L* in the oxygen band when relocating the electron at the transition metal site as follows

$$d_i^n + d_j^n \longrightarrow d_i^n + d_j^{n+1}\underline{L}, \qquad \Delta E = \Delta$$
(5)

Figure 3a shows the schematic representation of a Mott-Hubbard insulator, where the UHB and LHB are separated by the on-site energy U and the UHB and O 2p states are divided by the charge transfer energy Δ , with $\Delta > U$. On the other hand, Fig. 3b shows the scheme of a charge-transfer insulator, where the O 2p states lie between the UHB and LHB, with $\Delta < U$. In this case, the transition between the metallic and insulating phases is determined by the magnitude of Δ rather than U.

The ideas described above were comprised in a phase diagram (see Fig. 3c) by J. Zaanen, G. A. Sawatzky, and J. W. Allen [16]. The comparison of parameters involving the Coulomb interaction U, the charge transfer energy Δ , and the ligand and metal bandwidths determine whether a TMO is a Mott-Hubbard or charge transfer insulator. Through the 3d transition metal series, Δ decreases consistently, whereas U is known to increase [17, 18]. This tendency leads to the identification of oxide materials from the early 3d transition metal series as Mott-Hubbard insulators, whereas the late 3dtransition metals fall into the charge transfer regime [2]. Figure 3c shows the phase diagram where a dashed diagonal line separates the charge transfer and the Mott-Hubbard regions. According to the diagram, if U is sufficiently small, the material will become a metal (of d type), in agreement with the description of the MIT proposed by Mott (see Fig. 3 a). However, on the charge transfer side, a small (and even negative) Δ will not yield a metallic state. Although the UHB and the O 2p states might overlap, the metallic state is not achieved because a band gap opens due to intermixing effects. The region where the insulating behavior remains despite Δ being negative is called the covalent or negative charge transfer regime, [19–21] and it corresponds to the purple area observed in Fig. 3c. In contrast to Mott-Hubbard insulators where the charge fluctuations are described by Eq. 4, a negative charge transfer energy Δ will lead to a preferential $d^{n+1}L$ state over the d^n . Then, the expected charge fluctuations in the metallic state will be of the type

$$d^{n+1}\underline{L} + d^{n+1}\underline{L} \longrightarrow d^{n+1} + d^{n+1}\underline{L}^2, \qquad \Delta E = \mathbf{\Delta}, \quad \mathbf{\Delta} \lesssim 1$$
(6)

where the band gap arises due to the presence of p - p hole correlations. Finally, it is essential to point out that in addition to the localization effects mentioned above, other mechanisms not described in this chapter, such as the spin-orbit coupling and the crystal field effects, alter the bandwidth of certain systems producing delocalization.

Chapter 1

The Rare-Earth Nickelates

1.1 Bulk properties of perovskite nickelates

1.1.1 Introduction

The rare-earth nickelate perovskites are the family of materials with chemical formula $RENiO_3$, where RE = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Y, and Lu. Interest in these materials derives from their well established phase diagram, which includes a distinct metal-to-insulator transition (MIT). In addition, these compounds are appealing given their relation to other perovskite systems like cuprates, which show high-temperature superconductivity, and the manganites, which show colossal magnetoresistive effects. With the exception of LaNiO₃, all nickelates are characterized by having a very sharp transition from paramagnetic metal at high temperatures to antiferromagnetic insulator at low temperatures. The conductivity change at the MIT is also accompanied by a modification of the structure and a reduction of the symmetry from orthorhombic to monoclinic.

In this section, we present the development of research on bulk rare-earth nickelate perovskites from early-days synthesis and characterization to the description of the possible origins of the magnetic and electronic structures.

1.1.2 Synthesis

In the early days, synthesizing perovskite nickelates in polycrystalline bulk form required unusual external conditions. Contrary to nickel oxide, which was relatively straightforward to produce at temperatures close to 1000 °C and pressures below 1 bar, the $RENiO_3$ series required normally lower temperatures and/or higher pressures to attain the right oxidation state (i.e. Ni³⁺). Wold *et al.* applied the low temperature approach to synthesize LaNiO₃ at 800 ° with equal amounts of NCaO₃ and rare earth oxide [22]. By this approach, LaNiO₃ was found to have a Ni³⁺ valence state and a R $\overline{3}$ m crystal structure, whereas NdNiO₃ was not stoichiometric. On the high pressure side, Demazeau *et al.* were one of the first groups to produce most of the $RENiO_3$ series by heating together the initial ingredients at 950 °C under a local pressure of 60 kbar. The authors combined RE_2O_3 , NiO and KClO₃ in such a proportion that when heated, the potassium chlorate thermally decomposed to produce the high *in situ* oxygen pressure required to stabilize the perovskite phase and the Ni³⁺ oxidation state [23]. At the time, these procedures were difficult to reproduce because they required very special equipment and several runs to provide a significant amount of material, so it was unappealing for other groups to

follow the same route. Vassiliou *et al.* were able to synthesize $NdNiO_3$ at 1 bar O_2 and a temperature of 650 °C with the subsequent study of its magnetic and electronic properties. In this study various methods were performed, namely decomposition of solid nitrates, sol-gel precipitation decomposition, reaction of oxides and coprecipitation and rapid evaporation, with the former two being the successful ones [24]. Two years later, Lacorre *et al.* prepared $PrNiO_3$ for the first time and compared its properties with those of $LaNiO_3$, $NdNiO_3$ and $SmNiO_3$. To this end, the authors decomposed the corresponding nitrates together in a solution with the stoichiometric oxides and then created pellets which were kept at $1000 \,^{\circ}\text{C}$ and $200 \,^{\circ}\text{bar}$ of oxygen pressure for several days [25]. More recent methods, like the one performed by Alonso *et al.* require the combination of metal nitrates $Nd(NO_3)_3 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ together in a solution with destilled water [26]. This citrate-nitrate method is currently used by serveral groups for the sinthesis of policrystalline $RENiO_3$. At present, these and other modern synthesis methods and advanced equipment and techniques allow the growth of nickelates in various forms, such as thin films, superlattices and single crystals. In this section, the structural, electronic and magnetic properties of bulk rare-earth nickelates will be described, and in later sections some of their other forms will be discussed.

1.1.3 Structural properties

As mentioned in earlier sections, the ideal ABO₃ perovskite structure consists of a unit cell with a cubic lattice shape where one A element resides at the center and four BO₆ octahedra are located at the corners. In the case of nickelates, this ideal structure is not achieved because of the smaller size of the RE ion in comparison with Ni. The structure will then have a reduced size and the NiO₆ octahedra will have to either change in shape or rotate to occupy the space difference. It has been experimentally observed that the Ni-O-Ni distances remain constant in many nickelates [27]. Therefore, the NiO₆ octahedra can be regarded as a rigid structure and the changes of the system as a function of the rare earth ion can be described in terms of the Ni-O-Ni rotation angle. As will be seen in the next subsection, the reduction of the Ni-O-Ni angle will decrease the orbital overlap, pushing the system from a metallic-like behavior to an insulating one. In addition, one can introduce a term called the tolerance factor as in Eq. 1, which for the specific case of nickelates results.

$$t = \frac{d_{RE-O}}{\sqrt{2}d_{Ni-O}},$$

where t = 1 for the ideal perovskite structure and t < 1 for the rare earths, as they correspond to smaller d_{RE-O} distances. For example, for LaNiO₃, t is slightly less than 1 and the NiO₆ octahedra can be considered to tilt around the [111] cubic direction from the ideal perovskite structure [22]. For smaller rare earth ions, the octahedra will form an orthorhombic structure by rotating around the [001] and [110] cubic axes. In this regard, nickelates are described as orthorhombically distorted perovskites [27].

The phase diagram of the rare earth nickelates plotted as a function of temperature, tolerance factor (t) and the Ni-O-Ni angle (°) is shown in figure 1.1a. From this diagram it is possible to see that the tolerance factor and the bond angle decrease as the ionic radius goes from La to Lu. This change is accompanied by structural transformations such that for LaNiO₃ the crystal structure is rhombohedral with space group $R\overline{3}c$ and for the rest of the series (i.e. Pr - Lu) it becomes orthorhombic with symmetry *Pbnm* above the MIT line. Assuming purely ionic bounding, the borderline between these two space groups is



Figure 1.1: a) The phase diagram of bulk rare-earth nickelates divided into three regions: the paramagnetic metal (grey), the paramagnetic insulator (purple) and the antiferromagnetic insulator (green) phases of temperature as function of tolerance factor and Ni-O-Ni angle. The values for the tolerance factor were obtained from experiments and the scale for the Ni-O-Ni is not linear (reproduced from Ref. 3). The three main crystal structures present in the rare-earth nickelate perovskites, b) rhombohedral (LaNiO₃), c) orthorhombic and d) monoclinic (NdNiO₃), at different temperatures above and below the MIT, respectively. The data for the three structures were taken from Refs. 23, 26 and 28, and then drawn with the program VESTA [7].

drawn approximately around $t \approx 0.985$ [25]. However, as can be seen from Fig. 1.1 a, the experimentally observed values of the tolerance factor are significantly lower [3]. Below the MIT border, PrNiO₃ and the rest of the series undergo a structural transition to monoclinic with symmetry $P2_1/n$ (see Fig. 1.1 b). This monoclinic structure is accompanied by the formation of two inequivalent Ni sites in a bond-disproportionate (BD) state with short and long Ni-O bonds. The BD state can be described as a breathing distortion mode of the NiO₆ octahedra. In addition, as the ionic radius of the rare earth goes from La to Lu, the temperature at which the transition from orthorhombic to monoclinic takes place increases such that for Pr and Nd it occurs below room temperature, and for the rest of the series, above it. A related effect has been observed for samples under external pressure; for example, NdNiO₃ changes symmetry from Pbnm orthorhombic to R $\overline{3c}$ rhombohedral above 40 kbar [29]. Therefore, for the structure of the $RENiO_3$, applying high external pressures would have a similar effect as changing the rare earth for one with higher ionic radius (chemical pressure).

1.1.4 Transport and optical properties

Regarding the transport properties, and more specifically the electrical conductivity, Fig. 1.1 a shows that $LaNiO_3$ behaves like a metal down to the lowest measurable temperatures. In contrast, the rest of the rare-earth series undergoes a MIT with increasing temperatures. This transition as function of temperature is indeed one of the key properties of the rare-earth nickelates and is also accompanied by a crystallographic transformation (see previous section and figure 1.1a). Electrical resistivity measurements performed on NdNiO₃ and PrNiO₃ revealed that these materials present a thermal hysteresis around



Figure 1.2: a) Logarithmic resistance vs temperature measurement of NdNiO₃ for warming (circles) and cooling (squares) curves, reproduced from Ref. 31. The inset shows a magnification of the region near the first inflection point (see text) b) Optical conductivity (σ) for NdNiO₃ as function of energy ($\hbar\omega$) at various temperatures obtained from Ref. 34. Although distinct, both measurements show an abrupt change at $T_{MIT} \approx 180$ K.

 T_{MIT} . This phenomenon, which is consistent with a first order phase transition, was described by Granados *et al.* as the cumulative effect of various phases, i.e. the coexistence of the insulating (or semiconducting) and metallic phases over a small temperature range [30, 31]. The hysteresis behavior can be conveniently described if the resistivity versus temperature plot is divided into various regions: (i) for high temperatures only the metallic phase is observed; (ii) around T_{MIT} there is a first inflection point indicating that the semiconducting phase starts to appear, but with numerous metallic paths still active; (iii) for slightly lower temperatures there is a second inflection point suggesting the last metallic paths are vanishing and the semiconducting phase is consolidating; (iv) and finally, at low temperatures a single phase is again established, but in this case it is an insulating one (Fig. 1.2 a). In contrast, the same effect is not observed or is barely visible in the rest of the nickelate series [32, 33]. The possible explanation for this phenomenon is the increase of the thermal fluctuations at higher T_{MIT} that weaken the hysteresis.

Transport measurements also show that in both the metallic and semiconducting phases of $RENiO_3$ the charge carriers are electrons [30, 31]. Moreover, the charge carrier density in both phases is considerably low in comparison with single 3d transition metals. This contrast between materials allows for the classification of the rare-earth nickelates as poor metals. Despite this difference, it is important to mention that $RENiO_3$ are one of the few families of TMOs to show metallic behavior, which makes them attractive to study by means of theoretical models.

Study of the insulating state of the $RENiO_3$ ($RE \neq La$) gives quantitative and qualitative information about the size of the band gap. For instance, the resistivity curves of PrNiO₃ and NdNiO₃ can be fitted assuming a simple activated behavior within a specific temperature range. Fittings performed at low temperatures (below T_{MIT}) give activation energies for NdNiO₃ and PrNiO₃ of 25-28 meV and 22 meV, respectively [30, 31]. In comparison, optical measurements indicate the opening of a band gap as the temperature decreases, in accordance with the MIT observed in resistivity measurements (Fig. 1.2 b). The values of the band gap obtained from optical experiments oscillate around 200 meV and are distinct from the activation energies for the same materials [34].



Figure 1.3: a) Schematic representation of the ground state of Ni³⁺ in the ionic picture with the corresponding crystal field splitting and different orbitals (in blue). Three distinct cases can be observed: (i) charge distributed uniformly, (ii) octahedral configuration (NiO₆) with the splitting of the energy levels into eg and t_{2g} orbitals, and (iii) an elongated octahedral Jahn-Teller distortion which splits the energy levels into further orbitals. b) Sketch of the singleparticle density of states for (left) Mott-Hubbard, (center) charge-transfer and (right) negative Δ insulators reproduced from Ref. 35. The dashed and open areas represent ligands from the 3d and 2p orbitals, respectively. X-ray absorption measurement of various $RENiO_3$ performed at the c) O K-edge and d) Ni L-edges (reproduced from Ref. 36).

1.1.5 Electronic Structure

From a purely ionic point of view, the nominal valence state of Ni in the $RENiO_3$ should be 3+ with a $3d^7$ low spin electronic configuration $t_{2g}^6 e_g^1$ (see Fig. 1.3 a). However, it is well known that this simple picture cannot entirely explain the phenomena of various TMOs, including the nickelates. Nevertheless, theoretical works such as the one done by Zaanen *et al.* help to classify materials in a comprehensive way (see Fig. 3). According to the Zaanen-Sawatzky-Allen phase diagram, the rare earth nickelate perovskites fall into the charge transfer insulator regime, but very close to the metallic region with small charge transfer energy. The transition between the metallic and insulating states is then a consequence of the opening of a band gap with charge-transfer nature. As it was mentioned in earlier sections, the reduction of the Ni-O-Ni angle implies a decrease of the orbital overlap between the O 2p and the Ni 3d orbitals. This reduction of the superexchange angle can be achieved via the substitution of the rare earth by another with smaller ionic radius or by decreasing the temperature to produce a structural change that goes from orthorhombic to monoclinic. Within the charge transfer scheme, this effect will narrow the O 2p valence band, making the material an insulator. However, the charge transfer insulator is not the only scenario that has been proposed to explain the electronic structure of nickelate perovskites (Fig. 1.3 b).

Mizokawa *et al.* performed x-ray photoemission spectroscopy (XPS) together with cluster configuration-interaction calculations on NaCuO₂ and found that the charge transfer energy (Δ) was negative [35]. In addition, the authors suggested that Δ might behave in a similar manner with other uncommon valence states such as Fe⁴⁺ and Ni³⁺. Then, a localized state will originate by charge fluctuations such as the ones presented in Eq. 6. Under these conditions, for nickelate perovskites, the $3d^8\underline{L}$ configuration will be as probable as the ionic $3d^7$ and the band gap will neither be of the charge-transfer (p-d) type nor the Mott-Hubbard (d-d) type, but rather negative- Δ (p-p) [35].

X-ray spectroscopy experiments have helped to draw a more accurate picture by including the hybridization between the Ni-3d and O-2p orbitals. X-ray absorption measurements on the O K-edge of LaNiO₃, PrNiO₃ and NdNiO₃ show a characteristic peak around 528.6 eV (Fig. 1.3 c). The origin of this pre-peak can only be explained by introducing the Ni 3d and O 2p hybridization. In this regard, the configuration interaction method indicates that partial charge transfer from the anion to the cation is described by adding an admixture of configurations to the original ionic configuration, in which one or more electrons have been transferred [36]. In the case of the RENiO₃ the covalent ground state for a NiO₆ octahedra can be obtained by extending the ionic picture (see Fig. 1.3 a) as

$$|\Psi^{G}_{covalent}\rangle = \alpha |3d^{7}2p^{6}\rangle + \beta |3d^{8}\underline{L}\rangle + \gamma |3d^{9}\underline{L}^{2}\rangle + \delta |3d^{10}\underline{L}^{3}\rangle, \qquad \alpha + \beta + \gamma + \delta = 1 \quad (1.1)$$

where α , β , γ and δ are constants that can be obtained from measurements. By taking these considerations into account and comparing NiO with the *RE*NiO₃, Medarde *et al.* concluded that the hybridization between Ni 3*d* and O 2*p* in the former is weaker than in the latter [36]. Moreover, the authors stressed that in the *RE*NiO₃ series, the weight of the 3*d*⁷ configuration was more important than that of the 3*d*⁸*L* in contrast to the scenario suggested by Mizokawa and coworkers.

Further spectroscopic measurements, such as soft x-ray absorption at the Ni *L*-edges (E = 850 - 875 eV), also contribute to the understanding of each component of the covalent ground state (Eq. 1.1). Fig. 1.3 d shows the spectra of the Ni $L_{3,2}$ -edges for NdNiO₃, PrNiO₃ and NiO. In the case of NiO, each feature has been broadly studied such that it is possible to associate the main peak around 854 eV to the $3d^8$ configuration and the two small adjacent satellites to the contribution of $3d^9\underline{L}$ and $3d^{10}\underline{L}^2$, respectively. By simple inspection of the spectra of NdNiO₃ and PrNiO₃ it is possible to see a two-peak structure around 854 eV. This double-peak feature suggests relatively equal contribution from two configurations, which in this case could correspond to $3d^7$ and $3d^8\underline{L}$. This result is in contrast to the results obtained by previous authors, where the weight of one configuration was more important than the other [35, 36]. However, in light of these spectroscopic results, the negative Δ model (p - p) seems to be less probable than the charge transfer model (p - d). These discrepancies will be further addressed in the next section when we describe the results from measurements performed on epitaxial thin films.



Figure 1.4: a) G-type antiferromagnetic structure proposed for NdNiO₃ by Demazeau *et al.* (Ref. 23). b) Antiferromagnetism with ordering vector $\mathbf{k}_{pc} = (1/4, 1/4, 1/4)$ suggested by Garcia-Munoz *et al.* for very low temperatures (T < 30 K) drawn with the program VESTA (Refs. 7, 37, 38). The color code for the atoms is the same as in Figs. 1.1c,d. Both Nd and Ni have an effective magnetic moment represented by the (small = Ni, large = Nd) green arrows. c) Two possible scenarios for the origin of the magnetism observed in the *RE*NiO₃: (top) orbital sublattice and (bottom) Jahn-Teller distortion (reproduced from Ref. 39).

1.1.6 Magnetic structure and magnetic properties

Magnetic susceptibility and neutron diffraction measurements on LaNiO₃ demonstrated that this compound behaves like a paramagnet with no observable magnetic ordering down to the lowest temperatures [40, 41]. For NdNiO₃ and PrNiO₃ there is a change from the paramagnetic to antiferromagnetic phase that occurs at the same temperature as the MIT $(T_N = T_{MIT})$, indicating a first order phase transition. For the rest of the series (i.e. fro Sm to Lu) the transition to the antiferromagnetic state occurs at temperatures lower than the MIT, with the difference between T_N and T_{MIT} increasing as the ionic radius becomes smaller (see figure 1.1a). The first magnetic measurements performed on rare earth nickelates suggested an antiferromagnetic G-type structure (Fig. 1.4 a) [23]. For the orthorhombic structure of the $RENiO_3$ ($RE \neq La$), where the e_g energy levels split into $x^2 - y^2$ and $3z^2 - \mathbf{r}^2$, the low-spin orbital filling will place a single electron in one of these orbitals (Fig. 1.3 a). Considering the Goodenough-Kanamori rules for this case, an atiferromagnetic ordering of the Ni magnetic moments is expected for perovskite nickelates. However, as it was described in the previous section, the electronic structure of $RENiO_3$ cannot be explained in terms of the ionic picture and therefore a more complex magnetic structure could originate in these compounds. This notion was confirmed later by Garcia-Munoz et al. using polarized neutron diffraction measurements. The authors studied PrNiO₃ and NdNiO₃ and assigned a propagation vector $\mathbf{k} = (1/2, 0, 1/2)$ to the observed magnetic Bragg reflections [37]. This propagation vector $\mathbf{k} = (1/4, 1/4, 1/4)_{\rm pc}$ represents a very unusual magnetic structure where each Ni magnetic moment couples ferromagnetically to three of its six nearest neighbors and antiferromagnetically to the other three remaining magnetic moments (Fig. 1.4b). Shortly after, two possible explanations were proposed: (i) the magnetic ordering is a consequence of the development of an orbital superlattice suggested by the coexistence of ferromagnetic and antiferromagnetic

phases [37] and (ii) the observed magnetism is product of the orbital order induced by the cooperative Jahn-Teller effect (Fig. 1.4 c). As will be seen in next section, recent experiments performed on thin films enable the possibility to unveil the origin of the magnetic ordering in nickelates. Finally, with respect to the magnetic moments in the rare earth, studies indicate that in the case of Nd magnetic ordering appears below 30 K (Fig. 1.4 b). This polarization of the Nd magnetic moments is argued to arise due to the presence of an exchange field produced by Ni rather than from the Nd-Nd interactions [38].

1.2 Perovskite nickelate heterostructures

In the early days, the experimental study of $RENiO_3$ was constrained to polycrystaline samples (i.e., nm to mm sized crystal grains with different orientations). As it was described in the previous section, preparation and characterization of these materials was challenging due to the extreme conditions required in the synthesis process. Despite these difficulties, valuable information was obtained from the study of the polycrystals, such as the nickelate phase diagram. Nowadays, modern techniques allow for the fast production of other forms of these materials. For example, Pulsed Laser Deposition (PLD), Molecular Beam Epitaxy (MBE) and RF magnetron sputtering give the possibility of growing thin films and multilayers with atomic scale precision. These forms enable new control parameters to modify the electronic and magnetic response in materials which otherwise would behave differently in bulk. In addition, recent studies reported the successful growth of NdNiO₃ and LaNiO₃ single crystals using high pressure techniques [42–44]. In this section, we will focus on summarizing the recent studies regarding nickel oxide based thin films and superlattices and their implications on the understanding of the magnetic and electronic structures displayed by the nickelate family.

1.2.1 Epitaxial nickelate thin films

Electronic and magnetic properties

The synthesis of single crystal thin films has contributed remarkably to understanding the origin of the electronic and magnetic properties of the rare earth nickelates. As it was described in previous sections, various studies situated the ground state of bulk nickelates either in the charge transfer (p-p) or negative Δ (p-d) regime. However, recent theory and experimental studies performed on $RENiO_3$ thin films have strengthened the idea that the charge transfer energy can be small or even negative, indicating a prevalent contribution of the $3d^{8}L$ configuration [45–47]. Moreover, a combination of resonant inelastic x-ray scattering and x-ray absorption measurements together with cluster calculations show that the electronic structure of the $RENiO_3$ is characterized by the substantial contribution of the oxygen 2p bands (see Fig. 1.5 a) and that these systems exhibit a negative charge transfer energy [47]. This results are in line with various studies that suggest the band disproportionation model as an explanation for the occurrence of the MIT in nickelates. With respect to the metallic state, angle-resolved photoemission spectroscopy (ARPES) measurements show that the Fermi surface is formed by an electron pocket centered at the Γ point and by hole pockets at the M points (Fig. 1.5 b), suggesting two conduction channels [48-50]. In addition, thermoelectric measurements together with the Hall coefficient indicate the presence of p- and n-carriers, respectively, pointing towards a multiband nature in rare earth nickelates 51–55. Therefore, according to recent studies, nickelates can be regarded as materials with both n- and p-charge carriers, where the insulating state is governed by a negative charge transfer energy and the metallic state presents at least two conduction bands.

Regarding the magnetic structure, measurements performed on bulk $PrNiO_3$ and $NdNiO_3$ by Garcia *et al.* below T_N yielded as a result an antiferromagnetic state with ordering vector $\mathbf{k} = (1/4, 1/4, 1/4)_{pc}$. This wavevector is consistent with two scenarios were the spin arrangement is either collinear $(\uparrow\uparrow\downarrow\downarrow\downarrow)$ or non-collinear $(\uparrow\leftarrow\downarrow\rightarrow)$ along the $(111)_{pc}$ planes. These two scenarios correspond to the orbital order model produced by a Jahn-Teller distortion and the orbital sublattice model with ferromagnetic and anti-



Figure 1.5: a) Sketch of the charge transfer (left) and negative charge transfer (right) scenarios for the $RENiO_3$ (reproduced from Ref. 47). b) Fermi surface maps in the ΓXM plane obtained by ARPES (left) and GGA+DMFT (right) for two LaNiO₃ samples subjected to compressive (top) and tensile (bottom) strain (reproduced from Ref. 59). c) Non-collinear magnetic structure suggested by Scagnoli *et al.* for NdNiO₃ drawn with the program VESTA, (Refs. 7, 56, 58).

ferromagnetic regions described in the previous section (see Fig. 1.4 c). Various experimental studies performed on nickelates found no evidence of orbital ordering, but rather indications of charge ordering, making the collinear antiferromagnetism the less likely scenario [39,56,57]. Although Garcia *et al.* and other authors assigned a collinear (Fig. 1.4 b) nature to the antiferromagnetism of bulk nickelates, more recent experiments on thin films confirmed that the antiferromagnetic order in the nickelate family is non-collinear, as observed in Fig. 1.5 c [56,58].

Epitaxial strain and the MIT of $RENiO_3$ ($RE \neq La$)

The growth of RENiO₃ materials in thin film form enables the appearance of a new control variable that can substantially modify their structural, electronic and magnetic properties. In this regard, epitaxial strain (ε_{xx}) is defined as the force exerted on a thin film that has been grown on a single crystal substrate, which depends on the lattice mismatch between them. For example, when an epitaxial thin film is grown onto a substrate oriented along the (001)_{pc} direction, its in-plane lattice parameters (a, b) will have to accommodate (by elongation or shortening) in order to match those of the substrate. In this process, the thin film layers are subjected to a strain which can be quantified as

$$\varepsilon_{xx} = \frac{a_{\rm sub} - a_{\rm bulk}}{a_{\rm bulk}}$$

where $a_{\rm sub}$ and $a_{\rm bulk}$ represent the in-plane lattice parameters of the substrate and of the material in bulk form, respectively [3]. In addition, the out-of-plane constant (c) would have to readjust accordingly in order to keep the variation of the total volume to a minimum value. The corresponding reduction or increase of the lattice constants can then be achieved in two ways: (i) a Jahn-Teller distortion of the NiO₆ octahedra, which implies the elongation (compression) of the in-plane lattice constants and the compression (elongation) of the out-of-plane lattice constant for tensile (compressive) strain, or (ii) the rotation of the NiO₆ octahedra towards a different symmetry configuration, which reduces the Ni-O-Ni bond angle (See Fig. 1.1 a).

In nickelates, and more specifically for NdNiO₃, SmNiO₃ and EuNiO₃ samples grown on $(001)_{pc}$ oriented substrates, various authors have found that epitaxial strain has a huge impact on the MIT to such an extent that it can consistently tune T_{MIT} to different values in comparison to bulk, depending on the choice of the substrate [60-67]. For example, Liu *et al.* studied NdNiO₃ thin films grown on various substrates and found that T_{MIT} decreased as the strain goes from tensile to compressive (see Fig. 1.6 a). The authors also found that in the compressive strain regime, the antiferromagnetic phase is completely suppressed and the sample becomes metallic down to low temperatures, resembling a non-Fermi liquid state [68]. Similar results were obtained by Catalano *et al.* for SmNiO₃, where a regime with $T_N = T_{MIT}$ was achieved [60]. This first order transition arises in $SmNiO_3$ thin films grown on a NdAlO₃ substrate, which exerts a small copressive strain of $\varepsilon = -0.9\%$ (see Fig. 1.6 b). Along these lines, Meyers *et al.* performed electrical dc transport and resonant XAS together with first principles cluster calculations on $EuNiO_3$ samples. The authors concluded that compressive strain enhances the covalence of the Ni 3d and O 2p orbitals, leading to a shift of the second order Mott transition towards lower temperatures and eventually to a room temperature metallic state [65]. The agreement of these and other studies performed on different $RENiO_3$ grown under tensile and compressive strain points towards a common mechanism in response to epitaxial strain for nickelate thin films.

Figure $1.6 \,\mathrm{c}$ shows a comparison between the phase diagram of bulk nickelates (similar as the shown in Fig. 1.1 a) and the phase diagrams for NdNiO₃ and SmNiO₃ for temperature as function of strain. The first surprising observation is that for samples grown on substrates with almost no lattice mismatch, the MIT occurs at a different temperature as in bulk. In addition, all three diagrams show certain resemblance, indicating that at least in the compressive strain side, the results are equivalent to increasing the tolerance factor. The same is not true for the tensile regime, where an increase of the strain does not imply an increase or separation of T_{MIT} and T_N . In this regard, Cochon *et al.* concluded that the difference between compressive and tensile strain is due to the more energetically favourable formation of structural defects, such as dislocations or oxygen vacancies in the tensile regime [63]. Alternatively, Zhang *et al.* suggested that in contrast to tensile strain, where this films undergo a structural change from orthorhombic to monoclinic at the MIT, in compressive strain the films are not allowed to change the symmetry to $P2_1/n$ and therefore a MIT is not observed [70]. As it was described in earlier sections for bulk nickelates, applying external hydrostatic pressure will have the same effect as to increase the Ni-O-Ni bond angle or, equivalently, to change the RE cation for one with larger ionic radius. Since experimental results indicate that compressive strain produces similar results as straightening the Ni-O-Ni bond angle, the increase of symmetry by rotation of the NiO_6 octahedra seems to be a more plausible scenario for nickelates than the Jahn Teller distortion one.



Figure 1.6: The effects of epitaxial strain: Electrical resistivity of different a) NiNiO₃ and b) SmNiO₃ samples grown on different substrates. c) The phase diagram of nickelates as function of tolerance factor compared with the phase diagram as function of strain for NdNiO₃ and SmNiO₃. Figures a) and b) & c) are reproduced from Ref. 64 and Ref. 60 respectively. d) The nickelates phase diagram as function of the Ni-O-Ni bond angle together with two NdNiO₃ (111)_{pc} oriented samples grown under tensile and compressive strain (reproduced from Ref. 69).

In addition to the conventional growth of nickelate thin films on $(001)_{pc}$ oriented substrates, various groups have also studied alternative substrate orientations, such as $(110)_{\rm pc}$ and $(111)_{\rm pc}$. These orientations also have profound effects on the MIT of the nickelate thin films. For example, Liu *et al.* studied various $NdNiO_3$ thin films grown on NdGaO₃ substrates oriented along (100), (001) and (110) and observed that the MIT, occurred at different temperatures. The authors suggested that the anisotropic epitaxial strain produced by substrates with different orientations can efficiently tune the MIT given that an increasing averaged lattice mismatch causes the consistent shift of T_{MIT} towards higher values [71]. Along these lines, Catalano *et al.* found that $NdNiO_3$ grown on $(111)_{pc}$ oriented NdGaO₃ displayed a separation of T_N and T_{MIT} consistent with the $T_N \neq T_{MIT}$ of other members of the family with lower ionic radius. In this case the authors attributed their observations to the additional lattice matching conditions imposed by the substrate in this particular orientation [69]. In addition to the agreement with $(001)_{pc}$ regarding epitaxial strain, samples grown on substrates with different lattice orientations offer the possibility of exploring new electronic phases, such as the polar metals and honeycomb-like crystals experimentally realized for $(111)_{pc}$ oriented nickelates [72, 73].

Thickness dependent MIT in LaNiO₃

As was mentioned earlier, bulk LaNiO₃ is a paramagnetic metal that does not undergo a MIT at any temperature. This behavior is in contrast to the rest of the rare earth nickelate series, which experience a MIT as function of temperature. However, $LaNiO_3$ thin films go through a transition from a metallic state to a strongly localized one as the layer thickness reduces [49, 53, 74-78]. Son *et al.* who were one of the first groups to study this phenomenon, observed that the critical thickness (t_c) separating the metallic and insulating states shifted as function of strain [53]. Scherwitzl *et al.* performed a complementary detailed analysis in the region around t_c and observed metallic behavior with low-temperature resistivity upturns, which could be described in terms of the weak localization theory (see Fig. 1.7 a). Moreover, the authors observed an isotropic behavior of the magnetoresistance, which points towards a charge ordered antiferromagnetic state similar to that observed in the other rare earth nickelates [74]. Photoemission spectroscopy measurements performed by Sakai *et al.* showed that this weakly localized state resulted from the opening of a pseudogap at the Fermi energy, which then evolved to a full gap as the thickness was further decreased. These results indicated that the MIT as a function of thickness originated as a consequence of the dimensional crossover from 3D to 2D. Finally, combined studies of TEM, together with DFT calculations performed by Fowlie et al. suggested that the LaNiO₃ films separate into three regions (see Fig. 1.7 b) with different types of local structures driven by the boundaries with the substrate and surface [78].

Although so far long-range magnetic order has not been observed in LaNiO₃ thin films grown on $(001)_{pc}$ oriented substrates, recent studies show that some types of magnetism is present in other configurations of these materials. For example, Asaba *et al.* reported the observation of ferromagnetism in LaNiO₃ thin films grown on LaAlO₃ $(111)_{pc}$ substrates [80]. Anomalous Hall effect and magnetoresistance measurements (see Figs. 1.7 c & d) suggest that the origin of the long-range order is due to ferromagnetic superexchange interaction between Ni²⁺ and Ni³⁺ ions [79]. As it will be seen in the next section, the electronic and magnetic behavior observed for LaNiO₃ thin films can be translated to LaNiO₃-based superlattices with certain distinctions.

1.2.2 Nickelate superlattices

A Superlattice is a structure formed by the periodic arrangement of two or more material films grown on a single crystal substrate. This structure usually consist of two parts, one of which is conducting and the other of which is insulating. Heterostructures configured in this way allow the appearance of new and exiting phenomena that are not found in single thin films or bulk form, such as interfacial superconductivity, induced magnetism, quantum confinement and interfacial charge transfer, among others. In the case of nickelates, most of the research studies focus on LaNiO₃ superlattices, although heterostructures with other rare earths, like Pr, Nd and Sm, have also been explored. In this section we compile a series of experimental and theoretical works performed on nickelate superlattices in the last years which are relevant to the understanding of forthcoming results sections.

Dimensionality control and induced magnetism

As it was mentioned in earlier sections, $LaNiO_3$ does not undergo a MIT as a function of temperature but rather as a function of layer thickness (Sec. 1.2.1). A similar effect is also observed in various $LaNiO_3$ -based superlattices [81–85]. For example, May *et al.*



Figure 1.7: a) Sheet resistance plot for different LaNiO₃ samples with different thicknesses. The dashed line represents the quantum of resistance in 2D (reproduced from Ref. 74). b) ab initio DFT results for the Ni-O-Ni bond angle for LaNiO₃ thin films with different thickness (reproduced from Ref. 78) c) and d) Anomolous Hall effect loops for $(111)_{pc}$ oriented LaNiO₃ samples (reproduced from Ref. 79).

analyzed a series of LaNiO₃/SmMnO₃ superlattices with various LaNiO₃ layer sizes and detected a MIT transition as the thickness of the nickelate decreased [81]. In addition, Liu *et al.* studied a group of LaNiO₃/LaAlO₃ superlattices with dc transport and soft x-ray absorption spectroscopy and observed a transition from an itinerant electron behavior to a localized state attributed to the crossing of the quantum confinement limit [82]. The same configuration of materials was also probed with optical ellipsometry and low-energy muon spin rotation and showed a clear transition from the known paramagnetic metal to an antiferromagnetic insulator state as the LaNiO₃ layers reduce to two unit cells [83]. Using resonant x-ray diffraction, Frano *et al.* developed a detailed picture of the magnetic structure of these superlattices (see Fig. 1.8 a) and found a non-collinear 2D antiferromagnetism with the formation of a spin density wave predicted from theory [84]. Furthermore, theory calculations describe the emergence of the spin density wave in terms of the suppression of the charge instability and the dominance of the spin stability at $q = (1/4, 1/4, 1/4)_{\rm pc}$ [86]. The previous results demonstrate the tremendous effect that heterostructuring and dimensionality control have on the electronic and magnetic properties of materials, as antiferromagnetic ordering had not been observed in bulk or the $(001)_{\rm pc}$ oriented thin film counterpart of LaNiO₃.

Control of the orbital polarization

The interest in the study of nickelate superlattices originates in great part from theoretical predictions indicating the appearance of new phenomena when combining materials with well defined properties. In this regard, various authors have proposed the emergence of superconductivity in a combination of $LaNiO_3/LaMO_3$ (M = Al, Ga, Sc) superlattices [87, 88]. Experimental realizations of these theoretical ideas have been made by several authors with results that seem more complex than expected. For example, Jang et al. grew and characterized a $(LaNiO_3)_1/(LaAlO_3)_1$ superlattice and observed a semiconducting behavior rather than a superconducting one within the studied temperature range [89]. The authors attribute this behavior to the radical alteration of the electronic structure of the NiO_2 layers in the superlattice. Freeland *et al.* probed the electronic structure with polarized X-ray absorption measurements and found a distinct asymmetry between samples grown on substrates with tensile and compressive strain, such that the later show a splitting of the orbital energies while the former does not [90]. In both cases, the orbital polarization seems to be very small in comparison to predictions. Then, control of the 3d orbitals seems to be crucial to the development of electronic structures similar to the ones observed in high- T_c superconductors. A new methodology that serves to this end is the orbital reflectometry approach, where it is possible to quantify the layer-resolved orbital polarization by means of spectroscopic techniques [91]. This method was first used to determine the orbital polarization of a LaNiO₃/LaAlO₃ superlattice and it could resolve occupations with very high sensitivity (see Fig. 1.8 b). Later on, the same group performed a very detailed study of various LaNiO₃ superlattices and obtained orbital polarizations up to 25%. However, these experimental results indicate that the measured orbital polarization of the $LaNiO_3$ superlattices is significantly lower than the values calculated by theoretical studies [91, 92]. More recently, an alternative mechanism to doping the nickelate layers proposed the introduction of a third material into the superlattice, which would produce a large orbital energy splitting in the new heterostructure [93]. Along these lines, the experimental realization of a $LaTiO_3/LaNiO_3/LaAlO_3$ heterostructure yielded an orbital polarization of 50% with an electronic structure similar to a single-band Fermi surface 94.

Interfacial charge transfer

Superlattices containing a combination of nickelates and manganites have been extensively studied due to the presence of various rich phenomena such as charge transfer, exchange bias and interfacial magnetism [95–102]. Such effects can modify the spin and orbital degrees of freedom in a way that they ignite the emergence of novel electronic and magnetic states. In this regard, Gibert *et al.* studied various $(\text{LaNiO}_3)_n/(\text{LaMnO}_3)_m$ superlattices grown on (111) oriented SrTiO₃ and observed exchange bias, as the amount of layers of each material was $m = n \geq 3$. This effect, at the interfaces between a paramagnet and a ferromagnet, implies the formation of interfacial magnetism at the LaNiO₃ layers and it was not observed in the (001) oriented samples [95]. More specifically, for m = n = 7, the



Figure 1.8: a) Temperature dependence of the magnetic peak at (1/4, 1/4, 1/4) for various superlattices together with the electrical conductance for 2/2 and 4/4 layer samples (reproduced from Ref. 84). b) Schematic representation of a LaNiO₃/LaAlO₃ superlattice with an inhomogeneous orbital occupation along the nickelate layers (reproduced from Ref. 91).

samples show antiferromagnetic interlayer coupling and negative and positive exchange bias at different temperatures (see Fig. 1.9 a). The appearence of these effects can be explained in terms of the materialization of an antiferromagnetic structure with q =(1/4, 1/4, 1/4) at the LaNiO₃ layers, which was also present in the thin films but only below a certain critical thickness $(t_c < 7)$ [96]. Moreover, when the LaNiO₃/LaMnO₃ superlattices are doped with Sr the exchange bias can also be observed in (001) oriented samples. Xray absorption experiments indicate that in these superlattices the valence state and the magnetic behavior of Ni and Mn change such that they lead to the arrival of exchange bias [97]. Along these lines, interfacial magnetism was also observed in a $LaNiO_3/CaMnO_3$ superlattice, but only when the nickelate layers are metallic, i.e. when the these layers are above the critical MIT thickness. The appearance of this ferromagnetic state has also been attributed to the double exchange between the Mn⁴⁺ and Ni³⁺. Finally, charge transfer has been also observed in both Sr-doped and undoped LaNiO₃/LaMnO₃ superlattices together with the formation of non-collinear magnetic structure at the nickelate layers (see Fig. 1.9b) [98,99]. Thus, it seems that the structural configuration of the nickelatemanganite superlattices is intimately related to the presence of various exotic phases that can be tuned by means of layer thickness, chemical doping and substrate orientation.

Other $RENiO_3$ heterostructures

Recent studies also include the analysis of non-La based nickelate superlattices. One such studie incorporates the analysis of the charge transfer mechanism in various $RENiO_3/GdTiO_3$ (RE = La, Nd, Sm) superlattices. X-ray absorption and magnetic scattering measurements indicate hysteresis and ferromagnetic-like behavior [103]. A group of NdNiO₃/LaAlO₃ heterostructures with (111)_{pc} orientation were studied with x-ray absorption and *ab initio* calculations by Middey *et al.* (see Fig. 1.9 c). In their work, Middey and coworkers found antiferromagnetic correlations and orbital polarization that was not observed in


Figure 1.9: a) Sketch of the magnetic structures for a) a $\text{LaNiO}_3/\text{LaMnO}_3$ (111)_{pc} and b) a $\text{LaNiO}_3/\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (111)_{pc} oriented superlattice (reproduced from Refs. 96, 99). c) The (111)_{pc} orientation in a (top) perovskite unit cell and (bottom) a buckled honeycomb lattice in a NdNiO₃ heterostructure (reproduced from Ref. 73).

the $(001)_{pc}$ oriented samples [73]. Finally, Hepting *et al.* studied a PrNiO₃/PrAlO₃ superlattice and found a magnetically ordered ground state together with the suppression of the charge order when the heterostructures are grown under compressive strain [104]. These and previous experimental works on $RENiO_3$ point towards a promising future for modern electronics based on oxide heterostructures.

In this and previous sections we have presented a synthesised review of the evolution of research regarding the rare-earth nickelate perovskites in their bulk and thin film forms. For a more general description of these materials, we kindly refer the reader to reviews done by Medarde [27], Catalan [105], Middey *et al.*, [2] and Catalano *et al.* [3].

1.3 Superconductivity in infinite-layer nickelates

Unconventional superconductivity refers to superconducting materials where the pairing mechanism is not mediated by phonon exchange, but possibly by other means like antiferromagnetic spin fluctuations or interlayer coupling [106, 107]. The most notorious example of this phenomenon are the high- T_c cuprates, which were discovered more than three decades ago and continue to be intensively studied at present. Despite the vast amount of experiments, the mechanism by which high- T_c superconductivity takes place in these compounds is still a mystery. However, these experiments have allowed scientists to identify various crucial features for superconductivity in cuprates. These features are a quasi-two dimensionality, strong antiferromagnetic correlations, no orbital degeneracy, spin one-half and a broad doping range. Taking these characteristics into account, a new path focused on finding cuprate-like superconductors can be explored. Many years after the discovery of cuprates, scientists tried to find other materials with T_c comparable to the cuprates until the iron-based superconductors were discovered in 2006 [108,109], a finding which amplified the interest in the field. Although Fe-pnictides and cuprates have some attributes in common, like being layered systems, having important d-electron physics and a stable antiferromagnetic order, the former seem to be a distinct class of high- T_c superconductors on their own. More recently, the nickelates were added to the list of unconventional superconductors when superconductivity in Sr-doped $Nd_{1-x}Sr_xNiO_2$ thin films was found by Li and coworkers [110]. Although at present, the transition temperature of these superconducting nickelates is substantially low $(T_c \approx 15 \,\mathrm{K})$, their discovery is considered of huge importance because it allows scientists to give a step forward in unveiling the mechanism of high- T_c superconductors and subsequently towards the ultimate goal of room temperature superconductivity.

For decades, nickelates have been proposed to manifest superconductivity given that, in many aspects, they are similar to the high- T_c cuprates. Theory studies have suggested that Cu^{2+} could in principle be substituted by Ni¹⁺ in layered cuprates because it has the same crystal structure and identical e_g filling with two electrons in the $3z^2 - \mathbf{r}^2$ and one electron in the $x^2 - y^2$ orbitals. In addition, in a planar coordination like this, nickelates and cuprates have the same $3d^9$ electronic configuration. Anisimov *et al.* performed a detailed study using LDA+U calculations and found that the most promising nickelate to show superconductivity was one with fourfold planar coordination and Ni¹⁺/Ni²⁺ oxidation state [111]. Some examples of compounds that fulfilled the description are LaNiO₂, SrNiO₂ and LaSrNiO₂Cl₂, where an insulator with magnetic ordering was expected. Figure 1.10a shows the results from the LDA+U calculations performed by Anisimov *et al.* on LaNiO₂, where the O 2p states are completely filled and the Ni¹⁺ 3d hole resides in the $x^2 - y^2$ orbital.

Given all these similarities between nickelates and cuprates and the prospects of materials which could show high- T_c superconductivity, experimentalists acquire interest in nickelates, such that many nickel oxide systems have been studied in the last decades. Some of these systems include LaNiO₂, La₃Ni₂O₆ and La₄Ni₃O₈, which are members of the T'-type La_{n+1}Ni_nO_{2n+2} layered series. The T'-type group can be described as a two part structure with alternating blocks of infinite layer La_{n-1}Ni(NiO₂)_n and flourite-type layers of La-O₂-La. In this sense, LaNiO₂ would correspond to $n = \infty$ with Ni¹⁺ (3d⁹), La₃Ni₂O₆ to n = 2 and La₄Ni₃O₈ to n = 3, both with a mixed valence state Ni¹⁺/Ni²⁺ (3d⁹/3d⁸) (Fig. 1.10 b). These materials (except for LaNiO₂) have been shown to have a strong two-dimensional band character, with the rare earth 5d states completely de-



Figure 1.10: a) Total and partial densities of states (DOS) corresponding to the O 2p and Ni $e_g 3d$ of LaNiO₂ from calculations by Anisimov *et al.* (reproduced from Ref. 111). b) The crystal structure of three members of the T'-type series, namely La₃Ni₂O₆ (n = 2), La₄Ni₃O₈ (n = 3) and LaNiO₂ $(n = \infty)$ (reproduced fromRef. 68). c) The crystal structure of the superconductor Nd₆Ni₅O₁₂ reproduced from Ref. 115.

populated and a possible antiferromagnetic insulating ground state according to theory calculations [68, 112, 113]. Although these layered materials seem to be in closer analogy to cuprates than LaNiO₂, none of the previous works found signs of superconductivity in either of them. One reason for this might be the difficulty of obtaining highly pure compounds because they require two steps, namely the synthesis of the parent perovskite LaNiO₃ phase or the Ruddlesden-Popper La_{n+1}Ni_nO_{3n+1} series and the subsequent chemical treatment to remove the apical oxygen. In addition to the La-based materials, other rare earths like Nd and Pr and higher layer orders (n = 4, 5...) have been studied with promising results. Zhang *et al.* found that (La,Pr)₄Ni₃O₈ crystals carry various properties from the high- T_c superconducting cuprates, like a Ni low-spin state, a large orbital polarization with predominantly $x^2 - y^2$ states and a significant hybridization with O 2*p* states [114]. Very recently Pan *et al.* studied a quintuple-layer Nd₆Ni₅O₁₂ and found superconductivity around $T_c = 13$ K [115]. According to calculations, this new superconductor has an electronic structure that is intermediate between that of cuprates and infinite layer nickelates.

Following the technological advances in the synthesis of materials and heterostructures, theory studies also proposed that LaNiO₃/ABO₃ superlattices could host a suitable environment for superconductivity. In this case, the ordering of the $x^2 - y^2$ orbital, which is of d^7 type, is achieved by means of heterostructuring and strain. Chaloupka and Khaliullin suggested that a layered oxide LaNiO₃/LaMO₃ (M = Al, Ga) heterostructure could develop a planar orbital order in $x^2 - y^2$ induced by epitaxial strain and reduced dimensionality (Fig. 1.11 a) [87]. Moreover, the authors suggested that in superlattices with $3d^7$ nickelates and band gap insulators with trivalent cations as previously mentioned, an orbitally non-degenerate spin one-half electronic structure is possible. In the same line, based on LDA + DMFT calculations, Hansmann *et al.* found that the heterostructure of (LaNiO₃)₁/(LaAlO₃)₁ has a single-sheet cuprate-like Fermi surface (Fig. 1.11 b) [88]. In this case, although both $x^2 - y^2$ and $3z^2 - \mathbf{r}^2$ orbitals play an important role, the physics of this $3d^7$ nickelate-based superlattice still possess the main pieces of hightemperature superconductivity. Motivated by these ideas, many studies have been made



Figure 1.11: a) Sketch of the strain exerted on the NiO₆ octahedra in a LaNiO₃/LaMO₃ superlattice proposed by Chaloupka *et al.* (reproduced from Ref. 87). b) The cross section of the Fermi surface for LDA (top) and LDA + DMFT (bottom) by Hansmann *et al.* (reproduced from Ref. 88). c) Comparison of the DOS of LaNiO₂ and CaCuO₂ calculated with LDA (reproduced from Ref. 117).

on LaNiO₃/LaAlO₃ superlattices (see Sec. 1.2.2), but the experimental results do not show promising results [82, 89, 90, 116]. As a result, no superconductivity has been found in any d^7 nickelate heterostructure to date.

In addition to the marked similarities found between nickelates and cuprates, theoretical studies also indicate that there are significant differences between them. Lee et al. pointed out that even though Ni^{1+} and Cu^{2+} are isoelectronic, compounds like LaNiO₂ show a different electronic and magnetic behavior compared to $CaCuO_2$ [117]. For example, $LaNiO_2$ is weakly metallic with no long range magnetic order observed so far, while cuprates show an insulating behavior in the undoped state with antiferromagnetic ordering at finite temperatures T_N . There is a considerable mixing between the Ni $3d_{3z^2-r^2}$ and the La $5d_{3z^2-r^2}$ orbitals, which forms La 5d pockets at the Fermi surface that dope the Ni 3d band. Intermixing with oxygen is also different for both compounds, such that the hybridization of Ni 3d with O 2p is weak in comparison to the strong hybridization of Cu 3d with O 2p in cuprates (Fig. 1.11 c). These differences are the ones that can help to understand the key ingredients for superconductivity and special attention needs to be given to them. The observations made so far raise the question of which components are necessary for materials to show a superconducting state given that nickelates seem not to carry all the crucial ingredients for superconductivity in cuprates, and yet they show a superconducting transition at $T_c \approx 15$ K. However, current research indicates that nickelates could be regarded as a distinct group of superconducting materials. In the meantime, a lot of work is required regarding sample quality and reproducibility, since for the moment only a few groups have been able to reproduce superconducting nickelates, and their results, although comparable, have significant differences.

Taking the previous studies into account, the most comparable materials to the high- T_c cuprates seem to be the isostructural $RENiO_2$ with a nominal oxidation state of Ni¹⁺, which possess the same $3d^9$ electronic configuration as Cu²⁺ in cuprates. The process of obtaining $RENiO_2$ is very complex since it requires, at the first step, the synthesis of the precursor $RENiO_3$ and, second, the removal of apical oxygen by means of a process called topotactical reduction. This chemical process adds a new degree of difficulty as it

could give undesirable results, such as the formation of byproducts at the surface, regions with excess or lack of oxygen atoms and the inclusion of other small atoms in the apical sites. The first infinite layer nickelate to be synthesized was $LaNiO_2$ in 1983 using H₂ as a reducing agent [118]. According to the authors, the temperature at which the reduction takes place is crucial for obtaining the infinite layer $LaNiO_2$ from perovskite $LaNiO_3$. This means that different temperatures might give rise to undesired phases like intermediate $La_2Ni_2O_5$, or a mixture of phases, like $La_2O_3 + Ni$ and La_2NiO_4 . The work done by Crespin and coworkers to obtain LaNiO₂ was considered complex at the time, such that it required several years until similar results were obtained by different authors [119, 120]. Hayward et al. performed a low-temperature reduction with sodium hydride (NaH_2) to obtain $LaNiO_2$ and studied its structural and electronic properties. Their results showed that there was not long range antiferromagnetic order in contrast to isostructural cuprates. Later on, in 2003, $NdNiO_2$ was synthesized in bulk form and its properties could also be subsequently explored [121]. Both $NdNiO_2$ and $LaNiO_2$ showed similar electronic and magnetic properties with the resistivity displaying a semiconducting behavior rather than a superconducting one and paramagnetism instead of the well-known antiferromagnetic order in cuprates. More recently, Kawai *et al.* obtained thin films of $LaNiO_2$ by reducing epitaxial LaNiO₃ films grown on a $SrTiO_3$ substrate with CaH_2 [122, 123]. Remarkably, the topotactic reduction was so smooth that the structural framework was maintained and the samples could be subsequently annealed to obtain again the perovskite phase. The epitaxial film growth process adds an additional parameter to the group of variables that can be modified when obtaining the infinite-layer phase. This parameter is strain, and depending on the substrate it could be compressive or tensile. Kaneko et al. performed a substrate dependence study and concluded that the lattice matching between $LaNiO_2$ and the substrate is crucial for the stabilization of a c-axis oriented single phase [124]. Along these lines, both previous and other authors obtained a- and c-axis oriented films, and performed substrate and reduction time dependence analysis [123-125].

Previous experiments performed on undoped infinite layer nickelates NdNiO₂ and LaNiO₂ do not show any signatures of superconductivity¹ in either the bulk or thin film forms. However, it is well known that many cuprates are also not superconducting in their parent phase and superconductivity arises only when they are doped with charge carriers. The doping process adds an another difficulty for the synthesis of nickelates since the addition of charge carriers pushes the oxidation state of Ni away from stable 3+ in stoichiometric $RENiO_3$. For example, Sr- or Ca-doping inclines the balance towards an unstable 4+ oxidation state. Despite all these challenges, in 2019 Li et al. found superconductivity in a Sr-doped $Nd_{0.8}Sr_{0.2}NiO_2$ thin film grown on a $SrTiO_3$ substrate [110]. The authors grew first a perovskite $Nd_{0.8}Sr_{0.2}NiO_3$ thin film and then reduced it with CaH₂ by means of a low-temperature topochemical reaction in order to obtain the superconducting infinite layer $Nd_{0.8}Sr_{0.2}NiO_2$ sample (Fig. 1.12 a). While the parent reduced NdNiO₂ shows a metallic behavior with an pronounced resistivity upturn at low temperatures, the doped reduced sample $Nd_{0.8}Sr_{0.2}NiO_2$ is metallic at room temperature and undergoes a transition to zero-resistance at $T_c \approx 15 \,\mathrm{K}$ (Fig. 1.12 b). To date, superconductivity has been observed in three members of the rare-earth series, namely $Nd_{1-x}Sr_xNiO_2$, $Pr_{1-x}Sr_xNiO_2$ and $La_{1-x}Sr_xNiO_2$. Their corresponding phase diagrams of temperature versus hole-doping are shown in Fig. 1.12 d. Although distinct, all of them show a dome-like shape that covers a region between x > 0.1 and x < 0.25. The same shape is observed in cuprate superconductors but with significant differences, like a more

¹Recent results from Zeng *et al.* found superconductivity in undoped $LaNiO_2$ (See Fig. 1.12 d)



Figure 1.12: a) Sketch of the initial and final states of the reduction with CaH₂ from the perovskite Nd_{0.8}Sr_{0.2}NiO₃ to the infinite layer Nd_{0.8}Sr_{0.2}NiO₂. b) Resistivity measurement of reduced undoped NdNiO₂ (red) and doped Nd_{0.8}Sr_{0.2}NiO₂ (purple) samples. Both figures were taken from Ref. 110. c) phase diagram of temperature versus Sr concentration for La_{2-x}Sr_xCuO₄. d) Phase diagram for three rare earth infinite layer nickelates superconductors, Nd_{1-x}Sr_xNiO₂ (green), Pr_{1-x}Sr_xNiO₂ (blue) and La_{1-x}Sr_xNiO₂ (red). Figures c) and d) were taken from Ref. 126 and Ref. 127, respectively.

extended region in both temperature $T_c \gg 15$ and doping 0.05 < x < 0.25 (Fig. 1.12 c). Samples with doping concentrations above and below the superconducting regime show metallic behavior with a weak resistivity upturn at very low temperatures. This is in notable contrast with cuprates, since they are insulators in the underdoped regime and poor metals when overdoped.

After the first experimental report of superconductivity in $Nd_{0.8}Sr_{0.2}NiO_2$ epitaxial films, various groups have synthesized this compound in thin film form by two different growth methods of the parent $Nd_{0.8}Sr_{0.2}NiO_3$, namely Pulsed Laser Deposition (PLD) and Molecular Beam Epitaxy (MBE), and obtained comparable values of the superconducting transition temperature [127, 129-131]. Figures 1.12c and 1.12d show measurements performed by two different groups on various $Nd_{1-x}Sr_xNiO_2$ samples with different doping concentrations. From these results it is clear that the room temperature resistivity strongly depends on the reduction process and/or the initial conditions of the pristine sample. Therefore, in order to obtain a unified phase diagram, more measurements and higher sample quality are required. In comparison with the unreduced samples, the treated ones display higher resistivity values, which makes them fall into the regime of bad metals or even weak insulators. On the other hand, the study of $(Nd, La)_{0.8}Sr_{0.2}NiO_2$ polycrystaline and single crystals seems to be more challenging, such that, to date, no superconductivity has been observed in these samples [132-134]. Given these observations in bulk samples, Li et al. suggested that superconductivity in thin films might arise from effects happening at the interface, like strain [132]. In addition, from transport measurements, the authors



Figure 1.13: a) & b) Resistivity curves for various $Nd_{1-x}Sr_xNiO_2$ samples measured by two different groups, reproduced from Ref. 126 and Ref. 127, respectively c) & d) Hall coefficient for NdNiO₂ measured as a function of temperature and Sr doping. (reproduced from Ref. 126), e) & f) RIXS intensity maps of LaNiO₂ and NdNiO₂ parent compounds measured as a function of the photon energy at T = 20 K (reproduced from Ref. 128).

observed an insulating behavior in their polycrystaline samples that could be suppressed by applying high pressure. Moreover, Wang *et al.* suggested that some reasons why the samples were insulating and superconductivity was not observed in bulk include the lack of compaction and the presence of nickel impurities likely resulting from the reduction process, which is probably more disordered than in thin films [133]. In the single crystals side, things look more promising since samples like $La_{1-x}Ca_xNiO_2$ show a metallic behavior, comparable to that of weakly hole-doped thin films, making them a promising candidate to display superconductivity with the right amount of doping [134].

In an attempt to understand the origin of superconductivity in infinite layer nickelates, many experimental and theoretical works have been done. On the experimental side, Hall coefficient measurements performed on $Nd_{1-x}Sr_xNiO_2$ and $Pr_{1-x}Sr_xNiO_2$ show a change of sign as a function of temperature and hole-doping [126,135]. In regions were the doping is x = 0.20 and above and for temperatures below 100 K, the main charge carriers change from electrons to holes (Figs. 1.13 c,d). This kind of behavior of the Hall coefficient indicates a multiband character of nickelates that is different from cuprates. Moreover, similar measurements on superconducting $La_{1-x}Ca_xNiO_2$ show the same trend as in Sr-doped compounds but with a lower temperature threshold (35 K) [136]. Here, Zeng *et al.* suggested that the multiband structure of infinite layer nickelates is greatly influenced by the lattice correlations. Additional evidence supporting the multiband character of nickelates comes from RIXS measurements performed on the parent (La,Nd)NiO₂ compounds [128]. In addition to the main absorption peak associated with the presence of Ni 3d states at the Fermi surface, a second peak at lower energies is also visible that can associated with the hybridization between Ni and the rare earth, and thus invoking the contribution of multiple bands (Figs. 1.13e,f). Conversely, other RIXS measurements performed on doped $Nd_{1-x}Sr_xNiO_2$ samples concluded that nickelates resemble a system with a single Hubbard band, where doped holes localize in the $x^2 - y^2$ orbital forming a d^8 singlet state [137]. In this scenario, the behavior of the Hall coefficient is associated with electron correlations that influence the shape of the Fermi surface and not with multiband effects. Despite all these measurements, a conclusive interpretation of the effects of other orbitals in the physics of superconducting nickelates is still required.

Regarding magnetic measurements, previous powder neutron diffraction observed no long range magnetic order in either of the parent LaNiO₂ and NdNiO₂ compounds down to low temperatures [119, 121]. Instead of the well established antiferromagnetism observed in isostructural cuprates, infinite layer nickelates were regarded as paramagnets. More recent experiments, however, found evidence of antiferromagnetic fluctuations in powder doped Nd_{0.85}Sr_{0.15}NiO₂ samples [138]. These results from Cui *et al.* suggest the presence of short-range glassy antiferromagnetic behavior for temperatures below 40 K in addition to antiferromagnetic fluctuations at higher temperatures. In addition, Lu *et al.* used RIXS at the Ni L_3 -edge to measure the dispersion of magnetic excitations in NdNiO₂ [139]. These dispersive excitations in NdNiO₂ were then fitted using the linear spin wave theory obtained from a two-dimensional antiferromagnetic Heisenberg model. The results featured the importance of the coupling with the rare-earth electrons and the Mott-Hubbard nature of nickelates.

On the theory side, as early works have already pointed out, there are numerous similarities and differences between nickelates and cuprates. However, a revision and extension of previous ideas needs to be done in light of the discovery of superconductivity in Nd_{0.8}Sr_{0.2}NiO₂. In recent years, various studies focusing mainly on the electronic structure have been performed using the currently available theoretical tools. For example, single particle DFT calculations are in line with the experimentally proposed multiband nature of infinite layer nickelates [140–148]. The results show that the Fermi surface has electron pockets due to Ni 3d and the rare earth 5d states, which for the later can be interpreted as an effect of self-doping guided by the hybridization between the Ni-3d and RE-5d bands (Fig. 1.14 a). In cuprates this behavior is different, making the Fermi surface substantially distinct from nickelates. In addition, *ab initio* GW+EDMFT calculations on NdNiO₂ agree with the multiband description of nickelates at low energies [149]. Moreover, XAS and Hall coefficient experiments are consistent with the theoretical notion that the RE 5d states play an important role in nickelates, and together they strengthen the idea of multiband character for these materials.

DFT calculations, also give information about the difference of the on-site energy that stimulates the migration of charge from the O-2p to the Ni-3d orbitals. In terms of the Zaanen-Sawasky-Allen diagram [16], when this difference is compared to the Coulomb interaction U, it determines whether a material belongs to the Mott-Hubbard or the charge transfer regime. According to various literature, the nickelates have a charge transfer energy close to 4 eV, a value that is substantially higher (at this energy scale) than in cuprates (2 eV), situating them in different groups (Fig. 1.14 b) [150]. Ab initio GW self-energy calculations performed by Olevano *et al.* on LaNiO₂ found substantial differences with respect to DFT for the La 4f and O 2p states, although the *d*-bands and the Fermi surface were not drastically affected [151]. These results situated LaNiO₂ within the charge transfer region rather than in Mott-Hubbard one. From the correlations



Figure 1.14: a) Band structure, orbitally resolved density of states and Fermi surface of (top) CaCuO₂ and (bottom) LaNiO₂ (reproduced from Ref. 140). b) Sketch of a Mott insulator (nickelates) and a charge transfer insulator (cuprates), where Δ is the charge transfer energy parameter (reproduced from Ref. 150, 154).

perspective, infinite layer nickelates can be described by two distinct scenarios. In the first scenario, correlations are dominated by the Ni- $3d_{x^2-y^2}$ orbitals, invoking a single band Mott-Hubbard character [152]. The second scenario, the Ni- e_g states couple with the RE - 5d states, forming a bad metal that can be described within Hund's framework [149, 153].

With respect to magnetism, various theoretical studies have obtained a magnetic ground state [140, 155–158]. One of the main issues is, then, to understand why longrange magnetic order is not observed in experiments. Using DFT calculations Choi *et al.* obtained an antiferromagnetic ordered state but with a flat band one-dimensional-like van Hove singularity that appears at the Fermi surface [159]. This singularity makes the antiferromagnetic phase unstable to spin and charge density disproportionations and to lattice distortions, which hinder the antiferromagnetic tendencies but do not cancel them. Alternatively, Zhang *et al.* explains the suppression of the antiferromagnetic long-range order in Nd_{1-x}Sr_xNiO₂ in terms of the Kondo effect [160]. At low temperatures, the Nd-5d and Ni-3d_{x²-y²} conduction electrons couple to form Kondo spin singlets and thus extinguish the antiferromagnetism (Fig. 1.15 a). Both the magnetic and electronic structures of the infinite layer nickelates are objects of intensive study at present and more experiments are necessary to clarify the discrepancies found in theory.

An important aspect that can be theoretically addressed is the pairing mechanism of the new infinite layer superconductors. Almost from the beginning, s-wave superconductivity was ruled out in these nickelates [161], and a scenario analogous to cuprates (given their similarities), were spin fluctuations play an important role, was proposed [141,142]. From theory calculations using many-body correlations, like fluctuation exchange (FLEX), random phase approximation (RPA), multiorbital DDFT+DMFT and standard t-J model (Fig. 1.15 b), d-wave superconductivity was obtained [142,162–164]. On the other hand, contrary to the spin fluctuation scenario, Werner and Hoshino proposed that given the multiband nature of infinite layer nickelates suggested by experiments and theory, super-



Figure 1.15: a) Sketch of a two-dimensional NiO₂ square lattice of NdNiO₂. Blue and orange arrows represent the Ni spin and a Nd 5*d* electron, respectively (reproduced from Ref. 160) b) Band structure and density of states from first principles calculations for fully strained NdNiO₂ grown on SrTiO₃ (reproduced from Ref. 142) c) Illustration of the possible interfacial configurations for the LaNiO₂/SrTiO₃ superlattices (reproduced from Ref. 166).

conductivity in these materials can be explained in terms of the spin-freezing theory [165]. Moreover, the authors found that $Nd_{0.8}Sr_{0.2}NiO_2$ resides in a regime governed by two spin borders, one that correspond to the highly doped region with multiorbital character and the other to the low doped region with single-band nature.

Given that to date superconductivity in nickelates has only been observed in thin films and not in bulk samples, many scientists started to investigate the relevance of the reduction process as well as the possible surface and interface effects on these materials. One of the first works included the study of $RENiO_2/SrTiO_3$ superlattices by means of first-principle calculations (DFT) [166,167]. Bernardini *et al.* studied a LaNiO₂/SrTiO₃ superlattice with special focus on the stability of the interfaces and found substantial differences compared to bulk. For the synthesis of these materials, which require the growth of a parent LaNiO₃/SrTiO₃ and its subsequent reduction, various interfacial configurations are possible (LaO, SrO and Sr, see Fig. 1.15c). In particular, LaO (which is the most straightforward configuration) is found to be unstable upon reduction, and, therefore, removing the apical oxygen would be energetically challenging. The chemical reduction would then produce a sort of atomic reconstruction that affects the interface, locally doping it with holes [166]. For these heterostructures, the band structure analysis reveals that the contribution of the 5*d* orbital can be replaced by Ni-3*d* flat bands, which could be considered as the origin of new orders that can either compete or cooperate with superconductivity [166]. A similar behavior was also obtained for thin films with asymmetric interfaces [167]. Decoupled polar layers are formed at the interfaces and the surface with the formation of a two-dimensional electron gas [168]. Here it is important to mention that the previous results will be of great importance to understanding the phenomena occurring in the heterostructures analyzed in this thesis.

In this section, we compiled the most relevant results for our thesis on the field of superconducting nickelates. However, we stress that many other different experimental and theoretical studies have also been performed in this rapidly growing field. For more extended descriptions of superconductivity in nickelates, we kindly ask the reader to refer to works done by, Botana *et al.* [169], Yaoyao *et al.* [170] and Gu *et al.* [171].

Chapter 2

Synthesis: growth and chemical treatment

This chapter is dedicated to the description of the techniques involved in the creation of the nickelate materials studied in this thesis in all their forms. We outline each system from the synthesis, the modification employing solid-state chemical processes, and the monitoring at each stage. More specifically, we elucidate the basic principles of the fabrication of films by pulsed laser deposition (PLD). Then, we explain how the materials are treated by topotactic reactions until they reach their final optimized form. In chapter 5, we will briefly discuss the synthesis of polycrystalline nickelates performed by our collaborator A. Fuchs. So far, the materials studied in this thesis cannot be directly synthesized in a single step by any of the available growth techniques. Instead, the samples must undergo at least one additional step to transform into a new phase. The second step involves the topochemical treatment, which is a well-established method for the transformation of ABO₃ perovskite TMOs into either brownmillerite or infinite-layer phases [172–175].

2.1 Pulsed Laser Deposition (PLD)

At present, the successful growth of epitaxial films and heterostructures can be achieved by employing various techniques such as molecular beam epitaxy (MBE), chemical vapor deposition (CVD), sputtering deposition (SD), and pulsed laser deposition (PLD). All nickelate heterostructures studied in this thesis are synthesized using the latter system, given that the growth parameters for these materials are well established in our research group [84,91,92,104]. The PLD is a physical vapor deposition process usually performed in vacuum conditions or in the presence of a gas like oxygen for the case of films such as the $RENiO_3$. Fig. 2.1 shows the schematic representation of a typical PLD system composed of various internal and external elements to the main vacuum chamber. Among the external elements are the optical ones, including a high-energy laser source, mirrors that correct the laser beam orientation, and a focusing lens that increases or reduces the laser spot size. Other external equipment includes the temperature control and those generating adequate internal pressure, such as the vacuum system and the background gas (usually oxygen or argon). Inside the main chamber are the heating plate and the substrate where the thin film will be deposited. In addition, the target material connected to a rotating arm is situated vertically in line with the substrate such that the deposition process covers the entire surface. For the growth of superlattices and heterostructures, the upper holder (rotating arm) has space for allocating various material targets, which



Figure 2.1: Schematic of a PLD system. The internal mechanism consists of a rotating upper holder for the target(s) and bottom holder for the substrate and the heating system. The external equipment includes the vacuum system, the gas container and the laser together with the focusing lens and the directional mirrors, .

can be alternated to form periodic structures. To improve homogeneity, each target can rotate around its edge during the growth process.

The basic operation principle of the PLD involves pulses originating from a highpower laser and hitting a target of the material that needs to be deposited. As the laser hits the target, it goes through the material's surface with a certain penetration depth. This parameter depends on the absorption coefficient of the material and the laser wavelength, which is usually in the range of nanometers. At the surface of the material, the electrons oscillate resonantly with the electromagnetic field produced by the laser and transfer their kinetic energy to the lattice producing local heat and eventually the ejection of atoms. Then, at a specific energy density of the laser, the pulses ablate a small volume of the material, which then becomes a plasma plume. The shape of the plasma plume strongly depends on the pressure inside the PLD main chamber, and its density can be described in terms of the $\cos^n(x)$ law. The vaporized plume, which carries the essential elements for the growth process, is directed towards a heated substrate where the film will be deposited. When the ejected particles hit the substrate, they generate a region of condensation covering the entire heated surface. After a specific condensation rate, the films start to grow on the substrate, and thermal equilibrium is reached. The growth rate is determined by several parameters such as the laser fluence, measured in J/cm^2 , the background pressure, measured either in mbar or Torr, the morphology of the surface where the film will be deposited, i.e., substrate termination and miscut, and the temperature of the substrate (measured in $^{\circ}$ C) [176]. The process described above

occurs in a chamber with high vacuum conditions (Fig. 2.1). The PLD environment is compatible with a broad range of pressures going from 1 Torr to ultrahigh vacuum (UHV) $\approx 10^{-8}$ Torr. In the growth of oxide films, a small amount of oxygen pressure is allowed to be present inside the chamber.

In order to attain an optimal growth of films via PLD, it is essential to control the rate at which the ablated material is deposited on the substrate. This deposition rate is affected by various parameters, and they need to be determined individually for each material. For example, the temperature of the substrate is crucial for obtaining a thermal equilibrium of deposition [177]. This condition means that below a specific temperature, no film is deposited onto the substrate independently of the amount of time the plume is active. The type of pressure and gas inside the chamber also plays a vital role because they modulate the shape of the plume. In principle, the presence of a gas in the main chamber reduces the internal pressure and demands more laser energy to ablate the target. As was previously mentioned, laser fluence is an essential parameter for generating the plume for deposition. More specifically, the laser fluence determines whether the material from the target becomes the plume or just an evaporated flux. Another critical parameter is the distance between the substrate and the target, which controls the area hit by the plume. Given that the plume has a specific shape, the distance between the target and the substrate should not be higher than its extension; otherwise, the film's distribution on the substrate will not be homogeneous. Concerning the material used, the density of the target is relevant to determine the composition of the plume and, therefore, the phase that is formed on top of the substrate. In contrast with other parameters, the density of the target and its distance from the substrate can not be controlled during the growth process and are therefore assumed to be fixed. Finally, a parameter that is also necessary for determining an optimal deposition is the repetition rate of the laser [178]. The repetition rate is defined as the number of pulses generated by the laser per time unit. In the next section, we will discuss the procedure followed to obtain the optimal values of these parameters for the $RENiO_3$.

Compared with other epitaxial film growth techniques, PLD possesses various features that make it suitable for sample production. For example, the material released from the target as the laser impacts is stoichiometrically transferred to the substrate [176]. This mechanism is possible because the vaporization of the material is a non-equilibrium process where a small volume of the target absorbs a large amount of laser energy. In order to achieve consistent vaporization of the materials, the laser fluence should be above a specific value called the ablation threshold, which is determined by the absorption coefficient of the material. Below this limit, the laser pulses will only generate heat and a thermally evaporated flux dependent on the constituent cations' vapor pressure. Another feature of PLD is that material films with multiple cations can be deposited either using multiple targets of each element constituent or employing a single stoichiometric target of the material. These targets can be composed of polycrystalline ceramics, single crystals, or cations-only materials. In contrast with other growth techniques, PLD requires relatively low temperatures to operate due to a large amount of energy in the vaporized plume.

Growth of $RENiO_3$ heterostructures

We have used various targets for the growth of perovskite nickelates heterostructures, i.e. NdNiO₃ and LaNiO₃ together with the buffer layer targets of DyScO₃, GdScO₃, LaAlO₃, LaGaO₃ and SrTiO₃. Since all of them are oxide materials, adding oxygen as background gas is required during the growth process. Previous studies on $RENiO_3$ indicate that

the crystallinity of the target and the manipulation of the irradiation of excimer laser influence and develop the MIT in the nicklelates due to cation off-stoichiometry [179–181]. Our experimental results indicate that both the La- and Nd-based as-grown samples are stoichiometric and that a sharp MIT is observed in transport measurements of the NdNiO₃ (see Section 4.4 and Appendix B).

The process we followed for synthesizing nickelate heterostructures is described as follows: First, we prepared the stoichiometric target by attaching it to a target holder with a platinum paste. In order to fix the target to the holder, it was necessary to heat them together with the paste at $200 \,^{\circ}$ C for 2 h. The target was then polished before every process run to improve the surface homogeneity. Second, we cleaned the substrate with acetone (CH_3COCH_3) in an ultrasound sonicator for 10 min and then dried it with a pressurized N_2 gun. After the initial preparation, we placed the target and the substrate inside the main chamber (see Fig. 2.1) and proceeded to activate the vacuum pump to reach the desired pressure $(p \approx 1 \times 10^{-5} \text{ mbar})$. Once the required pressure is reached, we allow the flow of a small amount of oxygen $(p_{O_2} \approx 300 \text{ bar})$. After reaching the equilibrium state, we continued the preparation process by setting the temperature. For nickelates, a small range of temperatures is suitable, i.e., between 600 and 700 °C. As additional steps, we set the frequency of each pulse (usually 4 Hz) and the total number of pulses for the growth depending on the desired thickness. Finally, we activated and adjusted the laser fluence by measuring the averaged energy provided by the laser (a common value for perovskite nickelates is $F \approx 1.6 \,\mathrm{J/cm^2}$). We employed a KrF excimer laser with wavelength $\lambda = 248 \,\mathrm{nm}$ for the ablation. The PLD used for synthesizing nickelates also possesses a shutter that we can open and close during the growth process. This device is particularly useful for the growth of superlattices as it can be activated during the time we switch between the target materials of the desired heterostructure. In the case of superlattices, the first block to be deposited was always the nickelate, and the last was the blocking layer.

To obtain the desired thickness of the heterostructure, we optimized the growth rate parameter (Å/pulse). This optimization is done by first using growth parameters from previous samples or similar materials to fabricate test specimens and then measuring the thickness or bilayer thickness of the thin film or superlattice. The growth rates are related to the thicknesses in the following way:

$$th_{tf} = \rho_{\rm LNO} \cdot n \tag{2.1}$$

and for the superlattices

$$\begin{aligned} th_{\mathrm{SL}_{1}} &= \rho_{\mathrm{LNO}} \cdot n + \rho_{\mathrm{ABO}} \cdot m, \\ th_{\mathrm{SL}_{2}} &= \rho_{\mathrm{LNO}} \cdot m + \rho_{\mathrm{ABO}} \cdot n \end{aligned} \tag{2.2}$$

where n and m represent the number of pulses used for the growth of the test samples, ρ_{LNO} and ρ_{ABO} represent the growth rates of the nickelates and the blocking layer respectively and th_{tf,SL} represent the thicknesses of the thin film and the superlattice. For the determination of the growth rates in our superlattices we usually used the combination $SL_1 = (RENiO_3)_8/(ABO_3)_4$ and $SL_2 = (RENiO_3)_4/(ABO_3)_8$ to keep sufficient difference between the components of the heterostructure.

2.2 Topochemical reactions in oxides

The chemical processes involving oxygen reduction have recently attracted considerable attention, especially in the field of solid state research [172-175]. This increased interest is mainly associated with the possibility of synthesizing new materials with meta-stable phases, high homogeneity, and preservation of the structure, due to the low temperatures at which the transformation process takes place [182]. In the specific case of TMOs, which can have various non-stoichiometric oxygen ordered phases, these mechanisms can lead to new physical properties and phases with different symmetries without abruptly changing the structure. Furthermore, the removal and deficiency of oxygen in TMOs are intrinsically related to a lower oxidation state of the transition metal ions which means that rare valence states (not synthesized by conventional techniques) can be achieved. Along these lines, Sr-doped nickelates have been found to display superconductivity as the perovskite phase with Ni³⁺ valence is transformed to the infinite-layer phase with Ni^{1+} via the topochemical reaction that removes oxygen from the apical site [110]. In this context, the topochemical reaction is defined as a process associated with a definite site in the lattice and characterized by a profound relationship between the structural thermodynamic and kinetics aspects of the starting material and the resulting product [183]. In this thesis, we applied two distinct methods for the oxygen reduction from the nickelate heterostructures, namely the solid-to-solid topochemical reaction with calcium hydride (CaH₂), lithium hydride (LiH), lithium deuteride (LiD) and sodium hydride (NaH) and the hydrogen (H_2) gas-to-solid reaction, the former being the most successful from the two.

Solid-solid topochemical reaction

Calcium hydride is a chemical compound with a salt-like structure distinguished for being widely applied as a dissecant. This alkaline earth hydride, usually presented in the pure form of white powder, reacts violently with water and air releasing hydrogen gas. In recent years, it has been extensively used to reduce various TMO materials, including nickelates [122, 123, 125, 173, 184–187]. In the absence of any source of oxygen, this compound starts to decompose at temperatures above 800 °C to metal and gas $CaH_2 \rightarrow Ca(s)+H_2(g)$. On the other hand, in the presence of an oxide material such as the rare-earth nickelates, two products are possible according to the one-electron and two-electron processes, respectively

$$RENiO_3 + CaH_2 \rightarrow RENiO_2 + CaO + H_2, \qquad 2H^- \rightarrow H_2 + 2e^-$$
 (2.3)

$$RENiO_3 + CaH_2 \rightarrow RENiO_2 + Ca(OH)_2, \quad H^- \rightarrow H^+ + 2e^-$$
 (2.4)

which in both cases will lead to a reduced valence state of the transition metal ion as $Ni^{3+} + 2e^- \rightarrow Ni^{1+}$. Similar processes have been studied for the reduction of SrFeO₃ with CaH₂ [188]. In their work, Kobayashi *et. al.*, concluded that the dominance of the one-electron or two-electron processes depends most likely on the amount of oxide being reduced and not on the temperature of the reduction. In addition, the authors found that the reaction rate does not change with an increased amount of CaH₂, whereas it is inversely proportional to the distance between the treated material and the reducing agent. Interestingly, the two materials involved in the chemical process do not have to be in direct contact to reduce the oxide due to the local generation of H₂ gas. Additional studies on nickelate thin films established optimal reduction parameters to obtain the infinite layer

phase with a minimum molar ratio of 1:2 in favor of the reducing agent [122,123,185–187]. In principle, a 1:1 molar ratio should be sufficient for the reduction; however, the studies mentioned above did not obtain satisfactory results. For the specific case of LaNiO₂, it forms in a range of temperatures between 250 and 350 °C with an optimal value of 280 °C. Below these temperatures, La₂Ni₂O₅ is the dominant phase, and above them, the perovskite phase starts to decompose into La₂O₃ and Ni metal. Regarding time, LaNiO₂ thin films can be easily obtained after 120 min of reduction, whereas the bulk samples require several days of treatment [124, 189]. Naturally, these reduction times represent values observed in the literature, and they will vary depending on the preparation conditions.

Although we describe CaH_2 as a versatile compound to reduce TMOs, we have to point out that it is not the only hydride scientists have employed to treat these materials. For example Hayward and coworkers broadly used NaH to obtain LaNiO₂ and NdNiO₂ powders [119, 121]. Ikeda *et. al.*, compared the use of carbon powder, CaH_2 , and TiH_2 for the reduction of thin films and concluded that the latter two produced the samples with the lowest resistivity in LaNiO₂ [125]. Apart from nickelates, other materials such as the oxychloride $Sr_3Fe_2O_5Cl_2$ were reduced by Dixon *et. al.*, employing LiH to obtain $Sr_3Fe_2O_4Cl_2$ [190]. As was mentioned earlier, we have also performed reductions using LiH, LiD, and NaH. For example, we reduced nickelate superlattices with LiH and LiD to study the incorporation of hydrogen in the samples, given that neutron diffraction experiments can easily identify differences between the scattering factors of hydrogen and deuterium. Furthermore, in a similar way as Hayward and coworkers, we employed NaH to reduce powder NdNiO₃ samples, but we did not manage to reproduce the infinite-layer phase with this reactant. The three reducing agents mentioned above were used only for a few samples due to the complexity of the handling and the difficulties of removing their byproducts after reduction.

Finally, on the safety side, it is essential to keep in mind that these compounds should be handled under a controlled atmosphere, given the sensitivity of hydrides to air and the hazards related to releasing hydrogen (for example, a glove box with Ar gas). Indeed, as we will see in the next sections, we have followed a safety procedure to prepare the samples that were subsequently reduced.

Solid-gas reaction with hydrogen

The first oxygen reductions performed on nickelates are attributed to Crespin *et. al.*, who used hydrogen gas to obtain bulk LaNiO₂ from its perovskite form [118]. Unfortunately, due to the difficulty of the setup and reduction process, many scientists could not reproduce the results and attempted similar experiments with different reducing agents. Nevertheless, although these difficulties illustrate the complexity of the process when handling H₂ gas, many other experimentalists have applied hydrogen as a reducing agent on powder and thin-film samples [120, 124, 125]. Compared with hydrides, H₂ requires much less reduction time to reach the infinite-layer phase. This reduction process, which involves a solid-gas reaction, must be carried out at higher temperatures than the hydrides, i.e., between 350 - 600 °C. Given this temperature range, it is straightforward to identify why it is challenging to optimize the process, i.e., at such elevated temperatures, many TMOs start to decompose even without the presence of a reducing agent, narrowing down the optimal reduction window. The reaction process between perovskite nickelates and



Figure 2.2: Schematic representation of the furnaces used for the oxygen reduction with a) hydrides and b) hydrogen gas.

 H_2 can be described as follows

$$RENiO_3 + H_2 \rightarrow RENiO_2 + H_2O$$
 (2.5)

where water is generated as a byproduct, probably in the form of condensate at the surface of the samples. Since experiments involving H_2 include the constant flow of the gas, it is conceivable to think that this is a cleaner process compared with the hydrides, which are typically (but not necessarily) in contact with the sample and encapsulated in a sealed glass.

Safety procedures require using H_2 with extreme care due to its explosive potential. This precaution means that high purity H_2 requires special equipment to be employed. To avoid this complication, a mixture of hydrogen with inert gas can be used to reduce the risk of accidents (i.e., 95% Ar - 5% H₂). An example of a setup for the H_2 reduction process can be the use of a furnace able to contain a mechanism of constant gas flow which will have the advantage of immediately renewing the reducing agent and removing the byproduct.

Fig. 2.2 shows the equipment used to reduce the nickelate samples using hydrates and hydrogen gas. The treatment procedure with powder reactants involves a conventional ceramic lab furnace inside, which is then sealed in a glass tube with the sample to be treated (Fig. 2.2 a). To avoid the direct contact between the reducing agent and the sample, we use a small box of Al, Au, or Ag that lies on the powder with the sample inside. Under these conditions, the thickness of the box would determine the distance between the sample and the powder. The preparation of the content of the glass tube

is made inside a glove box under an inert gas atmosphere to prevent the hydride from reacting before being heated together with the sample. For the case of reductions with hydrogen gas, we connect a bottle containing low percentages of H_2 to the tube furnace (Fig. 2.2 b). The samples lie inside the tube previously vented with a turbo pump. The tube furnace guarantees a continuous flux of gas that will react with the sample. Both setups mentioned above are suitable for reducing powders, thin films, and superlattices and for the reoxidation of samples, considering the appropriate modifications.

Chapter 3

Characterization Techniques

In this chapter, we will discuss the group of techniques used to characterize the samples studied in this thesis. Among the techniques used to investigate nickelate-based materials are in-house systems such as x-ray diffraction (XRD). In addition, the transport properties measurements and electrical resistivity experiments were performed in the physical property measurement system (PPMS). Experiments involving x-ray absorption spectroscopy (XAS), resonant x-ray scattering (REXS), and resonant x-ray reflectivity (RXR), were performed at the BESSY II synchrotron in Berlin. Additionally, methods and techniques used by collaborators, which are important for our results, will not be described in this chapter. However, if needed, a summary of their operating principles will be given in the corresponding sections.

3.1 Elastic x-ray scattering

Elastic x-ray scattering is a family of techniques used to obtain information about materials' physical properties and crystal structure. These techniques include x-ray diffraction, resonant x-ray scattering, and resonant x-ray reflectivity. Elastic x-ray scattering involves processes where the energy of the incident light remains unchanged after interacting with the sample. The following sections discuss the basic principles of x-ray scattering and the interaction between light and matter. A more extended description of the theory of x-rays and matter can be found in Refs. 191, 192.

3.1.1 X-ray diffraction

X-ray diffraction is a powerful technique that has been widely employed to characterize the crystal structure of samples without causing damage to them. In a typical diffraction measurement, a beam of x-rays is directed towards the sample that needs to be analyzed. The interaction between the electrons in the periodic arrangement of atoms from the sample and the electromagnetic radiation in the incident beam produces the scattering of waves in various directions. The scattered rays, which travel through unequal optical path lengths, interfere with each other to produce a diffraction pattern. The pattern is then collected by a detector that can move radially around one of the sample's edge or rotation (see Fig. 3.1 a). The diffracted intensity measured with the detector can be described in terms of a momentum transfer vector, which depends on the momenta of the incoming and outgoing waves $\vec{q} = \vec{k}_f - \vec{k}_i$. This vector \vec{q} represents the momentum transferred to the photon, which has the same magnitude but opposite sign as the momentum transferred



Figure 3.1: a) Schematic representation of an x-ray diffraction measurement in real space. The waves are scattered in all directions, but only those hitting the detector contribute to the measured diffraction pattern. The bottom part shows a representation of the events happening at the atomic level. b) Schematic representation of the reciprocal space where the limit of the diffractometer is described by the green circle and the geometric limits of the sample are described by the white circles. The purple circle is the so-called Ewald's sphere whose radius is equal to $|\vec{k}_f| = |\vec{k}_i|$ [193].

to the scatterer. Then, the information about the spatial distribution of charges in the sample can be obtained through a scattering factor defined in terms of the charge density. From a classical point of view, an atom can be modeled as an electron density of spherical symmetry $\rho(\vec{r})$. In the particular case of non-resonant, elastic scattering from a single atom, the form factor is described as

$$f(\vec{q}) = \int \rho(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r}$$
(3.1)

with the integral carried out over all scattered waves from all positions $\vec{r_i}$ in the electron cloud. In the limiting case of $\vec{q} = 0$, which correspond to the contribution of all electrons excited by high-energetic x-rays, the integral yields simply the number of electrons in the atom $f(\vec{q} \to 0) = Z$. Eq. 3.1 is valid for an energy-independent form factor; however, for a more complete expression, it is necessary to include the energy of the incident photons $\hbar\omega$ which becomes important for energies close to the resonant edges. The energy-dependent form factor is expressed as,

$$f(\vec{q},\hbar\omega) = f(\vec{q}) + f'(\hbar\omega) + if''(\hbar\omega)$$
(3.2)

where f' and f'' account for the particular response of the electrons with different binding energies to the incoming field and the damping effect of the binding energies on the electron cloud, respectively. In the case of crystals, the atoms are arranged in the form of a periodic lattice, and the contribution of each atom must be summed over the amount of smallest repeating units to obtain information about the spatial distribution of ions. This sum yields the crystal structure factor

$$F(\vec{q}) = \sum_{\vec{R}_i} f(\vec{q}) e^{i\vec{q}\cdot\vec{R}_i}$$
(3.3)

here $\vec{R}_i = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$ is the vector that describes the position of an atom in the unit cell of the crystal. The scattered intensity $I_s = |F(\vec{q})|^2$ will be large when all scattered waves are in phase and the momentum transfer together with \vec{R}_i fulfil the following condition

$$\vec{q} \cdot \vec{R}_i = 2\pi n, \qquad n \in \mathbb{Z}$$

$$(3.4)$$

Eq. 3.4 is known as the Bragg's condition where all \vec{q} coincide with a reciprocal space vector defined as

$$\vec{b}_1^* = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \qquad \vec{b}_2^* = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \qquad \vec{b}_3^* = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \tag{3.5}$$

where $\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = V$ is the volume of the unit cell in the real space and the \vec{b}_i^* (i = 1, 2, 3) form a reciprocal space (see Fig. 3.1 b) described by the vector $\vec{G} = h\vec{b}_1^* + k\vec{b}_2^* + l\vec{b}_3^*$. A graphical representation of the condition in Eq. 3.4 is given in terms of a geometrical construction called the Ewald sphere (see Fig. 3.1 b) where diffraction will be possible only if the momentum transfer \vec{q} coincides with one of the points in the reciprocal space map. According to Eq. 3.1 and Eq. 3.3, the crystal structure factor becomes the discrete Fourier transform of the atomic form factors which in turn is the continuous Fourier transform of the charge density. However, when the unit cell of the crystal is composed by different atoms, the energy dependent structure factor becomes

$$F(\vec{q},\hbar\omega) = \sum_{\vec{r}_j}^{J} \sum_{\vec{R}_i}^{N} f(\vec{q},\hbar\omega) e^{i\vec{q}\cdot\vec{r}_j} e^{i\vec{q}\cdot\vec{R}_i}$$
(3.6)

with J corresponding to the number of different atoms in the unit cell and N to the number of unit cells in the crystal. Eq. 3.6 can be further generalized by including factors related to the polarization dependence of the beam source, absorption effects, the sample's preferential orientation, and the external equipment itself. Along these lines, an expression for the intensity in terms of the structure factor is given by

$$I_s \propto F(\vec{q}, \hbar\omega) \cdot F^*(\vec{q}, \hbar\omega) = |F(\vec{q}, \hbar\omega)|^2$$
(3.7)

where $F^*(\vec{q}, \hbar\omega)$ is the complex conjugate of the crystal structure factor. For an ideal scenario $F(\vec{q}, \hbar\omega)$ becomes a Dirac delta function as N tends to infinity (see Fig. 3.2 a). However, for real systems such as single crystal substrates, a broadening of this function has to be taken into account (see Fig. 3.2b). Moreover, the analysis of thin films and superlattices studied in this thesis involves the observation of additional features such as the Laue fringes, which determine the total thickness of the sample, and the superlattice Bragg peaks, which determine the size of the bilayer formed by two distinct materials (see Figs. 3.2 c,d). All points in the reciprocal space will be allowed for samples with high symmetry, i.e., cubic structures. However, lower symmetries yield combinations of *hkl*-values which suppress the term $e^{i\vec{q}\cdot\vec{R}_i}$. These are the well-known "selection rules" for x-ray diffraction, which allow for the identification of the crystallographic space group of a particular material. The previous observations are valid when the energies of the used x-rays are much higher than the energy required to excite the core electrons. However, when the energy of the photons is tuned to the resonance of the corresponding atomic absorption edges, the reflections prohibited by the selection rules can be observed. This phenomenon indicates anisotropy in the crystal and the distortion they produce on the electronic wave function.



Figure 3.2: a) Dirac delta function for the ideal case where $\lim_{N\to\infty} F(\vec{q},\hbar\omega)$ which would appear in each of the points (yellow) of the reciprocal space in Fig. 3.1 b. b) Typical pattern of an XRD measurement performed on a single crystal substrate where a clear broadening can be observed. This curve can be modelled by the function $\csc^2(2\pi a_z \sin(\theta)/\lambda)$. c) XRD pattern of a thin film grown on a substrate. The smaller peaks are called Laue oscillations and the spectra can be modelled using the function $\sin^2(2\pi na_z \sin(\theta)/\lambda)/\sin^2(\pi a_z \sin(\theta)/\lambda)$ known as the Laue function. d) XRD pattern of a superlattice composed of two materials grown on a substrate. In contrast to c) here, there are additional peaks associated with the superlattice and useful for determining the thickness of the bilayer. The independent axis is represented as $1/d = 2\sin(\theta)/\lambda$.

3.1.2 Theory of the interaction between light and matter

Spectroscopy is defined as the study of the interaction between matter and light, including the entire spectra of electromagnetic radiation. Based on this concept, spectroscopy techniques are used to obtain information about the physical properties of condensed matter systems by employing light as a probing mechanism. When a sample is exposed to external electromagnetic waves, its local properties deviate momentarily from the equilibrium. In the sub-atomic regime, when the incident photon reaches an atom, it couples a core electronic state with an unoccupied higher energy state. Depending on the energy of the incoming photon, it will be emitted, absorbed, or scattered, and the associated electron will be either ejected or just excited to another energy state within the atom. During this process, specific probing techniques can measure the excitations produced by the external field. The magnitude of the excitations will be proportional to that of the external field, and its duration will be determined by the interaction time. In this section, we focus mainly on describing two spectroscopic techniques, i.e., resonant elastic scattering and x-ray absorption employing the linear response theory.

In a similar fashion as with x-ray diffraction, electrons inside an ion will be perturbed by the presence of an external field $\vec{E}_i(\vec{r}, t)$. The polarization vector of such electrons will then respond linearly to the incoming field:

$$\vec{P} = \chi \vec{E}_i(\vec{r}, t), \qquad \vec{E}_i(\vec{r}, t) = \hat{\epsilon} E_0 e^{-i(\omega t - \vec{k} \cdot \vec{r})}$$
(3.8)

where χ is known as the electric susceptibility of the electron, $\hat{\epsilon}$ is a unitary vector directed along the polarization direction of the electromagnetic wave, E_0 is the amplitude of the field, and ω is its corresponding frequency. From the previous equation, it is possible to define an expression for the velocity and the acceleration of the electron as

$$\vec{j} = \frac{\partial \vec{P}}{\partial t} = -i\omega\chi\vec{E}_i(\vec{r},t), \qquad \vec{a} = \frac{\partial \vec{j}}{\partial t} = \omega^2\chi\vec{E}_i(\vec{r},t)$$
(3.9)

In this sense, the interaction of the electron and the electromagnetic field can be regarded as a harmonic oscillator with frequency ω . Then, the absorption process will be associated with the damping of the oscillatory motion of the electron. The power absorbed by the electron is obtained from the time-averaged work done in this process

$$W = \frac{1}{T} \int_0^T \vec{F} \cdot \vec{j} \, dt = \langle \vec{E}_i \cdot \vec{j} \rangle = \frac{1}{2} \operatorname{Re}[\vec{E}_i^* \cdot (-i\omega\chi)\vec{E}_i]$$
(3.10)

this expression can be further simplified by introducing the conductivity $\sigma(\hbar\omega) = \omega\chi$, which is generally not a scalar but a tensor of the second rank with complex components. The real and imaginary parts of this tensor are Kramers-Kronig related, and they are obtained by solving the differential equation of the damped oscillator. From Eq. 3.10 it is possible to derive an expression for the intensity of the absorption process:

$$I_{XAS}(\hbar\omega) = \frac{1}{2} \text{Im}[\hat{\epsilon}^* \cdot \sigma(\hbar\omega) \cdot \hat{\epsilon}]$$
(3.11)

In contrast to the absorption mechanism, the scattering process involves the fields present before and after the interaction. Then, the intensity of the resonant scattering will be given by the ratio between the radiated field from the electron and the initial incoming field as

$$I_{REXS}(\hbar\omega) = \frac{|\vec{E}_o|^2}{|\vec{E}_i|^2} \propto |\hat{\epsilon}_o^* \cdot \sigma(\hbar\omega) \cdot \hat{\epsilon}_i|^2$$
(3.12)

Equations 3.11 and 3.12 evidence the close relation between the scattering and absorption processes through the conductivity tensor σ . In addition, σ is associated with the atomic form factor $f(\vec{q}, \hbar\omega)$ such that

$$\sigma(\hbar\omega) \propto f'(\hbar\omega) + f''(\hbar\omega) \tag{3.13}$$

where the absorption process corresponds to the $f''(\hbar\omega)$ term. In the next section, we will extend the description of absorption spectroscopy and how it is applied to the particular case of TMOs.

3.1.3 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is a fundamental technique used to determine the materials' local geometric, electronic and orbital structure. This section will give a quantum mechanical description of the interaction between light and matter, along with the derivation of the XAS cross-section. According to the first-order perturbation theory [194], a system in which light and matter interact can be described by a Hamiltonian of the form

$$H = H_0 + H_{ext} \tag{3.14}$$

where H_0 is the term corresponding to the non-interacting system and H_{ext} appears from external perturbations such as the potential field produced by the light $\vec{A}(\vec{r},t)$. Since the light-matter interaction involves several processes, H_{ext} will be constituted by various factors

$$H_{ext} = H_1 + H_2 + H_3 + H_4$$

= $\frac{e^2}{2m}\vec{A}^2 - \frac{e}{mc}\vec{p}\cdot\vec{A} - \frac{e\hbar}{mc}\vec{s}\cdot\left(\nabla\times\vec{A}\right) - \frac{e\hbar}{2m^2c^3}\vec{s}\cdot\left(\frac{\partial\vec{A}}{\partial t}\times\frac{e}{c}\vec{A}\right)$ (3.15)

which account for processes such as the Thomson scattering, the resonant scattering, and the non-resonant magnetic scattering. Here $H_2 = -\frac{e}{mc} \vec{p} \cdot \vec{A}$ is the most relevant term for the resonant absorption process.

The rate of transition between different states produced by a perturbation of the system is given by the Fermi's Golden Rule, expressed as

$$I_{XAS} = \sum_{f} |\langle f | H_{ext} | i \rangle|^2 [\delta(\hbar\omega + E_i - E_f) + \delta(\hbar\omega - E_i + E_f)]$$
(3.16)

where *i* and *f* represent the initial and final states of the transition and E_i and E_f the respective energies. Here, $H_{ext} \approx H_2$ and the delta function δ is introduced to preserve the energy conservation theorem. In addition, the Dirac function can be replaced by a Lorentzian function to account for the lifetime-broadening of the states occurring in real experiments by using the following transformation

$$\delta(x) = -\mathrm{Im}\left[\lim_{\Gamma \to 0} \frac{1}{\pi(x + i\Gamma/2)}\right]$$
(3.17)

where Γ is a parameter specifying the width of the Lorentzian function. Combining the two previous equations leads to an expanded expression for the intensity as

$$I_{XAS} = -\frac{eE_0^2}{2m^2} \operatorname{Im}\left\{ \lim_{\Gamma \to 0} \left\langle i \left| \left(\hat{\epsilon} \cdot \vec{r} e^{i\vec{k} \cdot \vec{r}} \right)^{\dagger} \left[\frac{1}{\pi(\omega + E_i - H + i\Gamma/2)} \right] + \left(\frac{1}{\pi(\omega - E_i + H + i\Gamma/2)} \right) \left[\hat{\epsilon} \cdot \vec{r} e^{i\vec{k} \cdot \vec{r}} \right] \left| i \right\rangle \right\}$$
(3.18)

By comparing Equations 3.18 and 3.11 it is possible to obtain an expression for the conductivity as follows

$$\sigma = \frac{eE_0^2}{2m^2} \left\langle i \left| \vec{r} \left(\frac{1}{\omega + E_i - H + i\Gamma/2} + \frac{1}{\omega - E_i + H + i\Gamma/2} \right) \vec{r} \right| i \right\rangle$$
(3.19)



Figure 3.3: Schematic description of the 2p core-level spectroscopy in a 3*d*-TMO for a) the equilibrium state and b) the excited state where a photon induces a $2p \rightarrow 3d$ transition. In this particular case a $2p_{3/2}$ electron is excited to the 3*d* states (L_3 -edge). c) Plot of the real (red) and imaginary (blue) parts of the conductivity σ described by equation 3.20. Figure reproduced from Ref. 195.

where the Hamiltonian H appears twice in the equation because it acts two times on the system, one to drive it to an excited state and the other to return it to its original unperturbed state. Then, the conductivity σ can be calculated by obtaining the eigenvalues of the Hamiltonian.

In this thesis, the XAS analysis is mainly centered at the L absorption edge of 3d TMOs with the formula ABO₃. At the L edge, XAS can probe the 3d states of the TM ion by exciting 2p core-electrons to the unoccupied 3d states. More specifically, since the spin-orbit coupling divides the 2p states in to well separated $2p_{3/2}$ and $2p_{1/2}$ levels, the corresponding transitions become the L_2 ($2p_{1/2} \rightarrow 3d$) and L_3 ($2p_{3/2} \rightarrow 3d$) edges (see Figs. 3.3 a,b). In addition, it is possible to probe the oxygen anion K-edge and the A-site cation absorption edges, provided they lie withing the XAS energy range.

The conductivity σ can be further simplified by assuming a two-level system where a transition such as $|s\rangle \rightarrow |p\rangle$ takes place. Then, applying the previous condition to Eq. 3.19, it becomes

$$\sigma = \frac{e}{2\pi m^2} \left(\frac{1}{\omega + \omega_0 + i\Gamma/2} + \frac{1}{\omega - \omega_0 + i\Gamma/2} \right)$$
(3.20)

where ω_0 is the difference of energy $E_f - E_i$ between the two states. When the energy $\hbar\omega$ matches ω_0 , the denominator in the previous equation diverges, enhancing the scattering. Furthermore, the expression for σ in Eq. 3.20 can be separated into its real and imaginary parts through a Kramers-Kronig transformation. Fig. 3.3 c shows a plot of the real and imaginary parts of the conductivity σ , with $\omega_0 = 854 \text{ eV}$ and $\Gamma = 0.5 \text{ eV}$. In general, the conductivity σ is not a scalar but a tensor with a specific symmetry depending on the material. A common symmetry exhibited by many TMOs is tetragonal, and the corresponding conductivity tensor obtained from the absorption process is given by

$$\sigma_{\text{tetra}} = \begin{pmatrix} \sigma_{xx} & 0 & 0\\ 0 & \sigma_{xx} & 0\\ 0 & 0 & \sigma_{zz} \end{pmatrix}$$
(3.21)



Figure 3.4: a) Schematics of an XAS experiment performed on a 3*d* material (blue) grown on a substrate single crystal (grey) using unpolarized light approaching at a certain angle with respect to the sample's surface. Two detection mechanisms are depicted: the total electron yield (TEY) and fluorescence yield (FY). The light in a) can be separated into b) polarization $E \perp q_z$, which probes unoccupied states in the $3d_{x^2-y^2}$ orbitals, and c) polarization $E \parallel q_z$, which probes unoccupied states in the $3d_{3z^2-r^2}$ orbitals, following the electric dipole selection rules and assuming filled t_{2g} levels and partially filled e_g orbitals.

which produces at least two distinct types of spectra that can be collected by analyzing the system with light polarized parallel and perpendicular to the tetragonal arrangement. The difference between the two types of spectra is called linear dichroism and is often expressed in the normalized form

Norm. Lin. Dic. =
$$\frac{I_{E\perp q_z} - I_{E\parallel q_z}}{(2I'_{E\perp q_z} + I'_{E\parallel q_z})/3}$$
(3.22)

where $I_{E\perp q_z}$ and $I_{E\parallel q_z}$ represent the polarization parallel and perpendicular to the plane of the sample and $I'_{E\perp q_z, E\parallel q_z} = \int I_{E\perp q_z, E\parallel q_z}(E) dE$ are the integrated intensities at the absorption edges (i.e. between the $L_{3,2}$ -edges) (see Fig. 3.4 a). This quantity is a measurement of the preferential orbital occupation and the orbital energy level splitting of non-degenerate levels in many materials such as the TMOs. Moreover, these distinct polarizations couple with particular orbitals in the 3d states. For example for a system with the t_{2g} levels completely filled, the $I_{E\perp q_z}$ probes unoccupied states in the $3d_{x^2-y^2}$ orbitals whereas the $I_{E\parallel q_z}$ probes unoccupied states in the $3d_{3z^2-r^2}$ orbitals (see Figs. 3.4 b,c).

The dichroism obtained in Eq. 3.22 can be further analyzed for the specific case of 3d TMOs by taking into account sum rules considerations. The sum rules arise from the characteristic of the dipole operator, which are related to the symmetry of the system. According to the electron-dipole approximation, Eq. 3.18 is equivalent to

$$I_{XAS} \propto \langle \psi_i | \hat{\epsilon} \cdot \vec{r} | | \hat{\epsilon} \cdot \vec{r} | \psi_i \rangle \tag{3.23}$$

where ψ_i and ψ_f represent the wavefuctions of the initial and final states respectively and $\hat{\epsilon} \cdot \vec{r}$ is the dipole operator. These elements can be expressed in terms of the spherical harmonics [196] as $\psi = Y_l^m$ and $\hat{\epsilon} \cdot \vec{r} = rC_q^1$, where q = -1, 0, +1 depending on whether the incoming light is z-linearly (q = 0) or circularly ($q = \pm 1$) polarized. Then, the evaluation

of the integral $\langle Y_l^m | C_q^1 | Y_{l'}^{m'} \rangle$ will give the selection rules for the allowed transition process as

$$\Delta l = \pm 1 \qquad \Delta m = 0, \pm 1 \tag{3.24}$$

The sum rules can be written in terms of real orbitals for the case of intensities measured with linear polarized light in materials with excitations from the p to the d states

$$I_{x} = \frac{1}{h} \left[\frac{1}{2} h_{xy} + \frac{1}{2} h_{xz} + \frac{1}{6} h_{z^{2}} + \frac{1}{2} h_{x^{2}-y^{2}} - \sqrt{\frac{1}{12}} \left(d_{z^{2}} d_{x^{2}-y^{2}}^{\dagger} + d_{z^{2}}^{\dagger} d_{x^{2}-y^{2}} \right) \right]$$

$$I_{y} = \frac{1}{h} \left[\frac{1}{2} h_{xy} + \frac{1}{2} h_{yz} + \frac{1}{6} h_{z^{2}} + \frac{1}{2} h_{x^{2}-y^{2}} + \sqrt{\frac{1}{12}} \left(d_{z^{2}} d_{x^{2}-y^{2}}^{\dagger} + d_{z^{2}}^{\dagger} d_{x^{2}-y^{2}} \right) \right]$$

$$I_{z} = \frac{1}{h} \left(\frac{1}{2} h_{xz} + \frac{1}{2} h_{yz} + \frac{2}{3} h_{z^{2}} \right)$$

$$(3.25)$$

where the h_{ij} represents the hole occupation in the respective orbital and h is the total hole occupation. A more detailed description of the derivation of previous expressions is given in Refs. 197 and 198. For the particular case of a $3d^7 : t_{2g}^6 e_g^1$ system, such as for the Ni³⁺ ion with tetragonal symmetry, the intensities are given by the following expressions

$$I_x = I_y \equiv I_{E\perp q_z} = \frac{1}{6} h_{3z^2 - \mathbf{r}^2} + \frac{1}{2} h_{x^2 - y^2}$$

$$I_z \equiv I_{E\parallel q_z} = \frac{2}{3} h_{3z^2 - \mathbf{r}^2}$$
(3.26)

where $h_{x^2-y^2}$ and $h_{3z^2-\mathbf{r}^2}$ are the number of holes in the $3d_{x^2-y^2}$ and $3d_{3z^2-\mathbf{r}^2}$ orbitals, respectively. To obtain a quantitative measure of the imbalance between the e_g orbitals, it is possible to introduce a parameter X derived from the sum rules for linear dichroism, which relates the number of holes in each e_g orbital with the corresponding polarized intensities obtained from XAS [91, 199, 200]. Then, the hole ratio X is defined as

$$X = \frac{h_{3z^2 - \mathbf{r}^2}}{h_{x^2 - y^2}} = \frac{3I'_{E_z}}{4I'_{E_x} - I'_{E_z}}$$
(3.27)

where $I'_{E_x,E_z} = \int I_{x,z}(E)dE$ are the energy-integrated intensities at the absorption edges obtained from the XAS measurement. In addition, to quantify the unequal electronic occupation of orbitals, the orbital polarization P is defined as

$$P = \frac{n_{x^2 - y^2} - n_{3z^2 - \mathbf{r}^2}}{n_{x^2 - y^2} + n_{3z^2 - \mathbf{r}^2}} = \left(\frac{4}{n_{e_g}} - 1\right) \frac{X - 1}{X + 1}$$
(3.28)

where $n_{x^2-y^2} = 2 - h_{x^2-y^2}$ and $n_{3z^2-\mathbf{r}^2} = 2 - h_{3z^2-\mathbf{r}^2}$ are the number of electrons in the $3d_{x^2-y^2}$ and $3d_{3z^2-\mathbf{r}^2}$ orbitals, respectively, and $n_{e_g} = 4 - h_{e_g}$ is the total number of electrons in the e_g orbitals [92, 201, 202]. Both the hole ratio X and the orbital polarization P can be used to compare different heterostructures with the same Ni valence state. However, for comparing superlattices with different valence states it is preferable to only use X because it does not depend on the total number of electrons in the e_g orbitals.

3.1.4 Resonant x-ray reflectivity

X-ray reflectivity (XRR) is a technique used to characterize the surfaces and interfaces of thin films and superlattices. XRR is based on the principle of reflection of x-ray from a surface following the Fresnel equations. These equations are given in terms of the refractive indexes $N(\omega)$ of the different materials forming the heterostructure being analyzed. The refractive indexes are complex numbers that depend on the specific material's atomic number and the atomic form factor. From the optical approach described in section 3.1.2 and the theory for x-ray scattering presented in section 3.1.1, it is possible to obtain an expression for the refractive indexes in terms of the atomic form factor. Starting from the expression for the atomic form factor and assuming only forward scattering ($\vec{q} = 0$) Eq. 3.2 becomes

$$f(\vec{q} = 0, \hbar\omega) = Z^* + f'(\hbar\omega) + if''(\hbar\omega)$$
(3.29)

where $Z^* \approx (Z/82.5)^{2.37}$ is a small relativistic correction for the atomic number Z and $f'(\hbar\omega)$ and $f''(\hbar\omega)$ are the real and imaginary parts of the dispersion corrections, respectively. For x-rays, the complex refractive index [203] is defined as

$$N(\omega) = 1 - \delta(\omega) + i\beta(\omega) = 1 - \frac{\rho N_A r_0 \lambda^2}{2\pi A} (f'(\hbar\omega) - if''(\hbar\omega))$$
(3.30)

where δ and β are denoted as the optical constants, ρ is the mass density, N_A is the Avogadro's number, r_0 is the classical electron radius, λ the light's wavelength, A is the atomic mass and $\hbar\omega = E$. In addition, f' and f'' are Kramers-Kronig related by the following expression

$$f'(E) = Z^* + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon f''(\varepsilon)}{E^2 - \varepsilon^2} d\varepsilon$$
(3.31)

Then, a direct correspondence between the optical constants and the components of the dispersion correction [203] is given by

$$\delta(E) = \frac{\rho N_A r_0 \lambda^2}{2\pi A} f'(E), \qquad \beta(E) = \frac{\rho N_A r_0 \lambda^2}{2\pi A} f''(E)$$
(3.32)

For the specific case of reflectivity, we use the dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ which is related to the complex refractive index by the expression $N = \sqrt{\epsilon}$. This complex linear response function is related with the optical constants by the following expressions

$$\epsilon_1 = (1+\delta)^2 - \beta^2, \qquad \epsilon_2 = 2(1+\delta)\beta$$
 (3.33)

Similar to the definition of the conductivity σ in section 3.1.2, ϵ is a tensor with complex entries $\epsilon_{ij} = (\epsilon_1)_{ij} + i(\epsilon_2)_{ij}$, where i, j = x, y, z. Therefore, the dielectric function can be expressed as

$$\epsilon = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{xz} & \epsilon_{yz} & \epsilon_{zz} \end{pmatrix}$$
(3.34)

where some ϵ_{ij} terms can be simplified depending on the symmetry of the material. For example, for cubic, tetragonal and orthorhombic symmetries, the non-diagonal terms $(i \neq j)$ become zero and the diagonal elements (i = j) are defined as

$$\epsilon_{\text{cubic}} = \begin{pmatrix} \epsilon_{xx} & 0 & 0\\ 0 & \epsilon_{xx} & 0\\ 0 & 0 & \epsilon_{xx} \end{pmatrix} \quad \epsilon_{\text{tetra}} = \begin{pmatrix} \epsilon_{xx} & 0 & 0\\ 0 & \epsilon_{xx} & 0\\ 0 & 0 & \epsilon_{zz} \end{pmatrix} \quad \epsilon_{\text{ortho}} = \begin{pmatrix} \epsilon_{xx} & 0 & 0\\ 0 & \epsilon_{yy} & 0\\ 0 & 0 & \epsilon_{zz} \end{pmatrix} \quad (3.35)$$

For lower symmetry systems such as monoclinic ($\epsilon_{xz} = \epsilon_{zx} \neq 0$) and triclinic ($\epsilon_{ij} \neq 0, i \neq j$) some or all of the non-diagonal elements are different from zero [204]. In addition, in the case of magnetic materials such as, for example, a ferromagnet with cubic symmetry ($\epsilon_{yx} = -\epsilon_{xy} \neq 0$), some of the non-diagonal elements are also non-zero [205].

Orbital reflectometry of superlattices

Orbital reflectometry relates to the study and characterization of samples using light reflection as a mechanism. With this method, it is possible to quantitatively derive the layer resolved orbital polarization profiles obtained from resonant x-ray reflectivity and absorption data [91]. In this section, we describe the procedure to calculate the form and structure factors of TMOs heterostructures, taking a nickelate superlattice as an example. Similar to the relations obtained for x-ray diffraction in Sec. 3.1.1, the intensity in a reflectivity measurement is determined by the crystal structure factor

$$F_{(hkl)} = \sum_{j} f_{j} e^{2\pi i (hx + ky + lz)}$$
(3.36)

where h, k, and l are known as the Miller indices, and the x, y, and z are the corresponding space coordinates of a particular layer. The above expression can be further simplified by assuming the general case of specular reflection where all components are zero except for the out-of-plane lz. To explain the procedure of obtaining the structure factor of a given superlattice, we will take the particular case of a heterostructure with eight layers of material No. 1 (i.e., $RENiO_{2+\delta}$) and four layers of material No. 2 (i.e., ABO₃). In addition, we will assume that material No. 2 is homogeneous, whereas material No. 1 is not. These assumptions are possible in systems such as $RENiO_{2+\delta}/ABO_3$ where ABO₃ is a band gap insulator with similar electronic properties in all its layers. In the case of $RENiO_{2+\delta}$, the electronic structure is expected to be different for the interface layers compared with the inner layers due to effects such as polar discontinuity, spatial confinement, electronic reconstruction, layer intermixing, or oxygen deficiency.



Figure 3.5: Schematic representation of four different models of interface (IF) and inner (IN) layers combinations for a $(RENiO_{2+\delta})_8/(ABO_3)_4$ superlattice. The ellipsis indicates that the structure is repeated several times, and the slabs shown represent the basic bilayer of the whole structure.

Fig. 3.5 shows the possible configurations of different amounts of interface and inner layers for the specific case of an 8//4 superlattice. We consider four models: homogeneous case (no interface layers) and one, two, or three interface layers at each side of the superlattice. Then, following Eq. 3.36 and the assumptions made above, the complete structure factor for each reflection (superlattice peak) of $(RENiO_{2+\delta})_8/(ABO_3)_4$ is given by

$$F_{(00l)} = f_{ABO} e^{2\pi i \left(\frac{0}{12} \cdot l\right)} + f_{ABO} e^{2\pi i \left(\frac{1}{12} \cdot l\right)} + f_{ABO} e^{2\pi i \left(\frac{2}{12} \cdot l\right)} + f_{ABO} e^{2\pi i \left(\frac{3}{12} \cdot l\right)} + f_{ABO} e^{2\pi i$$

The previous equation can be conveniently simplified by employing the unit circle depicted in Fig. 3.6 a. The circle has been divided into 12 slices to account for the 8 + 4 layers of materials No. 1 and No. 2, respectively. Then, applying equation 3.37 and Fig. 3.6 for the first three superlattice reflections, the corresponding structure factors for model A are given by

$$F_{(001)} = (f_{ABO} - f_{RNO}) \left(\frac{\sqrt{3} + 3}{2}\right) (1+i)$$
(3.38)

$$F_{(002)} = (f_{\rm ABO} - f_{\rm RNO})\sqrt{3}\,i\tag{3.39}$$

$$F_{(003)} = 0 \tag{3.40}$$

In this case, the $RENiO_{2+\delta}$ layers are assumed to be homogeneous and therefore there is no difference between interface and inner layers. Both $F_{(001)}$ and $F_{(002)}$ depend on the difference between f_{ABO} and f_{RNO} multiplied by a constant factor whereas $F_{(003)}$ is zero. Therefore, the information about effects arising at the f_{ABO}/f_{RNO} interface is given by the first two superlattice reflections. Furthermore, a possible indication of the homogeneity of the system is the presence or absence of the $F_{(003n)}$ (n = 1, 2, ...) reflections.

A similar procedure as the one described above yields the first three structure factors of model ${\cal B}$

$$F_{(001)} = \left[f_{ABO} \left(\frac{\sqrt{3} + 3}{2} \right) - f_{RNO}^{IN} \left(\sqrt{3} + 1 \right) + f_{RNO}^{IF} \left(\frac{\sqrt{3} - 1}{2} \right) \right] (1+i)$$
(3.41)

$$F_{(002)} = (f_{ABO} - f_{RNO}^{IF})\sqrt{3}i$$
(3.42)

$$F_{(003)} = (f_{\rm RNO}^{\rm IF} - f_{\rm RNO}^{\rm IN})(1-i)$$
(3.43)

where F_{003} is graphically represented in Fig. 3.6 b. In this case, $F_{(001)}$ depends on the contribution from all layers, $F_{(002)}$ is sensitive to effects happening a the f_{ABO}/f_{RNO}^{IN} interface and $F_{(003)}$ is perceptive to effects at the $f_{RNO}^{IF}/f_{RNO}^{IN}$ interface exclusively. Therefore, a layer resolved description of the $RENiO_{2+\delta}$ part of the superlattice will be given by the analysis of $F_{(002)}$ and $F_{(003)}$ structure factors since they give an disentangled characterization of the relevant interfaces. For completeness, models C and D where also calculated and their results are shown in Appendix A.

The models proposed in Fig. 3.5 are made assuming integer amounts and symmetric distribution of layers on both sides of the superlattices. However, in real systems, it is plausible to observe asymmetry produced by conditions such as the substrate termination, which translate into the films as the growth process occurs. In other words,



Figure 3.6: a) Unit circle divided into 12 pieces to represent the complex coefficients $e^{(2\pi i l z)} = \cos(2\pi l z) + i \sin(2\pi l z)$ of a superlattice with 8 layers of material No. 1 plus 4 layers of material No. 2. The horizontal and vertical axis represent the real and imaginary parts respectively. b) Application of the unit circle for the calculation of the structure factor of the third superlattice reflection F_{003} in model *B* from Fig. 3.5.

it is conceivable to have systems with an odd number of interface layers, which will be equivalent to assigning a fraction number of layers on each side of the superlattice. For example, a $(RENiO_{2+\delta})_8/(ABO_3)_4$ sample with 3 interface and 5 inner nickelate layers can be obtained from equally distributed amounts of the mathematical equivalent $2 * f_{RNO}^{IF} : 5 * f_{RNO}^{IN} : 1 * f_{RNO}^{IF}, 1 * f_{RNO}^{IF} : 5 * f_{RNO}^{IN} : 2 * f_{RNO}^{IF}$ and $1.5 * f_{RNO}^{IF} : 5 * f_{RNO}^{IN} : 1.5 * f_{RNO}^{IF}$ configurations. In chapter 4 we will explore the appearance of asymmetric interfaces in the reflectivity analysis of superlattices with polar interfaces. Finally, it is important to point out that a standard reflectometry analysis like the one described above includes the evaluation of at least the four models presented in Fig. 3.5 and the choice of the adequate model is made based on the agreement between simulated and experimental data.

The formalism involved in x-ray reflectivity analysis

The XRR measurements have depth-resolved information about the system being analyzed; however, this knowledge is not immediately available after the measurement and needs to be extracted from the data. This proceeding is possible by performing a simulation of the reflectivity data for the different possible models (such as in Fig. 3.5) and then comparing the results with the measured data. This section describes the process of simulating the XRR spectra from the obtainment of the optical constants from the measured XAS data, the fitting of the reflectivity data using a program specifically designed to this end, and the derivation of the layer-resolved XAS spectra.

An XRR experiment intended to obtain the depth-resolved electronic structure of a heterostructure consist of two sub-type of measurements: (i) q_z -dependent scans attained by changing the incident angle of the beam (θ) while keeping the energy (E) constant and (b) E-dependent scans performed at specific q_z -values. The q_z -dependent scans, which can be either performed at resonant or non-resonant energies, are used to obtain the structural model of the sample. Then, the structure factors of the heterostructure are obtained by fitting the thicknesses and roughnesses of the different layers. After the fitting is done, the structural model parameters are kept fixed for the rest of the analysis. In the case of the E-dependent scans, which usually (but not always) coincide with the position of the superlattice reflections, they are used to extract the element and depth-dependent electronic structure of the heterostructure.

There are various programs commercially available to simulate reflectivity spectra [206–209]. In this thesis, we used the software tool RegMagX [208, 210] to perform the above fitting process. This program is based on both Parratt and full matrix formalisms to calculate the reflectivity data. Parratt's recursive method [211,212], whose author was one of the first to employ reflectivity for the analysis of surfaces of solids, uses a dynamical scattering approach including multiple reflections originating from each layer. Then, the total reflectivity $r_{j-1,j}$ between adjacent j-1 and j layers is given by

$$r_{j-1,j} = \frac{r'_{j-1,j} + r_{j,j+1} e^{iz_j q_j}}{1 + r'_{j-1,j} r_{j,j+1} e^{iz_j q_j}}$$
(3.44)

where q_j and z_j are the momentum transfer and the thickness of layer j respectively. The expression $e^{iz_jq_j}$ represents the phase shift between the reflected (j-1,j) and (j,j+1) beams. $r'_{j-1,j}$ is known as the Fresnel coefficient and it is related to the momentum transfer vector through

$$r'_{j-1,j} = \frac{q_{j-1} - q_j}{q_{j-1} + q_j}, \qquad q_j = 2k_j \sin \theta_j$$
(3.45)

where k_j is the incoming wave vector and θ_j is the incident angle at the *j* interface, which is related to the refraction index via the following expression

$$\theta_j = 2\pi \sqrt{n_j^2 - 1 + \sin\theta} \tag{3.46}$$

here θ represents the angle formed between the incoming beam and the sample's surface. Assuming that the substrate has an infinite thickness and that the incident light can be separated into perpendicular (σ) and parallel (π) polarizations to the reflecting plane, the Fresnel equations are given by

$$r_{j-1,j}^{\prime,\sigma} = \frac{q_{j-1} - q_j}{q_{j-1} + q_j}, \qquad t_{j-1,j}^{\prime,\sigma} = \frac{2 q_{j-1}}{q_{j-1} + q_j}$$

$$r_{j-1,j}^{\prime,\pi} = \frac{n_j^2 q_{j-1} - n_{j-1}^2 q_j}{n_j^2 q_{j-1} + n_{j-1}^2 q_j}, \qquad t_{j-1,j}^{\prime,\pi} = \frac{2 n_j^2 q_{j-1}}{n_j^2 q_{j-1} + n_{j-1}^2 q_j}$$

$$(3.47)$$

In addition, the roughness, a measure of the smoothness of the interfaces, is calculated using the Nevot-Croce method. This method is based on the assumption that the dielectric constant is related to depth according to measurements of the mean plane of the surface and that a Gaussian distribution can model the surface roughness [213].

$$r_{j-1,j}^{\prime \text{N-C}} = r_{j-1,j}^{\prime} e^{-2k_{j-1}k_{j}\gamma^{2}}$$
(3.48)

where γ is the roughness between layers j-1 and j, Parratt's formalism is suitable for fitting the q_z -dependent reflectivity curves and, therefore, for obtaining the structural model with the polarization averaged optical constants. However, for comparing experimental and calculated *E*-dependent data, it is necessary to employ a method that includes the full dielectric tensor (see Eq. 3.34). The full matrix formalism uses matrix representations of the incident and reflected wavevectors and includes both σ and π polarizations related to the plane of incidence. The propagation of the field vectors in a medium is described by the boundary field vector

$$\vec{F} = \mathbb{A} \times \vec{P} \tag{3.49}$$

where \mathbb{A} is the medium boundary matrix and \mathbb{P} is the wave propagation vector. According to Maxwell's equations, the field vector components tangential to the interfaces are continuous. Then, neighboring layers fulfill the following relation

$$\mathbb{A}_1 \vec{P}_1 = \mathbb{A}_2 \vec{P}_2 \tag{3.50}$$

In the case of multiple interfaces, the relation between the first and the last layer will be given in terms of a propagation matrix $\widetilde{\mathbb{D}}$ as

$$\vec{P}_i \mathbb{A}_i = \prod_m \left(\mathbb{A}_m \, \widetilde{\mathbb{D}}_m \, \mathbb{A}_m^{-1} \right) \vec{P}_j \mathbb{A}_j \tag{3.51}$$

where the substrate is assumed to have infinite thickness. The full matrix approach calculates the roughness by segmenting the layers and assuming gradual changes in the optical constants close to the interfaces. [214, 215].

Simulation of the x-ray reflectivity spectra

A depth-resolved analysis of the electronic properties of a sample includes the realization of both XRR and XAS measurements. The first step of this analysis consists of obtaining the optical constants from the measured XAS data. This procedure is possible because the imaginary part of the refractive index is related to the intensity of the XAS according to the following expression

$$I_{\rm XAS}(E) = -\frac{1}{E} \sum_{j=1}^{N} C_j f_j''(E) \to I_{\rm XAS}(E) \propto E\beta(E)$$
(3.52)

where C_j are the number of atoms of type j per formula unit and N are the number of different atoms of the compound. Then, δ can be derived using the Kramers-Kronig transformation (see Eq. 3.31) and their relation with the form factors. The optical constants used for reflectivity need to include a sufficiently large energy spectrum usually not covered by a typical XAS measurement. Therefore, it is necessary to include theoretical values of β (or f''), which can be obtained from tables of data such as the ones calculated by Henke [216] and Chantler [217, 218]. The authors use self-consistent Dirac-Hartree-Fock calculations for isolated atoms to obtain the absorption cross-section in the region between 10 eV and 40 keV, which agrees with experimental data taken at non-resonant energies. However, at resonant energies, the calculated data does not show the characteristic details of the fine structure at the absorption edges. Then, theory and measurements need to be merged by scaling and inserting the converted XAS (β) into the calculated data. Once both δ and β are calculated, they can be used as input for the reflectivity fitting. The analysis of the q_z -dependent reflectivity data is carried out using averaged (unpolarized) optical constants obtained according to

$$I_{\rm av} = \frac{1}{3} (2 \cdot I_{E\perp q_z} + I_{E\parallel q_z}) \tag{3.53}$$

where $I_{E\perp q_z}$ and $I_{E\parallel q_z}$ can be derived from I_σ and I_π polarizations according to the following relations

$$I_{\sigma} = I_{E\perp q_z}, \qquad I_{\pi} = I_{E\perp q_z} \cos^2 \theta + I_{E\parallel q_z} \sin^2 \theta \tag{3.54}$$

with θ representing the angle between the incoming light and the plane of the sample.

Once the q_z -dependent reflectivity fitting is satisfactory, the structural model is fixed and kept in this way for the rest of the analysis. The next step after obtaining the structural model is translating it from the Parratt method to the full matrix formalism. This adaptation is achieved by calculating the dielectric tensor elements according to Eq. 3.33 and taking into account the system's symmetry. In this thesis, we study mainly tetragonal systems where $\epsilon_{xx} = \epsilon_{yy}$ and $\epsilon_{ij} = 0, i \neq j$ (see Eq. 3.35). Now, since the structural model has to be kept fixed, the *E*-dependent reflectivity and the calculated data must be compared by modulating the dielectric tensor without modifying structural parameters. A method of modulation for heterostructures with four u.c. of each material was established by Benckiser et. al. [91] and subsequently applied by Wu et. al. [92, 197]. This modulation approach consists of the introduction of a parameter α , which determines whether the contribution to the total dichroism obtained by subtracting the polarization $(I_{E\perp q_z} - I_{E\parallel q_z})$ originates mainly from the interface layer or the inner layers. The modulation employing a parameter α was further extended by Radhakrishnan *et. al.* [219] to include superlattices with a dissimilar number of layers of each material. Then, the dielectric tensor is modified to redistribute the total dichroism observed in the XAS measurement to either the interface or inner layers. In this process, the calculated data and the measured E-dependent reflectivity data will either coincide or deviate depending on the conditions of the real system.

As an example of the modulation method, lets take the same heterostructure used in the previous section $(RENiO_{2+\delta})_8/(ABO_3)_4$. The $RENiO_{2+\delta}$ slab can be divided into different numbers of interface and inner layers according to the models seen in Fig. 3.5. Then, the elements of the dielectric tensor for the interface and inner layers will be given by the following expressions

$$\epsilon_{jj}^{\text{IF}} = (1 + m \alpha) \epsilon_{jj} - m \alpha \epsilon_{\text{cubic}}, \qquad \epsilon_{jj}^{\text{IN}} = (1 - n \alpha) \epsilon_{jj} + n \alpha \epsilon_{\text{cubic}}$$
(3.55)

where ϵ_{jj} are the averaged elements of the dielectric tensor obtained from XAS, the subscript $j = x, y, z, \epsilon_{\text{cubic}} = \frac{1}{3} (2 \cdot \epsilon_{xx} + \epsilon_{zz})$ and n : m is the ratio between interface and inner layers respectively. The corresponding ratios of the models presented in Fig. 3.5 are 1 : 3 (model *B*), 1 : 1 (model *C*) and 3 : 1 (model *D*). Moreover, in order to keep the measured XAS unchanged, *m* and *n* must fulfill the following condition

$$m \epsilon^{\text{IN}} + n \epsilon^{\text{IF}} = (m+n)\epsilon^{\text{XAS}}$$
(3.56)

In addition α is the modulation parameter with $\alpha \in [-1/m, 1/n]$. The values of α can be interpreted as follows: for $\alpha = 0$ the values of $\epsilon_{jj}^{\text{IF}}$ and $\epsilon_{jj}^{\text{IN}}$ are the same and therefore there is no difference between interface an inner layers. For $\alpha = 1/n$, $\epsilon_{jj}^{\text{IN}} \propto \epsilon_{cubic}$ and $\epsilon_{jj}^{\text{IF}}$ carries the majority of the total dichorism. Furthermore, for $\alpha = -1/m$, $\epsilon_{jj}^{\text{IF}} \propto \epsilon_{cubic}$ and most of the dichroism is produced by $\epsilon_{jj}^{\text{IN}}$ [219].

The modulation method presented above allows the fitting between the calculated and experimental *E*-dependent reflectivity data. The redistribution of the total dichroism achieved by the parameter α and by testing the possible models produce two distinct spectra corresponding to the interface and inner layers. The optical constants and the associated XAS intensities can be obtained by using the following relations

$$\delta = 1 - \sqrt{\left(\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}\right)/2}, \qquad \beta = \sqrt{(1 - \delta)^2 - \epsilon_1} \tag{3.57}$$


Figure 3.7: Description of the steps involved in the reflectivity analysis. The process starts with the treatment of the XAS raw data, followed by the preparation of the optical constants. Then β and δ are used as input for the q_z -dependent reflectivity fitting. The process continues with the modulation of α to fit the *E*-dependent reflectivity spectra. Finally, when the modulation is satisfactory, the layer-resolved XAS is plotted.

which are expressions derived from Eq. 3.33. Fig. 3.7 displays a detailed graphical description of the complete reflectivity analysis for the case of $(NdNiO_3)_8/(SrTiO_3)_4$. In Chapter 4, this method will be used to analyze infinite-layer nickelate superlattices.

3.2 X-ray sources

3.2.1 X-ray tube

The diffraction measurements described in section 3.1.1 are performed using x-rays generated by a high-energy source. This device is called the x-ray tube, and it is composed of an anode and cathode enclosed in a vacuum tube (see Fig. 3.8 a). Additional components include a high-voltage source connected to the ends of the anode and cathode and a cooling system attached to the former.

The generation of x-rays can be described as follows: A high voltage source generates the needed current to release electrons from the cathode. These electrons travel in vacuum towards an anode plate, where they impact with high velocity. At the atomic level, the electrons penetrate the plate and ionize the atoms by kicking out some core electrons. The ejected electrons leave holes that are immediately occupied by other electrons arriving from higher energy levels such that the equilibrium state is reached again. This process where the electrons fill the unoccupied states leaves, as a consequence, the production of x-rays.



Figure 3.8: a) Schematic representation of an x-ray tube constituted by a cathode, an anode, and a vacuum chamber. The x-rays are generated when the charged particles originating at the cathode hit the anode and release radiation. A high-voltage source is connected to the ends of the anode and cathode b) Typical x-ray spectrum for Mo and Cu with various distinct features: two intense peaks (K_{α}, K_{β}) and a continuum called "Bremsstrahlung." The K_{α} is composed by a two-peak structure labeled as K_{α_1} and K_{α_2} corresponding to the $2p_{3/2} \rightarrow 1s$ and $2p_{1/2} \rightarrow 1s$ transitions respectively.

More specifically, at the atomic level, electrons located at the 3p and $2p_{3/2,1/2}$ levels fill the empty places left by the 1s electrons in events denoted as K_{β} and $K_{\alpha_{1,2}}$ lines. The most common materials used for the anode are molybdenum and copper, and their emission spectrum is shown in Fig. 3.8 b. The K_{α} and K_{β} for Mo appear around 0.7093 Å and 0.6323 Å respectively whereas the corresponding wavelengths for Cu are 1.5406 Å and 1.3922 Å respectively. For x-ray diffraction measurements, only one of these lines is needed (usually K_{α}). Therefore, additional devices are used to suppress the K_{β} line, such as Ni filters located in front of the beam. The beam left after the filtering process is used to probe the samples.

3.2.2 Synchrotron radiation

Measurements performed at the resonant energies of transition metal oxides like those studied in this thesis need to be performed in large-scale facilities. The small dimensions of the samples analyzed to yield a poor scattering signal which cannot be collected by in-house equipment. In addition, signals appearing due to charge, magnetic and orbital order are very small in intensity, and they need apparatus with high brilliance to capture such phenomena. The x-ray absorption spectroscopy, resonant x-ray scattering, and resonant x-ray reflectivity experiments discussed in the previous sections were performed at a synchrotron that can generate x-rays with variable energy and polarization.

A synchrotron is a particle accelerator where electrons reach relativistic speed, generating x-ray radiation. Figure 3.9 a shows a schematic representation of the parts of a typical synchrotron. The generation of x-rays in these facilities is constituted by various steps, which can be described as follow: First, the electrons emitted from an electron gun are accelerated by a linear accelerator and directed towards a booster ring. When the electrons reach relativistic speeds, they leave the booster ring and pass to the storage ring, where they are confined. While the electrons travel through the storage ring, various devices are used to control their direction and shape. For example, radio-frequency (RF) cavities are used to keep the energy of the electrons stable. In addition, various types of dipole and quadrupole magnets are used to regulate the shape and direction of the electron beam.



Figure 3.9: a) Schematic representation of a synchrotron and its essential components, the booster and storage rings, the bending magnets, the insertion devices, and the experimental hutch where measurements are performed. The three types of magnets that produce x-ray in a synchrotron b) bending magnets, which change the electron's trajectory to circulate in the storage ring c) wigglers, formed by alternating magnetic dipoles that accelerate electrons in a sinusoidal path and c) undulators, which enhance the brilliance and intensity of the electron beam by constructive interference of the wavefronts. All figures were reproduced from Ref. 220.

The dynamics of the electrons and the radiation they produce in a synchrotron are governed by the relativistic Doppler effect. By this effect, the wavelength of light changes due to the relative motion of the electrons with respect to the observer. Then, the radiation generated by the fast-moving electrons is blue-shifted, and its emission is focused in the forward direction. In addition, at such high velocities, the Lorentz contraction narrows the dipole radiation shaped in the form of a cone which opens according to an



Figure 3.10: Schematic representation of the magnetic dipole arrays of undulators, a) horizontal polarization with no phase shift, b) vertical polarization with a phase shift of $\lambda_u/2$ and c) circular polarization with a phase shift of $\lambda_u/4$, where λ_u is the period of the undulator. All figures were adapted from the UE56 BESSY synchrotron facility website [221].

angle $1/\gamma = \sqrt{1 - v^2/c^2}$, where γ is called the Lorentz factor (see Fig. 3.9 b). Therefore, as a result of the effects mentioned above, the x-ray produced possesses a high intensity and a low divergence. This radiation is characterized by various parameters such as the beam size, the intensity, the degree of collimation, and the spectra distribution. All of these variables can be comprised of a single parameter called the brilliance, defined as

$$\mathfrak{B} = \frac{\text{photon/s}}{(\text{mrad})^2(\text{mm}^2 \text{ source area})(0:1\% \text{ bandwidth})}$$
(3.58)

which is also regarded as the flux per unit solid angle and unit source area.

The radiation required to perform experiments is produced in various types of magnets. For instance, the bending magnets are used to guide the electron beam through the storage ring (Fig. 3.9 b). In this case, the x-rays are generated due to the change in the direction of the electrons. In addition, special arrays of magnets called insertion devices are used to modify the characteristics of the beam according to the experimental requirements. One of such devices is the wiggler, which consists of a series of alternating magnets (similar to the bending magnets) that amplify the incoming intensity by a particular factor (see Fig. 3.9 c). On the other hand, the undulator is a device where the emitted radiation has increased intensity and narrowed dimensions such that the beam is focused in a smaller region (see Fig. 3.9 d). The undulator also consists of alternating magnets, however, the amplitude of oscillations of the electrons is much smaller, producing a more coherent beam. The insertion devices are classified according to a parameter

$$K = \frac{e B \lambda_u}{2\pi m_e c} \tag{3.59}$$

where e and m_e are the electron's charge and mass, B is the applied magnetic field, λ_u is the phase shift between the arrays of magnets, and c is the speed of light. According to this parameter, typical values of $K \gg 1$ correspond to wigglers, and $K \leq 1$ are assigned to undulators. In addition, the intensity in a wiggler is given by $I \propto N$, whereas for the undulator, the intensity scales as $I \propto N^2$, where N is the number of dipoles in the insertion device. For the particular case of the undulators, the emitted spectral range $\Delta E/E$ is very narrow, which translates into a higher brilliance. Moreover, the energy of the photons emitted by the undulator is discrete, given the sinusoidal nature of the electron's pathway. This energy is given by

$$E_n(\text{eV}) = 950 \frac{n E_e^2(\text{GeV})}{\lambda_u(\text{cm})(1 + K^2/2 + \lambda^2 \theta^2)}$$
(3.60)

where n is the n-th odd harmonic, E_e is the energy of the electrons, K is the parameter defined in equation 3.59, γ is the relativistic factor of the electrons, and θ is the polar angle of the undulator. The parameter K can be modified by adjusting the space between the magnetic dipoles in the undulator, changing the wavelength of the electron wave and thus the magnetic field strength.

Figure 3.10 shows the configuration of three types of undulators. These configurations produce linearly polarized light either parallel or perpendicular to the plane of the electrons by changing the phase shift of the array of magnets from 0 to $\lambda/2$ respectively (see Fig. 3.10 a & b). Furthermore, circular polarized light can be produced by changing the phase shift to $\lambda/4$ (see Fig. 3.10 c). The polarization of light is essential for probing the electronic and magnetic properties of materials. This requirement is because light can couple to specific orbitals in the material depending on its polarization. Depending on the geometry of the sample and its disposition in the experimental set-up, the incoming light can be divided into two components. However, for an electromagnetic wave, it is customary to define two polarization directions based on the direction of the electric field vector. The polarization perpendicular to the plane of the particle's direction is called σ , and the polarization parallel to it is named π . The (σ,π) notation will be useful for the next chapters when samples are analyzed with synchrotron radiation. A more extended description of the topics described above regarding synchrotron radiation can be found in Ref. 220.

3.3 Transport Measurements: Resistivity

Electrical resistivity is a property of materials describing how they oppose the flow of electrical current through them. A typical resistivity versus temperature measurement determines whether a material is metallic or insulator. The resistivity of the heterostructures analyzed in this thesis was measured using the physical property measurement system (PPMS). Among the type of measurements performed in the PPMS are the two-and four-point probe and the van der Pauw method [222, 223], the latter being the one used most often in this thesis.



Figure 3.11: a) Sketch of an mm-sized sample with four contacts MNOP usually made from Au or Ag. Typical two-channel configuration for the van der Pauw measurement corresponding to sample in a). c) Curve describing the relation between the factor f and the ratio $R_{MN,OP}/R_{NO,PM}$ in Fig. 3.62 (reproduced from Ref. 223). d) Curve of resistivity versus temperature for two materials, an insulator (red) and a metal (blue), fitted with an expression representing a non-Fermi liquid and a localization activated by the variable range hopping.

The first step to performing a van der Pauw measurement is to put metallic contacts on the four edges of the sample that needs to be analyzed, as shown in Fig. 3.11 a. Then, we select two points where the current is supplied and two points where the PPMS collects the voltage. At least two independent configurations can be measured based on the desired combinations of MNOP points. For example Fig. 3.11 b shows one channel where the current goes from M to N and the voltage is collected in O and P giving rise to the resistance $R_{MN,OP}$. Similarly, one can obtain the corresponding resistance $R_{NO,PM}$. Then, the resistivity of the sample is given by the following expression

$$\exp(-\frac{\pi d}{\rho}R_{MN,OP}) + \exp(-\frac{\pi d}{\rho}R_{NO,PM}) = 1$$
(3.61)

where ρ is the resistivity of the sample and d is its thickness. Eq. 3.61 can be further simplified by introducing a proportionality factor f which relates the ratio between the resistances as shown in Fig. 3.11 c. The resistivity is then given by

$$\rho = \frac{\pi d}{\log(2)} \frac{R_{MN,OP} + R_{NO,PM}}{2} f$$
(3.62)

For most of our samples, the values of f were close to unity, indicating that the factor can be disregarded.

Electrical transport properties of nickelates

Several authors have widely studied the electrical transport properties of perovskite nickelates [224–229]. Among the rare-earth nickelates, the one that has been mainly studied is LaNiO₃, as it exhibits a metallic behavior at all measurable temperatures. However, works like the one done by Herranz *et. al.* state that an insulating behavior can be observed due to disorder that leads to Anderson-type localization [224]. In this sense, localization is assumed to be activated by the variable range hopping (VRH) process leading to

$$\rho(T) = \rho_0 \, e^{\left(\frac{T_0}{T}\right)^{1/4}}, \qquad T_0 = \frac{5.7 \, \alpha^3}{k_B N(E_F)} \tag{3.63}$$

where ρ_0 is a constat denoted as the residual resistivity, $N(E_F)$ is the density of states at the Fermi level, and α is the localization length. Nevertheless, most recent studies regard nickelates as non-Fermi liquids (NFL) [64, 230] with a temperature-dependent resistivity given by

$$\rho(T) = \rho_0 + b T^{\alpha} \tag{3.64}$$

where $\alpha < 2$ will correspond to the non-Fermi liquid regime, and $\alpha = 2$ will characterize the material as a Landau Fermi liquid (LFL).

At low temperatures, quantum corrections to the conductivity are expected, since some samples present a small resistivity upturn. These corrections can originate due to weak localization effects (WLE), the Kondo effect based on spin-dependent scattering or localization caused by the renormalized electron-electron interaction (REEI) or a combination of these effects [229]. For example, a combination of the WLE and REEI contributions [230] leads to expressions for the resistivity such as

$$\rho_{3D}(T) = \frac{1}{\sigma_0 + a_1 T^{p/2} + a_2 T^{1/2}} + b T^2, \qquad \rho_{2D}(T) = \frac{1}{\sigma_0 + a \ln T} + b T^2 \qquad (3.65)$$

where $\sigma_0 = 1/\rho_0$ is the residual conductivity, $a_1T^{p/2}$ is the term corresponding to WLE (with p = 2 for electron electron interactions and p = 3 for electron-phonon interactions), $a_2T^{1/2}$ is the term related to REEI, $a \ln T$ includes both WL and REEI effects, and bT^2 is the electron-electron Boltzmann term [225]. For some doped systems, the above expressions will be modified to include contributions originating from the Kondo effect (i.e. a logarithmic term such as $c_1 \ln T$) [229]. In the next chapter we will use these equations to fit both the perovskite and infinite-layer phases of the nickelates superlattices.

Chapter 4

Infinite-layer nickelate heterostructures

4.1 Introduction

The discovery of unconventional superconductivity in cuprates with an unusually high- T_c initiated much research on similar 3d TMOs with the hope that they can also show this fascinating state of matter. In this regard, nickelates became an excellent candidate given that they can possess similar properties such as a spin s = 1/2 in a planar d orbital and a comparable crystal structure. Recently, the scientific efforts to reproduce the properties characteristic of cuprates in other compounds yielded good results with the detection of superconductivity in a NdNiO₂ thin film doped with Sr [110]. However, these results were initially difficult to reproduce, and it took time until other groups obtained similar outcomes on their samples [127, 136, 231–233]. The reasons for this delay in the reproduction are associated with the narrow growth conditions and the subsequent chemical treatment that is required [234].

Nowadays, experiments have allowed visualizing the phase diagram of the infinite-layer nickelates, which shows a dome-like shape of the transition temperature as a function of doping concentration, another essential characteristic of cuprates [126, 127, 135]. The highest point of this dome is at $T_c \approx 15 \,\mathrm{K}$ for the $\mathrm{Nd}_{0.8}\mathrm{Sr}_{0.2}\mathrm{NiO}_2$ compound, which is much lower than the corresponding value for cuprates (See Fig. 4.1). This nickelate material can be obtained by a two-step process in which a $Nd_{0.8}Sr_{0.2}NiO_3$ thin film is first grown and then topochemically reduced with CaH_2 . Each of the previous steps are difficult to attain because they require specific conditions that different set-ups can easily miss. First, the addition of Sr to the synthesis of nickelates decreases the growth window for the perovskite phase and increases it for other phases such as the Ruddlesden-Popper [234]. Second, the reduction process leaves room for the appearance of phases with excess or deficiency of oxygen in the treated films, which might be undetectable for certain characterization techniques. Although, at present, Pr- and La-based nickelates have also been found to show superconductivity, and their corresponding phase diagrams have been drawn (see Fig. 4.1 b), many questions about the magnetic and electronic properties of these new materials still need to be addressed [135, 136, 235].

The topotactic chemical treatment to extract oxygen from nickelates has been studied for many years, and in the specific case of LaNiO_x , various stable states have been found. [118–120, 122, 124, 187, 236]. Between the perovskite LaNiO_3 and the desired infinitelayer LaNiO_2 phase, there are at least two other stable phases. As the oxygen atoms are removed, these phases are obtained by substituting some octahedral columns with square planar chains. In the $\text{LaNiO}_{2.75}$, a ferromagnetic insulator, the ratio of perovskite



Figure 4.1: a) Phase diagram of the superconducting cuprates (top) and layered T'-type nickelates (bottom). The *n* originate from the formula $RE_{n+1}Ni_nO_{2n+2}$, AFI and SC are the antiferromagnetic insulator and superconducting regions respectively. Figure reproduced from Ref. 115. b) Combined phased diagram for the $RE_{1-x}[Sr/Ca]_xNiO_2$, (RE = Nd, Pr, La). Figure reproduced from Ref. 136.

and square-planar chains is 3:1, whereas in LaNiO_{2.5}, an antiferromagnetic insulator, the corresponding ratio is 1:1 (see Fig. 4.2) [26, 237]. With respect to the pseudocubic lattice parameters, the out-of-plane constant changes considerably from 3.84 Å in LaNiO₃ to 3.38 Å in LaNiO₂ whereas the in-plane parameters shift from 3.84 Å to 3.96 Å respectively [118,187]. This relatively large difference in the out-of-plane lattice constants allows the detection of changes by characterization techniques such as x-ray diffraction.

The numerous similarities between superconducting nickelates and cuprates, reinvigorate the theoretical interest in the former materials [88, 111, 140, 146, 154, 156, 238-243]. In addition, the differences between these materials can provide important clues for understanding unconventional superconductivity. Some theories suggest similar magnetic correlations as in cuprates [238] in agreement with recent results from paramagnon dispersion analysis [244]. Other theoretical studies arrive to different conclusions regarding the magnetic properties [245]. More specifically, the antiferromagnetic coupling between spins is believed to be smaller in nickelates than in cuprates, which might hinder magnetic ordering tendencies. Along these lines, experimental results regard undoped infinite-layer nickelates as paramagnetic metals with a weak insulating behavior at low temperatures and no signs of long-range magnetic order, whereas cuprates are well-known antiferromagnetic insulators. Furthermore, the hybridization strength between Ni¹⁺ and the oxygen ligands appears to be smaller than the one of Cu^{2+} in cuprates [117, 128]. Finally, it is important to point out that despite the absence of long-range order in the parent NdNiO₂ compound [121], it shows magnetic modes that agree with the model of a Mott insulator upon doping [139].

In this chapter, we propose an alternative approach to hole doping infinite-layer nickelates that relies on the layer-selective reduction [248] of various $[(\text{La},\text{Nd})\text{NiO}_3]_m/[\text{ABO}_3]_n$ superlattices grown on different perovskite substrates. The proposed idea can be explained as follows: an oxygen-deficient nickelate/band-gap insulator superlattice is obtained through a layer-selective reduction process, which results from the different stability of the layers upon CaH₂ reduction. In case that the band insulator slabs remains unchanged, an interesting situation arises in the nickelate layers, where the apical oxygen



Figure 4.2: Crystal structure of the oxygen deficient a) $LaNiO_{2.5}$ and b) $LaNiO_{2.75}$ compounds. The crystallographic data for the structures have been obtained from Refs. 246 and 247 respectively. Figures have been drawn with the program VESTA [7].

in the interfaces layers remain, while the inner layers of the nickelate slab are reduced to the square-planar structure (see Figs. 4.3 d, e, f). This assumption is supported by density functional theory calculations, which study the interface between an ABO₃ insulator and the $RENiO_2$ [146, 167]. Suppose we now assume the additional charge induced by the remaining apical oxygen ion is homogeneously redistributed across the entire LNO layer stack. In that case, this will allow tuning the doping level by controlling the number of m layers. Then the nickel valence state is given by $Ni^{1+\frac{2}{m}}$ (see Figs. 4.3 d, e, f). In addition, a similar doping mechanism is expected to occur in reduced Ruddlesden-Popper single crystals of $(La, Pr)_4Ni_3O_8$ [114], and in the newly discovered superconducting T'type structure $Nd_6Ni_5O_{12}$ [115]. Furthermore, it is important to mention that superconductivity was found in analogous infinite-layer cuprate superlattices [249–251]. In these heterostructures, superconductivity arises due to the injection of charge carriers into the CuO_2 planes either by a metallic buffer layer or by the interface between the cuprate and the band gap insulator, which act as a charge reservoir. Finally, contrary to the difficult growing conditions in the chemically doped infinite-layer nickelates, the synthesis of the pristine superlattices has been widely studied, the growth conditions are much more stable, and the required parameters are well-known [92].

In this thesis, we describe the study of various nickelate pristine and reduced superlattices in combination with band-gap insulting perovskite compounds (also called blocking layers), such as $GdScO_3$, $DyScO_3$, $LaGaO_3$, $LaAlO_3$, and $SrTiO_3$. Our main objective is to produce a heterostructure with nickelate layers in the square-planar configuration, which can be doped through the interface with the blocking layers to attain superconductivity. The superlattice configuration includes control parameters that can facilitate the doping of the square-planar nickelate layers, such as electronic and spatial confinement, charge transfer, superexchange interactions, and structural distortions. The different superlattices are divided into three groups: (i) La- and Nd-based nickelates combined with scandates grown on the same material as the blocking layer (see Figs. 4.3 a, d). This group of materials was chosen considering the lattice matching between the infinite-layer nickelates and scandates, which is believed to produce small structural distortions. (ii) La-based nickelates together with materials that make no A-cation change across the interface, i.e. LaBO₃ (see Figs. 4.3 b, e). The continuity of the A-cation atomic layers between the nickelate and the blocking layer is expected to yield less disorder at the



Figure 4.3: The three types of nickelate superlattices analyzed in this thesis. The yellow arrows describe the distinctiveness of each group. a) & d) nicklelate/scandate superlattices are expected to have a good in-plane lattice matching upon reduction in addition to the cooperative tensile strain produced by the substrate. b) & e) nickelate/LaBO₃ superlattices keep the A-cation site unchanged across the interface. c) & f) nickelate/titanate have charge discontinuity at interfaces which can lead to charge doping. The structures correspond to LaNiO_{2+ δ}/DyScO₃, LaNiO_{2+ δ}/LaGaO₃ and LaNiO_{2+ δ}/SrTiO₃, where $\delta = 1$ for a), b) & c) and it is expected that $\delta \approx 0.25$ for d), e) & f) respectively.

interface. (iii) La- and Nd-based nickelates combined with and grown on SrTiO₃ (see Figs. 4.3 c, f). Perovskite oxides of the form $RE^{3+}Ni^{3+}O_3$ are polar materials, whereas $Sr^{2+}Ti^{4+}O_3$ is considered to be a non-polar compound. This polarity is based on the charge difference between the AO and BO₂ planes, which leads to 0 in STO and +1/-1 in LNO. Therefore, a nickelate/titanate superlattice has a charge discontinuity at the interface that might lead to an effective hole or electron doping. In this regard, systems such as the nickelate/titanates are prone to charge transfer, which seeks to counterbalance the polar discontinuity at the interface by injecting charge from one B-cation to the other. As we will see in the next sections, the reduced structures depicted in Figs. 4.3 are different from the real structures obtained from the experimental analysis, except for the LaNiO_{2+ δ}/LaBO₃ superlattices case.

4.2 Nickelate/scandate superlattices

We start our study of infinite-layer nickelate superlattices by analyzing heterostructures combined with scandates. Although our main objective is to find a heterostructure that shows superconductivity, our first task is to see if the structure depicted in Figs. 4.3 d, e, f can be achieved by a topochemical treatment. In this regard, we selected the nickelate/scandate configuration as the first candidate to attain the infinite-layer phase in the nickelate part and the layer-selective reduction of the superlattice. The choice of scandates as blocking layers was made based on the small difference in the in-plane lattice mismatch expected upon reduction, which might lead to more stable structures. In addition, nickelates and scandates have the same polarity of atomic layers along $(001)_{pc}^{-1}$. Moreover, $DyScO_3$ and $GdScO_3$ are considered to be very stable against reduction, and their growth conditions are well established in our group [84, 92, 252]. Earlier experimental studies on similar heterostructures include x-ray absorption, resonant reflectivity, and diffraction on a series of $LaNiO_3/DyScO_3$ superlattices. For example, France *et al.* found a quasitwo-dimensional noncollinear antiferromagnetic structure in the $(\text{LaNiO}_3)_m/(\text{DyScO}_3)_n$ superlattice (m = n = 2) [84]. In addition, Bluschke *et al.* studied the interaction between the magnetic moments of Ni and Dy in a group of $(LaNiO)_2/(DyScO)_2$ superlattices and found that exchange interactions between the 3d and 4f spins influence the nickelate order and in turn induce a similar periodicity in the interfacial Dy sublattice [252]. In a $(LaNiO_3)_4/(DyScO_3)_4$ sample, Wu *et al.* obtained orbital polarization as high as 22% and 16% for the interface and inner nickelate layers respectively, showing the impact of epitaxial strain on the enhancement of a preferential orbital occupation [92]. On the theoretical side, a recent study suggest that superconductivity can be achieved in a $(LaNiO_3)_1/(DyScO_3)_3$ superlattice [253]. The reason for choosing this configuration resides in a group of effects produced at the interface, such as the tensile strain, oxygen octahedral distortions, and a polarized internal electric field. The studies mentioned above describe two important phenomena: (i) the magnetic moments of Ni are aligned for superlattices with two nickelate and scandate layers, and (ii) the tensile strain exerted by the substrate (in this case, $DyScO_3$ or $GdScO_3$) on the epitaxially grown superlattice produces a significantly large polarization of about 25% in favor of the $d_{x^2-y^2}$ orbitals for the nickelate slabs. Later in this chapter, we will compare the orbital polarization values from Ref. 92 with the corresponding percentages obtained in our samples to determine if the layer stacking impacts the measured orbital polarization. Additionally, we will contrast the orbital polarization produced by strain and oxygen removal.

In this section, we study three types of superlattices, namely LaNiO_{2+ δ}/DyScO₃ (LNO/DSO), NdNiO_{2+ δ}/DyScO₃ (NNO/DSO), and LaNiO_{2+ δ}/GdScO₃ (LNO/GSO). The first successful reduction of superlattices occurred in a group of nickelate/scandate heterostructures, including LNO/GSO, which were grown on a (110) oriented GdScO₃ substrate [254]. We attribute this to the specific epitaxial conditions of the pristine samples and the lattice matching between the components of the expected reduced superlattice. Pristine LNO has a bulk pseudocubic lattice constant of 3.840 Å [255], whereas GSO and DSO have pseudocubic lattice parameters of 3.965 Å and 3.945 Å, respectively [256–259]. This difference produces a significant amount of tensile strain (3.3%, 2.8% respectively, see Eq. 1.2.1) that could facilitate the removal of apical oxygen in the subsequent reduction process since the reduced infinite-layer LNO has bulk in-plane lattice constants of 3.960 Å [236], which is close to the pseudocubic in-plane values of the scandates. This

¹Here pc refers to pseudo-cubic, for orthorhombic indexing, no subscript will be used

agreement of lattice parameters might be useful to reduce the formation of distortions and structural faults in the reduction process that could originate from lattice mismatch.

The considerations mentioned above made the nickelate/scandate superlattices the most promising candidates for the realization of infinite-layer/blocking-layer heterostructures and motivated their synthesis, characterization, and reduction. The superlattices were synthesized by pulsed-laser deposition (PLD) using high-density stoichiometric targets of LaNiO₃, NdNiO₃, DyScO₃ and GdScO₃, and following the growth conditions established in Ref. 92. The samples with initial dimensions of $5 \times 5 \,\mathrm{mm}^2$ were cut into four equal pieces, one of which was kept pristine, and the rest were used to optimize the reduction process. This procedure is expected to decrease the effect of subtle differences between the structure of superlattices obtained in different PLD growth runs. The reduced samples were obtained by using CaH_2 powder as a reductant. The reduction process can be described as follows: The cut pieces were prepared inside a Glove Box under Aratmosphere and placed in an open box usually made of gold or aluminum foil. Then, the boxes were placed inside a small glass/quartz tube on top of approximately $50 - 100 \,\mathrm{mg}$ of CaH₂ powder. Later, the tubes were sealed in a vacuum $(10^{-6} \text{ to } 10^{-7} \text{ mbar})$ and subsequently annealed in an oven at 280° C for various times ranging from 12 - 192 h. After this time, the samples were carefully subtracted from the glass tubes and washed in acetone (CH_3COCH_3) .

Based on all reduction attempts, we concluded that not all layer combinations are possible [254]. A careful study of the successfully reduced superlattices reveals two trends: (i) In general, it was more challenging to reduce samples where the number of nickelate layers $(m_{\rm LNO})$ was equal or lower than the number of blocking layers $(n_{\rm DSO(GSO)})$. A possible explanation for this phenomenon is that a large number of DSO (GSO) layers can produce structural distortions at the interfaces with the LNO layers that slow down or completely prevent the reduction process from happening. (ii) Samples with less than four nickelate layers could not be reduced. This observation could be linked to the restrictions imposed by the buffer layers regarding oxygen removal, which could extend to more than one layer, making less efficient the reduction process in superlattices with m < 4. Keeping in mind the previous considerations and in order to perform a complete study of the reduced nickelate superlattices, various layer combinations need to be tested. In our previous work, we performed successful reductions on various LNO/GSO and LNO/DSO superlattices, where the number of nickelate (m = 4, 6) and scandate (n = 1, 2, 3, 4) layers varied methodically. Although the samples changed structurally upon reduction, no signs of superconductivity were found; instead, a metallic or semiconducting behavior was observed [254]. In this section, we continue the analysis of the nickelate/scandate superlattices for other layer combinations in the search for a system that shows superconductivity.

$LaNiO_{2+\delta}/DyScO_3$

We start our analysis with a specific type of superlattices, where we keep the number of LNO layers fixed, and the amount of DSO is changed systematically. At first sight, one might expect no change in the structural and electronic properties of the Ni ions as a function of the number of blocking layers, but given the observation (i) described above, it becomes necessary to test different amounts of buffer layers in search of the most stable structure. Fig. 4.4 shows a group of x-ray diffraction and electrical resistivity measurements of various LNO/DSO samples. We studied three different configurations, namely $(\text{LNO})_8/(\text{DSO})_2$, $(\text{LNO})_8/(\text{DSO})_4$ and $(\text{LNO})_8/(\text{DSO})_6$ grown on (110) oriented



Figure 4.4: a) XRD of a group of pristine and reduced $(\text{LNO})_m/(\text{DSO})_n$ superlattices. The region comprises the $(001)_{\text{pc}}$ and $(002)_{\text{pc}}$ substrate peaks. The dashed vertical line represent the position of the main Bragg peak of the reduced samples. The asterisks mark peaks arising due to the gold contacts on some samples used for transport measurements. b) Resistivity of the same group of (top) pristine and (bottom) reduced samples. The orange dashed lines represent fittings of the data according to Eq. 3.64. Data in a) has been vertically translated for clarity.

DyScO₃ in order to investigate how the structural and transport properties of the reduced superlattices change as a function of the number of DSO layers. We observed that samples with n = 2 DSO layers required substantially less treatment time than samples with n = 4and 6, which required comparable times. Although all samples analyzed had the same repetition and, therefore, significantly different thicknesses, we believe that the contrasting reduction times are not related to this thickness difference due to the large time scale used in the topotactic process (1-8 days).

X-ray diffraction measurements to characterize the samples were performed in a fourcircle single-crystal diffractometer, equipped with a Cu- $K_{\alpha 1}$ source and a Dectris MYTHEN line detector (see Fig. 4.4 a). Compared with the pristine samples, all peaks of the reduced samples are shifted to higher values of 1/d, consistent with a smaller out-of-plane lattice constant. In particular, next to the $(001)_{pc}$ substrate reflection, all reduced samples show a peak around $c \approx 3.69$ Å. The out-of-plane parameter of a superlattice Bragg peak is given by the average of its constituent layers [260]. This result arises from the fact that the individual out-of-plane parameter (c_{pc}) of LNO and DSO are not resolvable along the stacking direction due to the resolution limits imposed by the quasi-two dimensionality of the structure. Therefore, the peak center is determined by the averaged value:

$$\overline{c}_{\rm SL} = \frac{m_{\rm LNO}c_{\rm LNO} + n_{\rm DSO}c_{\rm DSO}}{m_{\rm LNO} + n_{\rm DSO}} \tag{4.1}$$

where $m_{\rm LNO}$ and $m_{\rm DSO}$ are the number of layers of LNO and DSO respectively and $c_{\rm LNO}$ and $c_{\rm DSO}$, the corresponding out-of-plane lattice constants. Assuming that the lattice constant of the DSO layers is approximately the same as the substrate (bulk) and that we can subtract the DSO contribution (i.e. by solving Eq. 4.1 for $c_{\rm LNO}$), the averaged LNO out-of-plane lattice constant is $c_{\rm LNO} = 3.55$ Å, which is far from the value for bulk LaNiO₂ $c_{\rm LNO,bulk} \approx 3.38$ Å [236] and thin films $c_{\rm LNO,TF} \approx 3.40$ Å [122]. This result indicates that probably not all nickelate layers are reduced. However, we rule out that further reduction is possible, as the diffraction patterns observed in XRD did not change significantly after a certain minimum reduction time. Therefore, we infer that interfacial effects prevent the complete reduction of the LNO part in the superlattices. In addition, while literature data do not indicate a significant variation between samples grown on different substrates [124], we conclude that strain cannot account for such a difference between the LNO lattice constants of bulk and superlattices.

Once we calculated c_{LNO} for all superlattices, we would like to estimate how many layers, on average, have been reduced to the infinite-layer phase. To accomplish this, we assume that the LNO slabs are structurally composed only by integral layers of the known reduced stable forms, i.e., LaNiO_{2.5} and LaNiO₂. In principle, the reduced part of the superlattice might be constituted by various intermediate phases of LaNiO_{2+ δ}; however, here, we will only employ $\delta = 0, 0.5$ as an approximation of the actual scenario. In the following sections, we will see that this is a reasonable assumption as the results agree with the fitting performed on the XRD data and spectroscopic measurements. We use the formula

$$c_{\rm LNO} = \frac{p_{\rm LNO_{2.5}} c_{\rm LNO_{2.5}} + q_{\rm LNO_2} c_{\rm LNO_2}}{p_{\rm LNO_{2.5}} + q_{\rm LNO_2}}$$
(4.2)

where $c_{\text{LNO}2.5}$ and $c_{\text{LNO}2}$ are the out-of-plane lattice constants of the epitaxial strained LaNiO₂ and LaNiO_{2.5} thin films respectively and $p_{\text{LNO}2.5}$ and $q_{\text{LNO}2}$, their corresponding number of layers. Using values of $c_{\text{LNO}2} = 3.40$ Å and $c_{\text{LNO}2.5} = 3.74$ Å [122, 123, 125], we find that the best agreement between the c_{LNO} obtained with Eqs. 4.1 and 4.2 occurs when $p_{\text{LNO}2.5} = 4$ u.c. and $q_{\text{LNO}2} = 4$ u.c. With this information, we can obtain the corresponding chemical formula and valence state of the reduced LNO part of the heterostructure. Then, the nickelate slab can be written as $\text{LaNiO}_{2+\delta}$ with $\delta \approx 0.25$ and a corresponding valence state of Ni^{1.5+}. The previous results are only an estimation of the approximate value of the out-of-plane lattice constant and the averaged valence state and represent an indirect measure of the amount of oxygen vacancies, which helps to compare different superlattices and their maximum reduction stages.

Figure 4.4 b shows the electrical resistivity measurements of the $(LNO)_8/(DSO)_n$, (n = 2, 4, 6) pristine and reduced samples. The pristine samples plotted in the top panel have comparable curves from 300 K to 2 K. On the other hand, the reduced samples plotted in the bottom panel present a metallic behavior with small upturns at low temperatures. Various authors have done a detailed analysis of the resistivity versus temperature dependence in LaNiO₃ thin films [225, 227, 228, 230, 261]. At relatively high temperatures, the curves can be fitted by equation 3.64 and depending on the value of α , the materials will be classified as non-Fermi liquids ($\alpha < 2$) or Landau Fermi-liquids ($\alpha = 2$). Our fittings performed on the untreated samples yielded values of $\alpha \approx 4/3$, whereas, in the case of the reduced samples, they gave $\alpha \approx 3/2$, in good agreement with literature values [225,230]. Moreover, the value of α for the reduced samples is in close agreement with fitting results performed on the normal state of the infinite-layer $Nd_{1-x}Sr_xNiO_2$ [262]. At low temperatures, however, there are other effects involved, and quantum corrections, including renormalization of electron-electron interaction (REEI) and weak localization effects (WLE), have to be taken into account (see Sec. 3.3) [224, 263]. If we consider both REEI and WLE effects, the fitting procedure for the pristine samples gives a good agreement with the 3D case, whereas the reduced samples are best described by the 2D case (see Eq. 3.65) [224].



Figure 4.5: a) XRD of a group of pristine and reduced $(\text{LNO})_m/(\text{GSO})_n$ superlattices. The region comprises the $(001)_{\text{pc}}$ and $(002)_{\text{pc}}$ substrate peaks. The dashed vertical line represent the position of the main Bragg peak of the reduced samples. b) Resistivity of the same group of (top) pristine and (bottom) reduced samples. The red dashed lines represent fittings of the data according to Eq. 3.64 and 3.63. Data in a) has been vertically translated for clarity.

$LaNiO_{2+\delta}/GdScO_3$

As a part of the study of nickelate/scandate superlattices, we also used GSO as a blocking layer to investigate the effects of the A-cation change $(Dy \rightarrow Gd)$ on the crystal and electronic structure of the superlattices. In this regard, we studied three different configurations, namely $(LNO)_8/(GSO)_2$, $(LNO)_8/(GSO)_4$ and $(LNO)_6/(GSO)_4$ grown on (110) oriented GdScO₃. Fig. 4.5 shows a set of XRD and electrical transport measurements for the pristine and reduced LNO/GSO heterostructures. Similar to the LNO/DSO samples, the LNO/GSO superlattices show high crystallinity in both pristine and reduced forms. A careful study of the region around the $(001)_{pc}$ substrate reflection retrieves an averaged LNO/GSO out-of-plane lattice constant of 3.68 Å, which is very close to the value obtained for the LNO/DSO superlattices. However, given that GSO posses slightly larger lattice constants, the c-axis lattice parameter for the LNO slab will be lower i.e. $c_{\rm LNO} = 3.53 \,\text{\AA}$ (see Eq. 4.1) suggesting a lower oxygen content than in LNO/DSO. In addition, Fig. 4.5 b shows the electrical transport measurements for the pristine (top) and reduced (bottom) LNO/GSO superlattices. Again, the pristine samples show the same resistivity range for both LNO/DSO and LNO/GSO superlattices. Concerning the reduced heterostructures, the results are comparable to the LNO/DSO superlattices except for the $(LNO)_8/(GSO)_2$ sample, which shows a semiconducting trend. In this case, the behavior of the sample is best described by the variable range hopping mechanism (VRH) with the characteristic temperature dependence of $\rho(T) = \rho_0 \exp(T_0/T)^{1/(d-1)}$ (see Eq. 3.63), where d = 3 is used for the three-dimensional resistance. In this regard, the Mott VRH model describes how resistivity behaves as a function of temperature in disordered systems with localized charge carriers, and it has been already applied to nickelates case [224, 264]. Then, the high resistivity values together with the low-intensity Bragg peaks (see Fig. $4.5 \,\mathrm{a}$) of the sample with n = 2 suggest the presence of structural disorder appearing after the reduction process.

In order to get insight into the local, electronic structure of the involved elements in the nickelate/scandate superlattices, we performed X-ray absorption measurements on all previous samples. The experiments were performed at the UE46 PGM-1 undulator beamline of the BESSY-II synchrotron at Helmholtz-Zentrum Berlin, which provides two types of linear polarization, i.e., σ and π -polarized light. For all XAS measurements, we used the averaged XAS spectra obtained for each polarization (σ, π). The two distinct spectra were measured alternately and at least twice to increase the accuracy of the results. In addition, a background line and a normalization factor after the Ni- L_2 edge were applied, and in all cases the La- M_4 line was also subtracted by a Lorentzian fit. Finally, to obtain I_x and I_z , we employed the Eq. 3.54 defined in section 3.1.4.

Fig. 4.6 shows the polarization-dependent XAS and linear dichroism of various reduced LNO/DSO and LNO/GSO samples at the Ni- $L_{2,3}$ edges. For completeness, the corresponding XAS spectra for the pristine samples are shown in the Appendix B.1, and they are in qualitative agreement with previous measurements of Ni³⁺ heterostructures [92]. Moreover, XAS measurements at the Dy- $M_{4,5}$, Gd- $M_{4,5}$, and Sc- $L_{2,3}$ edges, which are shown in the Appendix C.1 and C.2, display no difference between the treated and non-treated samples, indicating the layer selectness of the reduction process in the nickelate/scandate superlattices. Both graphs in Fig. 4.6 show various features that need to be discussed in detail. For example, LNO/DSO and LNO/GSO samples with n = 2show low-intensity peaks at the Ni- $L_{2,3}$ edges and a subtle preferential hole occupation of the $d_{x^2-y^2}$ orbitals. However, there are some regions where the $d_{3z^2-\mathbf{r}^2}$ orbitals are also dominant (e.g., $\approx 852.9 \,\text{eV}$). One possible explanation for these results is that a low number of buffer layers $(n \leq 2)$ allow regions with a- and c-axis oriented infinite layer planes resembling the thin film case [122]. However, evidence of such regions was not found on the corresponding XRD measurements, probably because the Bragg reflections of this phase might be buried under the superlattice peaks. Another possible interpretation of the results could be that for this configuration, other phases, such as the ones containing Ni^{2+} dominate the spectrum at the resonant edges. In this regard, we have inspected our diffraction measurements for Bragg reflections belonging to La₂NiO₄ and NiO, but we found no evidence of these phases. On the other hand, samples with n > 2 show a clear peak structure at the Ni- $L_{2,3}$ edges. These peaks indicate a higher hole density in the $d_{x^2-y^2}$ orbitals resembling a $3d^9$ system, which is remarkably similar in all samples, albeit such peaks are slightly more intense in the LNO/DSO than in the LNO/GSO samples.

$NdNiO_{2+\delta}/DyScO_3$

In this section, we focus on a group of nickelate/scandate superlattices where we employ NNO (Nd-based nickelate) instead of LNO. Interestingly we found that these superlattices require substantially less reduction temperature and time in comparison with their LNO counterparts ($T = 260 \,^{\circ}$ C, $t < 1 \,^{d}$ ay). In the following, we describe the result obtained from a pair of pristine and reduced pieces of the same cut sample with the stacking (NNO)₈/(DSO)₄. The x-ray characterization of the pristine and reduced samples is shown in Fig. 4.7 a. As in the LNO superlattices, the NNO/DSO samples show well-defined structural patterns, and their main Bragg peaks are shifted with respect to each other. Similarly, as for the LNO superlattices, we can assume that the treated sample is composed only of the known reduced stable forms Nd₃Ni₃O₇ (Ni^{1.66+}) and NdNiO₂ (Ni¹⁺). In terms of single-phase layers, separating the DSO contribution with Eq. 4.1, and using $c_{\rm NNO_2} = 3.30 \,^{\rm A}$ and $c_{\rm NNO_{2.33}} = 3.765 \,^{\rm A}$ [265, 266] in Eq. 4.2, we obtain results that suggest that only three layers from the nickelate slab are reduced to the infinite-layer phase and that intermediate reduction phases might dominate the electronic properties of the superlattice.



Figure 4.6: Polarization dependent XAS (I_x, I_z) at the Ni- $L_{2,3}$ edges of a group of reduced a) LNO/DSO and b) LNO/GSO superlattices. In both sets of data, the La- M_4 line and the edge jumps (Ni- $L_{2,3}$) have been removed. The top parts of the spectra have been vertically translated for clarity. The bottom parts of the spectra are the normalized linear dichroism calculated according to Eq. 3.22 and multiplied by a factor of 300.

Contrary to LNO, which has no magnetic ordering transition unless the amount of layers is very small, NNO possesses an antiferromagnetic ordering below $T_N \approx 200 \,\mathrm{K}$ [64, 84]. This condition makes NNO suitable for magnetic studies on oxygen deficient samples. A similar analysis of the oxygen vacancies in $\text{SmNiO}_{2+\delta}$ thin films was done by Li et. al. [267]. In their work, the authors found that the magnetic order represented by a Bragg peak at q = (1/4, 1/4, 1/4), is rapidly diminished upon oxygen removal. We have performed resonant x-ray scattering to achieve a detailed characterization of the magnetic ordering in pristine and reduced NNO/DSO superlattices. Fig. 4.7 b shows resonant reciprocal space scans at the Ni- L_3 edge ($E = 853.4 \,\mathrm{eV}$) for both pristine and reduced samples. At base temperature (T = 10 K), the pristine sample shows a small, but visible resonant Bragg reflection at $\mathbf{q}_0 = (1/4, 1/4, L)$, in accordance to similar experiments on NNO heterostructures [64, 268]. On the other hand, the reduced sample shows a more intense peak at a similar \mathbf{q}_0 . We performed temperature and polarization dependence measurements on the reduced sample to understand the nature of the observed peak. On the temperature side, Fig. 4.7 c indicates that the peak detected in the reduced sample, persist even at high temperatures $(T = 300 \,\mathrm{K})$. In addition, while the treated sample shows almost no difference between distinct polarizations (I_{σ}, I_{π}) at T = 10 K, it clearly displays a small difference at $T = 300 \,\mathrm{K}$ (see Fig. 4.7 b). Moreover, a comparison of the energy dependence of the diffracted intensity at \mathbf{q}_0 with the XAS yields similar results with small but clear differences between I_{σ} and I_{π} at both temperatures (see Fig. 4.7 d). Determining whether the origin of the peak observed in the treated sample is magnetic or structural related is difficult. Nevertheless, hereunder we briefly discuss the possible source of this Bragg reflection. Given that in nickelates, the magnetic order seems to decrease abruptly as a function of oxygen content [267] and that no long-range magnetic order has been observed in NdNiO₂ [139, 269], we conclude that the square planar phase is probably not the source of such Bragg reflection. Based on the out-of-plane lattice constant calculations, it is possible that the treated superlattice possesses intermediate phases such as Nd₃Ni₃O₇ [266, 270]. According to Moriga *et. al.*, Nd₃Ni₃O₇ is a weak ferromagnet with $T_C = 340 \,\mathrm{K}$ and it could be the responsible for the appearance of such peak [270]. Additionally, the Nd₃Ni₃O₇ structure can be regarded as a supercell with



Figure 4.7: a) XRD of a pair of pristine and reduced (NNO)₈/(DSO)₄ superlattices around the $(001)_{pc}$ substrate peak. b) Polarization-dependent scans around $\mathbf{q}_0 = (1/4, 1/4, L)$ for the same pristine and reduced samples at T = 10 K and E = 853.4 eV. The dashed line is used as a guide. c) Polarization-dependent comparison between the XAS (multiplied by a factor of 3.5) and the photon energy dependence of the magnetic Bragg intensity at \mathbf{q}_0 around the Ni- L_3 edge of the reduced sample, which shows similar line shapes for 10 K and 300 K. d) The Bragg peak of the reduced sample at various temperatures as a function of the angle of incidence.

 $3a_0 \times a_0 \times 3a_0$, where a_0 is the perovskite subcell, which could structurally produce such observed Bragg reflection [266]. Therefore we suggest that the possible origin of this Brag reflection is an intermediate phase between NdNiO₃ and NdNiO₂, although further work is required for a conclusive statement.

Our study of nickelate/scandate heterostructures led us to create a new type of superlattice where various layers within the nickelate slab are reduced to in the square-planar configuration. In addition, we found that the amount of blocking layers is an essential parameter in modifying the physical properties in our superlattices. Given that samples with n = 2 might be affected by structural disorder upon reduction or intermixing effects at the interfaces and samples with n = 6 (or more) are unsuitable for surface-sensitive experiments (as the blocking layer is the last deposited slab), we conclude that the most favorable amount of blocking layers is n = 4. In the following sections, we will see similar results with other materials used as blocking layers. The substitution of the A-cation (Dy \rightarrow Gd) in the buffer layer produces no significant changes in the XAS spectrum at the Ni resonant edges for samples with the same stacking. In contrast, a change from n = 2 to $n \ge 4$ gives a distinct spectrum at the Ni- $L_{2,3}$ edges in both LNO/DSO and LNO/GSO. On the other hand, a substitution of the A-cation (La \rightarrow Nd) in the nickelate side of a superlattice with the same stacking yields significantly different reduction conditions. Our study of the main Bragg reflections in our superlattices observed by XRD indicates that our initial assumption depicted in Fig. 4.3 d is not correct and that fewer layers are reduced to the infinite-layer phase. Moreover, the analysis of the *c*-axis lattice parameter in all superlattices suggests that only four layers in LNO/(D,G)SO and three layers in NNO/DSO are in the square-planar configuration.

Despite the treatment of various superlattice configurations, superconductivity has not been observed in any samples. Our assumption of homogeneous charge distribution and the analysis of the transport data, the averaged *c*-axis parameter, and estimated valence state yield a possible explanation: The superlattices reduced so far show poor metallicity with small resistivity upturns at low temperatures and probably lie on the over-doped or in principle also, the under-doped regime in comparison to the superconducting nickelate (and cuprate) thin films (see Fig. 4.1). A complete study of the charge distribution within the nickelate blocks will be given in the next section with the help of theoretical calculations performed by collaborators. On the other hand, the NNO/DSO sample shows a surprising result where a clear Bragg reflection at $\mathbf{q}_0 = (1/4, 1/4, 1/4)$ appears on the reduced sample. This Bragg peak has a small polarization dependence and persists up to room temperature (see Fig. 4.7). We attribute the possible origin of such peak to intermediate states between the pure perovskite and square planar phases, although additional measurements will be necessary to demonstrate this interpretation.

4.3 $LaNiO_{2-\delta}/LaBO_3$ (B = Ga, Al) superlattices

Our search for a heterostructure composed of infinite-layer nickelate slabs, which have a similar doping level as the superconducting $Nd_{1-x}Sr_xNiO_2$ thin films (in contrast to the nickelate/scandate superlattices, which were regarded as overdoped) led us to perform a study on LaNiO_{2+ δ}/LaBO₃, (B = Ga, Al) superlattices. In particular, we focus on the $(\text{LaNiO}_{2+\delta})_{m=8}/(\text{LaBO}_3)_{n=4}$ superlattices grown on a (001) oriented SrTiO₃ substrate (see Fig. 4.8 a). The substrate with pseudocubic lattice constants of $c_{\rm sto} = 3.905$ exerts a moderate tensile strain over the pristine samples while it induces a substantial amount of compressive strain on the reduced samples. We selected LaGaO₃ and LaAlO₃ as blocking layers to promote the layer-selective reduction, given that the Ga^{3+} and Al^{3+} ions have a closed-shell configuration and are therefore less prone to reduction. In addition, the A-cation site is kept unchanged across the interfaces, as La is used in the two materials forming the superlattice. This condition is believed to reduce the structural disorder generated due to cation intermixing at the interface. In this section, we show experimental results obtained for the LNO/LGO samples; however, similar measurements and comparable results are shown in Fig. 4.13 for the case of the LNO/LAO superlattices at the end of this section.



Figure 4.8: a) Schematic representation of the $(\text{LaNiO}_{2+\delta})_m/(\text{LaGaO}_3)_n$ superlattices with m = 8 and n = 4, for the pristine/re-oxidized (left) and reduced (right) samples grown on a (001) oriented SrTiO₃ substrate. The layers of the nickelate slab are labeled L1 to L4, and the rest are a mirror image (indicated by the dashed line) within the LNO block. b) XRD spectra of a group of pristine, reduced, and re-oxidized heterostructures. The plot includes the (001) and (002) reflections of the SrTiO₃ substrate. The asterisks indicate peaks originating from the $K_{\beta 1}$ reflection arising from the substrate. c) Resistivity of the same group of samples. The inset shows schematics of the cut samples.

The superlattices were grown by PLD following the conditions established in Ref. 92. The reduction process was performed in a similar way as for the nickelate/scandate



Figure 4.9: a) Resistivity of a group of pristine (dark crosses) and reoxidized (light circles) nickelate superlattices with different stacking and buffer layer compositions. All reoxidized samples show lower resistivity as their pristine counterparts. b) XRD of a group of reduced $(LNO)_8/(LGO)_4$ superlattices. The region comprises the (001) and (002) substrate peaks. The data has been vertically shifted for clarity.

superlattices. One of the reduced samples was subsequently used for reoxidation (see Fig. 4.8 b, c). The reoxidized stage was achieved by heating the reduced samples in an oven that was open to the atmosphere. The reoxidation is simpler than the reduction process in terms of preparation and time, as it only requires the heating of the sample under an O₂ atmosphere during a 2h period.

XRD measurements (see Fig. 4.8 b) show that both pristine and reduced samples have good crystalline quality as the corresponding Bragg/SL peaks around the substrate main reflections are well resolved. Both XRD and resistivity measurements show that the reduction process is reversible and therefore that the structural frame is preserved during the chemical treatment (see Figs. $4.8 \,\mathrm{b,c}$). The reversibility of a topotactic reduction process has also been observed in nickelate thin films [122], and other TMOs-based superlattices [248]. The electrical transport of pristine and reoxidized samples performed in Van der Pauw mode (see Section 3.3) shows metallic behavior in agreement with measurements performed on the LNO/DSO and LNO/GSO superlattices and comparable to literature values for LaNiO₃ thin films and bulk samples [122, 124, 237, 271]. The resistivity of the reduced superlattices shows a semiconducting temperature dependence, which can be fitted by Eq. 3.63 (Fig. 4.8 c). A comparative study between the transport data of pristine and reoxidized samples indicates that the resistivity is consistently lower in the latter ones (see Fig. $4.9 \,\mathrm{a}$). The previous results, together with the slightly larger c-axis parameter observed in the reoxidized samples, suggest that there are oxygen vacancies present in the as-grown samples. These findings are surprising given that the last step of the growth process is to anneal the samples at 690°C in a 1 bar oxygen atmosphere. Then, the direct annealing of samples after deposition is less efficient than the reduction and subsequent ambient annealing in an oven. This behavior occurs because the immediate annealing of pristine samples is limited by oxygen diffusion, whereas for reoxidized samples, the restrain disappears when the apical oxygen sites are first emptied and then refilled.

A fitting performed with the simulation software QUAD [272] on the XRD data from Fig. 4.8 b provides further insight into structural details through the evaluation of relative



Figure 4.10: Simulations of the XRD data shown in Fig. 4.8 for the (002) SrTiO₃ substrate region performed with the program QUAD. a) LaNiO₃ with octahedral structure b) LaNiO_{2+ δ} with two possible configurations, the interfacial quadratic pyramidal plus inner square planar structure (black box inset) and the pure square planar (grey box inset) configuration.

peak intensities of the diffraction pattern. Figs. 4.10 a, b show the results plotted around the (002) substrate peak, which confirm the interfacial structure proposed in Fig. 4.8 a (right). More specifically, the relative intensities of the (0023), (0024) and (0025) superlattice reflections (high-low-high) of the reduced samples are in good agreement with the simulation of a structure with inner square planar plus interfacial quadratic pyramidal Ni-O coordination. On the other hand, a monotonic increase in the intensity pattern for the same group of superlattice reflections, which indicates square-planar coordination, disagrees with the experimental data. This intensity pattern was consistent in several treated samples after the topotactic reduction (see Fig. 4.9 b). The averaged lattice constant of the superlattice ($\bar{c}_{\rm SL} = 3.61$ Å) obtained with XRD is in good agreement with the results from TEM measurements, and DFT calculations performed on the same samples [273]. Moreover, an analysis performed following equations 4.1 and 4.2 yields an averaged out-of-plane lattice constant $c_{\rm LNO} = 3.47$ Å, which can be obtained by using $p_{\rm LNO_{2.5}} = 2$ and $q_{\rm LNO_2} = 6$. This result is in agreement with the fittings performed to the XRD data and to the structure proposed in Fig. 4.3 e.

X-ray absorption spectroscopy

We use soft x-ray absorption spectroscopy (XAS) to analyze the differences in the electronic configuration of all ions in the pristine and reduced samples. All measurements were carried out at room temperature and energies covering relevant element-specific absorption edges. We recorded data from two types of detection modes at the same time. The first one, total-electron yield (TEY), is a surface-sensitive detection mode with a sampling depth of a few nm due to the small escape depth of the electrons. The second, fluorescence yield (FY), has a much larger probing depth (about the attenuation length); however, it can be influenced by saturation effects, and self-absorption effects [274]. The XAS measurements with distinct polarizations were executed at a fixed angle of 45°. According to this geometry (see inset of Fig. 4.11 d) the $E \parallel c$ and $E \perp c$ polarizations will be given by

$$I_{E\perp c} = I_{\sigma}, \qquad I_{E\parallel c} = 2I_{\pi} - I_{E\perp c},$$



Figure 4.11: Polarization-averaged XAS spectra (see Eq. 3.53) around a) the La- $M_{5,4}$ and Ni- $L_{2,3}$ edges, b) the Ga- $L_{2,3}$ edges (smoothed due to the lower flux provided at these high energies), and c) the O-K edge. The data for pristine (blue) and reduced (red) samples are vertically translated for clarity. d) Polarization-dependent XAS for pristine and reduced samples across the Ni- $L_{2,3}$ absorption edges, where the La- M_4 lines have been subtracted. The top and middle panels show spectra taken with x-ray polarization $E \parallel c$ and $E \perp c$. The bottom panel shows the normalized linear dichroism obtained from the difference of intensities as in Eq. 3.22. The spectra for a), b), and c) were measured in total-electron yield detection mode, whereas the spectra in d) were measured in fluorescence yield mode.

where the previous expressions have been obtained from the general formula 3.54 [275]. The previous expressions allow the determination of the linear dichroism, which is a measure of the preferential orbital occupation in partially filled energy levels.

Fig. 4.11 a shows polarization-averaged spectra, calculated according to Eq. 3.53, around the La- $M_{5,4}$ ($3d \rightarrow 4f$) and Ni- $L_{2,3}$ ($2p \rightarrow 3d$) absorption edges. The center of mass of the Ni-L spectra in the reduced samples is shifted towards lower energies with respect to the pristine sample. This displacement of the white lines of approximately 1.5 eV indicates a reduced valence state that goes from Ni³⁺ in the as-grown samples towards Ni¹⁺ in the treated samples. No changes are observed in the La-M and Ga-Lspectral regions, which indicates an invariant valence state of these ions upon reduction (see Fig. 4.11 b, c). These results agree with transmission electron microscopy (HRTEM) images taken by our collaborators F. Misják and U. Kaiser, which show thinner LNO slabs, but equally thick LGO blocks in the reduced samples compared to the untreated samples [273]. Concerning the O-K edge, the reduced samples show the absence of a pre-peak, which is present in the as-grown samples around 528 eV (Fig. 4.11 c). Given that perovskite nickelates are regarded as charge-transfer materials, the Ni ground state is dominated by the $3d^8 \underline{L}$ configuration, where \underline{L} denotes a ligand hole (see Eq. 4.7 and 1.1) [5]. This configuration is translated into a strong hybridization between Ni-O, resulting in a pronounced pre-peak at the O-K edge. A close inspection of the spectra for the reduced sample indicates that the pre-peak is substantially decreased and shifted towards higher energies, suggesting a loss of hybridization and a change in the valence state of Ni and the ligand coordination. Similar behavior has been observed with resonant inelastic x-ray scattering in other infinite-layer nickelates samples [128]. In their work, Hepting et. al. studied LaNiO₂ and NdNiO₂ thin films with XAS and found that the pre-peak in the O-K edge was absent. In addition, theory calculations classify infinite-layer nickelates as Mott-Hubbard materials instead of the negative- Δ nature of the perovskite counterparts [150]. This designation is in agreement with the semiconducting behavior observed in the resistivity measurements of the reduced samples (see Fig. 4.8 c) as Mott-Hubbard systems are prone to localization.

The top and middle panels of Fig. 4.11 d show the polarization-dependent XAS spectra for the pristine (blue) and reduced (red) samples. For LaNiO₃ with $3d^{8}\underline{L}$ electronic configuration in a cubic ligand field, the expected dichroism is much smaller [91,92], since the hole occupation of $d_{x^2-y^2}$ and $d_{3z^2-\mathbf{r}^2}$ is very similar. In superlattices similar to the studied in this chapter, there is a small variation associated with effects such as the tensile strain produced by the substrate and the electronic confinement from the insulating blocking layers [92]. This variation is what we observe in the normalized dichroism (defined as in Eq. 3.22) of the pristine sample plotted in the bottom panel of Fig. 4.11 d (blue curve). Concerning LaNiO₂, a large anisotropy between measurements performed with perpendicular polarizations $(I_{E\parallel c}, I_{E\perp c})$ is anticipated in analogy to cuprates where the Cu^{2+} ions (similarly to Ni¹⁺) are surrounded by oxygen in the square planar coordination. More specifically, the single hole in the $d_{x^2-y^2}$ orbital will result in spectral gain at the Ni- $L_{3,2}$ -edges for $I_{E\perp c}$ whereas for $I_{E\parallel c}$, no spectral gain is expected due to full occupancy of the $d_{3z^2-\mathbf{r}^2}$ orbitals. As expected, the dichroism observed in the reduced sample implies a preferential occupation of holes in the $d_{x^2-y^2}$. This dichroism is comparable in shape to the corresponding pattern observed in the Cu^{2+} ions of the high- T_c cuprates [276]. Then, the dichroism observed for the reduced samples could be regarded as a characteristic of $3d^9$ systems. However, comparing the normalized dichroic signals in both materials yields a large difference in favor of Cu^{2+} [276]. A possible explanation for this difference is that charge could be non-homogeneously distributed within the LaNiO_{2+ δ} blocks. The theory calculations performed by collaborators and described in the following paragraphs will address this issue. Furthermore, in section 4.5 we will apply resonant x-ray reflectivity to extract the deep layer-resolved valence profiles in various infinite-layer nickelate superlattices.

Theory: Model and methods

In order to understand how the dopants distribute across the nickelate layers of the reduced superlattices, our collaborators H. Menke and P. Hansmann performed calculations for the superlattice structure depicted in Fig. 4.8 a (right). Two aspects were addressed: (i) a non-interacting reference model and (ii) the effect of electronic correlations within Dynamical Mean-Field Theory (DMFT). From the non-interacting Density Functional Theory (DFT) calculations, they obtained the layer (L1-L4) and orbital resolved partial Density of States (pDOS). Fig. 4.12 a shows that the Ni 3d states are partially filled be-



Figure 4.12: a) Partial density of states for the LaNiO_{2+ δ} layers in the LNO/LGO superlattice with respect to electronic orbitals near the Fermi level ε_F obtained from DFT calculations. b) Layer- and orbital-resolved distribution of the density Δn at the different Ni sites for cases including additional charge ΔN . c) Layer-resolved spin density $\rho(S)$ as a function of the spin S. Figures were made by colaborators H. Menke and P. Hansmann (see Ref. 273).

tween the O 2p and the La 5d states and the most prominent states around the Fermi energy ε_F are the Ni $d_{x^2-y^2}$. Given that one apical oxygen is present in the interface layers (*L*1) but not in the inner ones (*L*2-*L*4), there are clearly significant differences between these two groups of layers from the electronic structure point of view. For *L*1, peaks near the Fermi level appear for $d_{3x^2-r^2}$ and $d_{x^2-y^2}$ due to antibonding combination and hybridization with $2p_z$ respectively. Concerning the d_{xz}/d_{yz} orbitals, they are also affected by the apical oxygen such that their spectral weight is pushed towards the Fermi level at the interface. For *L*2-*L*4, the pDOS of the $d_{3x^2-r^2}$ orbitals are significantly lowered compared to *L*1 due to the missing apical oxygen. A comparison of *L*1 and *L*2-*L*4 through electronic configuration considerations in the ionic limit shows that the hybridization with apical oxygen at the interface layer increases the Ni-projected charge. In contrast, the absence of this hybridization in the inner layers depletes it. More interesting is the ligand field effect on $d_{3z^2-r^2}$ orbitals, whose spectral weight is pushed towards or away from the Fermi level for the interface and inner layers, respectively, due to the presence or absence



Figure 4.13: a) XRD of a group of pristine and reduced $(LNO)_8/(LAO)_4$ superlattices. b) resistivity of the same group of samples. c) Polarization-averaged XAS spectra (see Eq. 3.53) around the O-K edge. The data for pristine (blue) and reduced (red) samples are vertically translated for clarity.d) Polarization-dependent XAS for pristine and reduced samples across the Ni- $L_{2,3}$ absorption edges, where the La- M_4 lines have been subtracted. The top and middle panels show spectra taken with x-ray polarization $E \parallel c$ and $E \perp c$. The bottom panel shows the linear dichroism obtained from the difference in intensities as in Eq. 3.22.

of apical oxygen.

To explain how the charge is distributed across the reduced nickelate layers, our collaborators performed DMFT calculations, including the addition of electrons and holes. Fig. 4.12 b shows an histogram of the layer- and orbital-resolved projected densities of each Ni site. When electrons are added to the system, they distribute evenly across the layers, filling up the $d_{x^2-y^2}$ states. In contrast, when the system is doped with holes, they get trapped at the interface layers, initially in the $d_{3z^2-r^2}$ and then in the $d_{xz/yz}$ when the $d_{3z^2-r^2}$ becomes half-filled. The reason for this difference can be explained by considering the spin configurations of the local Ni moments, which indicate the formation of a strongly correlated Hund's metal and local high-spin configurations (see Fig. 4.12 c).

An analogous study performed on the LNO/LAO superlattices yields various similarities but also some differences with respect to LNO/LGO. In the case of the pristine samples, the measurements show qualitative agreement between LNO/LGO and LNO/LAO, while this is not the case for the treated samples. For example, the XRD pattern of the reduced LNO/LAO superlattices (Fig. 4.13 a) shows low intensity but visible Bragg peaks, which seem no to follow the same pattern as in the LNO/LGO superlattices. An analysis of the out-of-plane lattice constant yields $c_{\text{LNO}} = 3.52 \text{ Å}$, which translates into $p_{\text{LNO}_{2.5}}/q_{\text{LNO}_2} = 3/5$ in contrast to $p_{\text{LNO}_{2.5}}/q_{\text{LNO}_2} = 2/6$ for LNO/LGO. This difference might be the reason for the distinct XRD pattern observed between the two superlattice types. Concerning the transport measurements, the LNO/LAO reduced sample (Fig. 4.13b) shows a semiconducting behavior that is an order of magnitude larger than in the LNO/LGO counterparts. Measurements at the O-K edge for the reduced samples (Fig. 4.13 c) show a significantly lower pre-peak around 530 eV in both LNO/LGO and LNO/LAO superlattices. This pre-peak could originate from the interaction between the Ni ion and the remaining apical oxygen at the interface with the buffer layer (see section 4.6). Finally, the normalized dichroic signal (Fig. 4.13 d) in the reduced LNO/LAO sample is substantially lower than in the LNO/LGO superlattices with the appearance of regions where the hole occupation is preferentially siting a the $d_{3z^2-\mathbf{r}^2}$ orbitals. In contrast to the comparison made between LNO/DSO and LNO/GSO, where a change in the A-cation element of the buffer layer produces almost no change in the Ni electronic configuration, the change of Ga for Al in the blocking layers leads to a distinct hole occupation at the Ni e_g orbitals. These results evidence the effect produced by different buffer layers on the structural and electronic properties of such nickelate systems.

Our study of the LNO/LGO superlattices leads us to the realization of a heterostructure where the nickelate slabs are composed of inner square-planar and interfacial pyramidal layers as predicted in Fig. 4.3e. Transport measurements show that the reduced LNO/LBO samples are semiconducting in contrast to the metallic trend displayed by the nickelate/scandate superlattices. However, these experiments, together with XRD measurements, indicate that the reduction process can be reversed to obtain samples with similar properties as the pristine ones. Spectroscopic measurements show similar results between LNO/LGO and LNO/(D,G)SO superlattices. For example, we confirm the selectiveness of the reduction process by observing no changes in the Ga- $L_{2,3}$ absorption edges. In addition, the normalized dichroism obtained from polarization-dependent measurements is similar for both nickelate/gallate and nickelate/scandate superlattices, although it is slightly higher in the samples containing scandates. Theory calculations indicate that our superlattice cannot achieve the desired doping concentration because the doped holes do not distribute homogeneously within the nickelate block. However, the same calculations yield insight into the electron doping, which distributes evenly across the nickelate slabs.

4.4 Nickelate/SrTiO₃ superlattices

So far, we have discussed two types of infinite-layer superlattices (nickelate/scandate and LNO/LBO) and find that the excess of charge resulting from the reduction process seems not to distribute evenly. Our next objective is to find a blocking layer that we can combine with the nickelates to produce an even charge distribution, i.e., more homogeneous doping of the infinite-layer stacks. This blocking layer could be the case of $SrTiO_3$, a non-polar material that could produce an excess of holes at the nickelate layers due to charge transfer as it occurs in other titanate superlattices [277, 278]. In this section we focus on the study of $(La,Nd)NiO_{2+\delta}/SrTiO_3$ (L,N)NO/STO superlattices grown on a (001) oriented $SrTiO_3$ substrate. However, before describing these heterostructures, it is important to review the literature regarding their parent compounds ($\delta = 1$). There are various experimental and theoretical studies on nickelate/titanate superlattices, with the majority of them focusing on $LaNiO_3/SrTiO_3$ and a few studying NdNiO₃ and BaTiO₃ [279–288]. Unlike the non-polar structures analyzed in previous sections, (i.e., LNO/DSO, LNO/GSO, LNO/LGO and LNO/LAO) the interfaces of these heterostructures are characterized by a discontinuity which can lead to either a n-type or p-type doping. This discontinuity arises because the superlattices combine the correlated polar metals (La,Nd)NiO₃ with the non-polar band insulator $SrTiO_3$. When stacked along the $(001)_{pc}$ direction, LNO has LaO^{+1} and NiO_2^{-1} atomic layers, while STO shows charge-neutral SrO and TiO_2 layers.

Earlier experimental studies like the one performed by Son and coworkers demonstrated an enhancement of the conductivity by changing the number of bilayers (p) in a $[(\text{LaNiO}_3)_4/(\text{SrTiO}_3)_3]_p$ superlattice grown on (001) oriented $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT) [279]. The authors proposed two mechanisms to explain such phenomenon, i.e., the conduction via parallel-connected layers and the coupling of layers, each of which is close to the MIT threshold. Using standing-wave soft x-ray photoelectron spectroscopy (SXPS), Kaiser et. al. found a suppression of the electronic states around the Fermi level of the LNO interface layers of the same configuration of superlattices with p = 10. This suppression of charge carries, which extends over one u.c., is believed to be the origin of the MIT in LNO thin films [280]. These results, where the depletion of DOS near the Fermi energy is associated with the MIT, were later confirmed by ARPES [285]. Along these lines, scanning transmission electron microscopy (STEM) experiments performed by Hwang et. al. yielded important results regarding the structural properties of these heterostructures. Contrary to the LNO thin films grown on STO, which have a non-bulk-like structure near the substrate interface, the $LaNiO_3$ layers in an LNO/STO superlattice relax their octahedral tilts pattern towards bulk values, resulting in an enhanced conductivity in comparison to the LNO thin films [281]. More recently, a similar study was performed by Chen et. al. for a combination of NdNiO₃/SrTiO₃ superlattices grown on $(001)_{pc}$ oriented NdGaO₃. The study consisted on measuring various $(NNO)_m/(STO)_n$ superlattices for which the amount of STO layers were kept fixed at n = 4, while the NNO layer number was varied from m = 2 to m = 8. Using STEM, the authors found a crossover from a modulated octahedral superstructure at m = 8 to an uniform non-tilt pattern at m = 4 [287]. This crossover indicates that the layer-thickness dependence of the oxygen octahedral rotations may cause the observed MIT and antiferromagnetic transitions found at lower temperatures as the octahedra are straightened. Altogether, we note that oxygen octahedral rotations and reduced dimensionality are important effects that determine the physical properties of these superlattices.

Theoretical studies have concentrated on the effects at the interface between the nick-

elate and STO layers. Using first-principles DFT calculations, Han et. al. found that the reduction of the DOS at the Fermi level observed by experiments such as XPS and ARPES occurs without charge transfer across the interface to the insulating STO. In contrast to other interface effects such as the orbital and valence reconstruction, in the LNO/STO superlattices, the Fermi level DOS is strongly modulated depending on the position of the Ni atoms with respect to the interface. This modulation was found to originate from heterostructuring itself without any change in the valence or oxidation state [283]. Kim et. al. studied an $(LNO)_1/(STO)_1$ heterostructure employing first-principles DFT considering different doping simulation methods. Experimentally, doping could be realized through chemical doping, electric field, and even oxygen vacancies, the latter producing structural distortions that originate from the removal of the apical Ni-O bond. The results indicate an increase of the apical oxygen to Ni distance and a decrease of the orbital polarization as more electrons are introduced to the system [284]. A recent study analyzed the charge discontinuity at the LNO/STO interface, leading to either *n*-type or *p*-type doping. Using DFT+U, Geisler *et. al.* found that both n- and p-type doping are accommodated by changing the occupation of bands within the $LaNiO_3$ slab. In addition, two important observations are made: the oxygen octahedral rotations of LNO are extended to the STO layers, and an electric field is generated at the interface between materials of opposite polarity [286]. The experimental and theoretical studies described above not only shed light on the effects at the interface of pristine perovskite (L,N)NO/STO superlattices but also help to envision the behavior of their large oxygen-deficient counterparts, the infinite-layer nickelate heterostructures.

This thesis presents results from two types of nickelate-titanate superlattices, namely LNO/STO and NNO/STO. However, in this section, we will focus mainly on the NNO/STO samples as the results seem to be in close analogy with the LNO/STO counterparts (see Appendix D). Our study of NNO/STO superlattices compiles a layer-dependent analysis divided into two groups: the first with n = 2 and the second with n = 4 STO layers. Our goal is to study the changes in the electronic and transport properties of the superlattices as a function of the number of NNO layers (m). In addition, we test two different amounts of STO layers (n) to compare the results with the nickelate/scandate superlattices discussed in Sec. 4.2. We start with the analysis of superlattices, where the amount of STO layers is kept fixed at n = 2, and the NNO layers vary from m = 4 to m = 8. Figs. 4.14 a, b show the XRD and electrical resistivity measurements on three pairs of pristine and reduced samples: $(NNO)_4/(STO)_2$, $(NNO)_6/(STO)_2$ and $(NNO)_8/(STO)_2$. All pristine samples show well-resolved Bragg peaks and Laue fringes, signaling a high crystallinity and smooth interfaces (see Fig. 4.14 a). For the reduced samples, the Bragg peaks are shifted towards higher 1/d values, in agreement with the results obtained for other infinite-layer nickelate superlattices. The top panel in Fig. 4.14b show the corresponding resistivity curves of the pristine superlattices, where it seems that the MIT together with the hysteresis disappear (or shift) as the amount of NNO layers decreases. A similar change in the resistivity as a function of the number of NNO layers is also observed in Ref. 287 although with a lower MIT, probably due to the reduced epitaxial strain produced by the substrate (NdGaO₃). For the reduced samples, an NNO thickness-dependent trend is also observed (bottom panel of Fig. 4.14 b), where the resistivity increases as the number of NNO decreases. In addition, the temperature dependence also changes, from metal (decreasing with T) for m = 8 to semiconducting in m = 4. Here is important to point out that these results on the XRD pattern and the transport measurements are consistent and not related to the reduction stage of the samples as we have prepared and



Figure 4.14: XRD of a group of $(NNO)_m/(STO)_n$ superlattices with variable NNO and STO fixed at a) n = 2 and c) n = 4. b) & d) The corresponding electrical resistivity measurements of the NNO/STO (top) pristine and (bottom) reduced superlattices. The solid (open) circles represent measurements upon cooling (warming) for the pristine samples. The XRD data has been vertically translated for clarity.

reduced different superlattices with the same stacking, and all of them give similar results after certain reduction time threshold (see Fig. 4.15).

Now we turn to superlattices with thicker buffer layers, namely (NNO)₆/(STO)₄, (NNO)₈/(STO)₄, (NNO)₁₀/(STO)₄ and (NNO)₁₂/(STO)₄. Figs. 4.14 c, d show the corresponding XRD and electrical resistivity curves for the four pairs of pristine and reduced samples. The XRD measurements show well-defined peaks for all pristine and reduced samples, although it seems that the intensity of the Bragg reflections decreases as a function of the LNO layers in the treated samples. Regarding the electrical transport data, all pristine samples show a clear MIT together with visible hysteresis at around $T_N \approx 175$ K. Interestingly, all reduced samples with n = 4 show a metallic behavior with the resistivity curves having a similar shape around the same order of magnitude. A careful examination of the averaged lattice parameter ($\bar{c}_{\rm SL}$) of all NNO/STO superlattices yields values between 3.66 and 3.54 Å with the larger values belonging to superlattices with m = 4 and 6 NNO layers. Subtracting the contribution of STO from these values, the lattice constant ($c_{\rm NNO}$) for the NNO slabs gives values between 3.40 and 3.54 Å, which are very close to the experimentally observed value for infinite-layer nickelates c = 3.30 Å grown



Figure 4.15: a) XRD measurements of a group of $(\text{NNO})_m/(\text{STO})_n$ superlattices with (top) m = 8/n = 2 and (bottom) m = 8/n = 4 stacking, reduced at different times. b) Resistivity of the same group of superlattices with (top) m = 8/n = 2 and (bottom) m = 8/n = 4 stacking.

on STO [265]. These results indicate (as in the previous section) that regions within the nickelate slab have or cannot be reduced independently of the treatment time. In the next sections, and similarly, as for the LNO/LGO superlattices, we will see that these layers with different oxygen coordination regions are confined at the interfaces with the buffer layers.

In addition to the XRD and transport measurements described above, XAS contributes with valuable information regarding the valence electron configuration. Fig. 4.16 shows the XAS measurements at the Ni- $L_{2,3}$ edges for the two groups of reduced NNO/STO samples. For the case of the heterostructures with n = 2 (Fig. 4.16 a), the normalized linear dichroism shows regions with multiple-peak structures in both absorption edges. For example, the Ni- L_3 edge, there are two peaks at 853.8 and 855.6 eV with hole-occupation being predominantly at the $d_{x^2-y^2}$ orbitals and a peak at 852.5 eV with $d_{3z^2-\mathbf{r}^2}$ character. Moreover, for the Ni- L_2 edge, the samples show a triple peak structure at 869.0, 870.7 and 871.8 eV respectively, all with $d_{x^2-y^2}$ nature. Things are significantly different for the samples with n = 4 as only two peaks at 853.3 and 870.0 eV corresponding to the Ni- L_3 and $-L_2$ edges are observed. Additionally, the observed peaks in the samples with n = 4 seem to be shifted toward lower energy values with respect to the samples with n = 2, indicating a lower valence state of Ni or a stronger crystal field effect in the former. Moreover, a change from a multiple peak structure to a single peak structure at each Ni edge from m = 2 to m = 4 suggests that the contribution to the spectral weight originates mainly from a single valence state such as Ni¹⁺. However, both groups of samples show a significant negative dichroism in the region between the Ni- $L_{2,3}$ edges. This negative dichroism is also observed in the region around the $Cu-L_{2,3}$ absorption edges of the cuprates superconductors [276]. For completeness, the corresponding XAS spectra of the pristine samples are shown in Appendix B.2.

We have performed a similar analysis with x-ray diffraction, electrical transport and xray absorption measurements for a series of $(\text{LNO})_m/(\text{STO})_n$ superlattices (see Appendix D.1 & D.2). As in the $(\text{NNO})_m/(\text{STO})_4$ superlattices, the x-ray diffraction measurements show clear Bragg reflections in both pristine and reduced samples. Concerning the resistivity measurements, all pristine and reduced samples show a metallic behavior, with the



Figure 4.16: Polarization-dependent XAS for a group of $(NNO)_m/(STO)_n$ with a) n = 2 and b) n = 4, superlattices. The data in the upper panels have been vertically translated for clarity. The bottom panels are the normalized dichroism obtained from Eq. 3.22 and multiplied by a factor of 300.

treated samples being one order of magnitude less conducting and without any electronic transition. Furthermore, the XAS measurements show remarkably similar spectral shapes between NNO/STO and the LNO/STO heterostructures and their respective stacking, although the LNO/STO samples seem to have lower orbital polarization.

Although, so far, we have studied in detail the structural and electronic properties of various infinite-layer nickelate superlattices, indications of superconductivity have not been observed. However, we have identified clear trends where the pristine samples show a shift of the MIT as a function of NNO layers (i.e., a decrease in T_{MI} with decreasing NNO thickness), similarly to in Ref. 287. Concerning the reduced superlattices, for samples with n = 2 STO layers, conductivity is enhanced as the number of NNO layers increases. For samples with n = 4 STO layers, resistivity shows a minimum in the case of the 8/4 stacking sequence. The differences observed by XAS between samples with n = 2and n = 4 are also seen in the nickelate/scandate superlattices, suggesting a threshold between these two amounts of buffer layers. A comparison of NNO and LNO superlattices shows a subtle shift of the dichroic peaks as a function of the number of nickelate layers indicating the presence of more low valence Ni¹⁺ in the thicker nickelate slabs. Finally, Fig. 4.17 shows a direct comparison between XAS spectra of our NNO/STO superlattice and La_{1.84}Sr_{0.16}CuO₄, a member of the family of cuprate superconductors. The intensity of the dichroism produced by the cuprate superconductor is approximately four times larger than the one originating from the superlattice. This result is surprising given that one might expect a similar hole occupation for systems with the same electronic configuration $(3d^9)$. Therefore, we assume that other effects occurring probably at the interfaces or during the reduction process might weaken the observed polarization in the superlattice.

As was mentioned in previous sections, the calculations obtained from the averaged *c*-axis lattice parameter give us only an estimated value of the valence state in all layers assuming a homogeneous charge distribution. However, theoretical studies indicate the segregation of charge towards the interfaces, which cannot be reconciled with the homogeneous charge distribution scenario. These results call for the employment of an experimental technique that allows us to accurately determine the valence state in a layer-resolved fashion in the nickelate part of the superlattices. One of the techniques



Figure 4.17: Polarization dependent XAS for a pair of a) $La_{1.84}Sr_{0.16}CuO_4$ and b) $(NNO)_8/(STO)_4$ samples. The bottom panels are the normalized dichroism obtained from Eq. 3.22.

that could be used is electron energy loss spectroscopy (EELS), which can measure the valence state of certain atoms with very high spatial resolution. However, EELS requires TEM specimen preparation and high electron energies to reach an atomic resolution, both requirements that can cause damage or modify the sample, leading to inaccurate results. Another technique that can be used is resonant x-ray reflectivity, which can perform a layer-resolved characterization of heterostructures and is particularly efficient for analyzing surfaces and interfaces. We have chosen this technique because of its non-destructive nature, although it has uncertainties (which will be discussed in the next section). More specifically, we will experimentally resolve the electronic configuration at the interfaces and inner layers of the nickelate/titanate superlattices employing x-ray reflectometry.

4.5 Orbital reflectometry of infinite-layer nickelate superlattices

In this section, we present the analysis of resonant x-ray reflectivity (RXR) made to obtain the orbital polarization and valence state depth profiles of different infinite-layer (La,Nd)NiO_{2+ δ}/ABO₃ superlattices (ABO₃ = LaGaO₃, SrTiO₃). The infinite-layer phase was obtained by reducing the precursors (La,Nd)NiO₃/ABO₃ with CaH₂. The characterization employing x-ray diffraction, electrical transport, and soft x-ray absorption was discussed in the previous sections (see Secs. 4.3, 4.4). Our data analysis, which involved two distinct methods for obtaining the local Ni electronic structure, reveals that the average hole occupation of $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals in the interface layers next to ABO₃ is different compared to the inner layers in the reduced (La,Nd)NiO_{2+ δ} slabs. The same effect can be reproduced by a structure with interfacial Ni²⁺ and inner Ni¹⁺ layers whose spectra were calculated from cluster calculations with tight-binding parameters obtained from a fit to the DFT band structure. These experimental results agree with the conclusions obtained in Sec. 4.3, where the reduced superlattices contain regions with segregated charges in the nickelate slabs with both pyramidal and square-planar ligand coordination (see Fig. 4.18 a).



Figure 4.18: a) Proposed electronic configuration for the nickelate layers in a pristine and reduced superlattice. b) Hole ratio X_{AV} obtained by sum rule considerations (see Eq. 3.27) versus the out-of-plane lattice constant \bar{c}_{SL} of (square) (NNO)_m/(STO)_n, (circle) (LNO)_m/(LGO)_n and (triangle) (LNO)_m/(STO)_n, all with m = 8 and n = 4.

We focus our analysis on three different types of infinite-layer nickelate superlattices with equal layer stacking, namely $(\text{LaNiO}_{2+\delta})_8/(\text{LaGaO}_3)_4$, $(\text{LaNiO}_{2+\delta})_8/(\text{SrTiO}_3)_4$ and $(\text{NdNiO}_{2+\delta})_8/(\text{SrTiO}_3)_4$. XAS and RXR measurements using linear polarized soft x-rays (with σ and π polarizations) were performed on all samples at the UE46 PGM-1 beamline of the BESSY-II synchrotron at Helmholtz-Zentrum Berlin. To obtain $E \parallel c$ and $E \perp c$, we applied Eq. 3.54 to the corresponding XAS measurements, which were performed in TEY mode, and at two angles, i.e $\theta = 30^\circ$, 45° . We compare the XAS results obtained for all samples by calculating the hole ratio (X_{av}) introduced in Eq. 3.27. X_{av} is a quantity that relates the amount of holes in each e_g band and it can give an estimate of the orbital polarization in our superlattices. More specifically, X_{av} will be greater than unity when the amount of holes in $d_{3z^2-r^2}$ exceed the number of holes in $d_{x^2-y^2}$, and it will be less than unity in the opposite case. The corresponding values are shown in Fig. 4.18 b as function
of the out-of-plane lattice constant. All pristine samples show a value of $X_{av} \approx 1$ which translates into a small orbital polarization due to strain and confinement, in agreement with previous studies [91, 92, 197]. The reduced samples, on the other hand, show a clear preferential orbital polarization with $X_{av} \leq 0.75$. The regions where the pristine and reduced samples are located are clearly separated in Fig. 4.18 b (white areas). This separation between regions, suggest that the treated and non-treated samples can be easily identified based on the values of \bar{c}_{sL} and X_{AV} .

Resonant x-ray reflectivity

The need to understand the electronic configuration of individual atomic layers in the nickelate slabs led us to employ RXR, a surface- and interface-sensitive technique used to obtain the spin, charge, and orbital deep profiles in heterostructures such as the ones considered in this chapter. The complete set of reflectivity measurements consists of two groups of experiments performed in specular mode (q is always perpendicular to the surface of the sample) at constant energy and momentum transfer. The first reflectivity experiment (E = const.) involved measurements taken at three different energies, i.e., one off-resonant energy of 8047 eV, and two resonant energies at the Ni- $L_{2,3}$ edges. All spectra show well-resolved thickness fringes (also called Kiessig fringes) and up to three superlattice peaks (Figs. 4.20 a, b, c). While Kiessig fringes reflecting the vacuum-sample and sample-substrate contrast are pronounced at all energies, the superlattice reflections are enhanced at Ni energies, exemplifying the resonance effect. The second measurement type (Figs. 4.20 d, e, f) was made at constant q_z values, which corresponded to positions of the superlattice peaks observed in the energy-fixed scans (see orange dashed lines in Fig. 4.20). We measured the spectra at two different q_z values for each sample to get information about the nickelate/buffer-layer and the (interfacial)nickelate/(inner)nickelate interfaces. In order to obtain this information, we have to fit both sets of data simultaneously, something that a reflectivity fitting program such as ReMagX can accomplish [208, 210]. To prevent the alteration of our measurements due to possible charging effects, we decided to perform all experiments at room temperature. Sample charging is an effect appearing in systems with insulating regions, which can modify the spectra originating from intrinsic properties.

As a preliminary step of our analysis, we obtained the optical constants required for fitting the reflectometry data. To this end, we used the averaged XAS spectra obtained for each polarization (Fig. 4.19 a). These spectra have been already presented in previous sections in Figs. 4.11 d, 4.16 b and D.2 b. Then, we merged the averaged data, which was scaled with the energy (E), together with data of atomic scattering factors found in literature, i.e., Chantler tables (Fig. 4.19 b, c) [217, 218]. To obtain the real part of the merged spectra, we used the program dbEditor designed by S. Brück and S. Macke [289], which is able to perform the Kramers-Kronig transformation (Fig. 4.19 d). Finally, to obtain the optical constants (δ, β) , we applied Eqs. 3.32 to the data obtained in the previous step. We point out that this process is not uncertainty-free, and that small errors in the merging process might occur. However, we indicate that within the energy resolution, all features present in the measured spectra are displayed in the final merged data.

Once we generated the optical constants for each block of pristine and reduced samples, we used them as input of the ReMagX software [208,210]. We obtained each superlattice's structural model by simultaneously fitting all q_z -dependent reflectivity curves. The fittings (solid black lines) in Figs. 4.20 a, b, c were obtained using the polarization averaged optical



Figure 4.19: a) Averaged XAS spectra taken with linearly polarized light. b) Scattering factors obtained from Chantler table [217,218]. c) Scattering factor obtained from merging the data in a) and b). d) Scattering factors obtained by Kramers-Kronig transformation using the program dbEditor [289].

constants (see Eq. 3.53) as inputs under the Parrat formalism [211] plus a line to account for the background signal appearing in the measurement. For all superlattices, the best agreement was obtained when the first nickelate and the last blocking layer slabs were allowed to have different thicknesses and roughness, and the rest of the blocks were coupled to the same thickness [91]. After a good fitting was found, the structural model was kept fixed for the rest of the analysis. The structural parameters derived from the reflectivity fittings are summarized in the table of Appendix E.1. In addition, we performed the same procedure for the pristine samples, and the results are in good agreement with experiments performed in Ref. 92 (see Appendix E.1).

The second step simulates the energy-dependent reflectivity at constant q_z and compares the results to the experimental curves. A direct comparison between the *E*-dependent fits generated by the averaged XAS optical constants in the fitting program and the experimental data yields a large discrepancy between the two data sets (see Appendix F.1). This outcome agrees with the results obtained in previous sections, where the interfacial and inner layers of the nickelate slabs are found to have different electronic properties. Therefore, we require a mechanism to redistribute the averaged *E*-dependent spectra between the layers within the nickelate slabs in order to fit the measured spectra. This redistribution is accomplished by: (i) separating the nickelate blocks into two groups (interface and inner layers) and assigning them a specific number of layers, which account for a total of eight unit cells, and (ii) by finding a method that changes the weight of the spectra between the two groups of layers.

We start by addressing (i) with the initial assumption that the nickelate layer stacks are composed of two interface layers with scattering factor $f_{\rm IF}$ and six inner layers with $f_{\rm IN}$ (see Fig. 4.8 a). For a non-symmetric superlattice, the intensity of the (003) and (002) superlattice reflections, which were derived in Eqs. 3.41 and 3.43, are determined by

$$F^{(002)} = (f_{\text{ABO}} - f_{\text{RNO,IF}})\sqrt{3}i, \qquad F^{(003)} = (f_{\text{RNO,IF}} - f_{\text{RNO,IN}})(1-i)$$

where f_{ABO} is the scattering factor of the blocking layer, and $f_{RNO,IF}$ and $f_{RNO,IN}$ are the scattering factors of the interface and inner nickelate layers, respectively [290]. Given



Figure 4.20: Reflectivity as a function of q_z for the reduced a) NNO/STO, b) LNO/STO, and c) LNO/LGO superlattices. Each panel shows three curves corresponding to one off-resonant (green) and two resonant (blue and red) measurements at the Ni- $L_{2,3}$ edges. The dashed vertical lines correspond to the position of the (001), (002), and (003) superlattice peaks. Reflectivity constant- q_z energy scans for the d) NNO/STO, e) LNO/STO, and f) LNO/LGO superlattices. All measurements were performed at the (002) and (003) superlattice peaks except e), where the (001) peak was investigated. The dashed lines in e) and f) correspond to the position of the La- M_4 line. π^* corresponds to $\pi_{pol} \times [\cos(2\theta)^{-2}]$ which is a correction to the intensity minimum in the proximity of the Brewster angle.

that these superlattice reflections are particular sensitive to $f_{\rm IF}/f_{\rm IN}$ and $f_{\rm ABO}/f_{\rm IF}$ interfaces, we will study the polarization dependence at the (002) and the (003) superlattice peaks (Figs. 4.20 d, e, f). In principle, one can also use the (001) superlattice peak $(F^{(001)} = f_{\rm ABO} c_1 - f_{\rm RNO,IN} c_2 + f_{\rm RNO,IF} c_3)$ in the analysis, however, its structural factor has contributions from both interfaces, making it less suitable for investigation.

A close inspection of the spectral shape in the q_z -fixed scans of Fig. 4.20 indicates that they strongly depend on the value of q_z and, therefore, are different from the XAS profiles. The spectra also indicate that interface and inner layers might contribute with different weights to the measured XAS. Moreover, the single-peak lineshape observed for π -polarization at the Ni-L₃ edge is significantly more prominent than for the σ -polarization giving rise to pronounced negative dichroism. The Parrat formalism used to obtain the structural model is based on scalar scattering factors, i.e., it is impossible to treat any dichroism requiring a scattering tensor of at least tetragonal symmetry. Therefore for this second step, we used the Full Matrix Formalism (FMF) that requires individual optical constants in each spatial direction as an input [91]. The reduced superlattices of interest here pose a particular challenge to this form of modeling since not only the orbital polarization of nickel in the individual atomic layers can be different, but also its valence state and the ligand field in which the ions are located can change at the same time. Since the resonant scattering tensors cannot be calculated exactly, they are usually obtained from the experimental XAS spectra described above. Given that in XAS, a layer-averaged spectrum is measured (with a certain depth weighting), it cannot be readily broken down into the individual contributions required as input for a proper model for these superlattices. Hence, we use two distinct methods to obtain the optical constants for the scattering factors $f_{\rm IF}$ and $f_{\rm IN}$ and to address point (ii).

The first method is the one introduced in Ref. 91, where a parameter α was defined to redistribute the orbital polarization (dichroism) from the XAS data between the central and outer nickelate layers as

$$\left(\varepsilon_{\text{IN(IF)}}\right)_{jj} = (1 \mp \alpha) \,\varepsilon^{jj} \pm \alpha \,\varepsilon_{\text{cubic}}, \qquad \alpha \in [0, 1], \tag{4.3}$$

where $\varepsilon^{jj} = \varepsilon_1^{jj} + i\varepsilon_2^{jj}$ (j = x, z) are the complex entries related to the scattering factors $f_{\rm IF}$ and $f_{\rm IN}$, and $\varepsilon_{\rm cubic} = \frac{1}{3} (2\varepsilon^{xx} + \varepsilon^{zz})$. This approach will not capture any energy-dependent variations of the dichroism since possible spectra changes due to different Ni valence or ligand fields are not captured. According to Benckiser *et al.*, a value of $\alpha = 0$ represents the homogeneous case, where both interface and inner layers produce the same dichroism. On the other hand, a value of $\alpha = 1$ corresponds to dichroism produced by the interface layers only [91]. However, for our superlattices, we would like to include values of α that allow the majority of dichroism to be produced by the inner layers. This result is achieved by extending the original range to [-1, 1]. In addition, the case presented in Ref. 91 (and also in Ref. 92) corresponds to a symmetric distribution of interface and inner layers (i.e., two interface and two inner layers), whereas the stacking of our superlattices incorporates additional possibilities (see Sec. 3.1.4). In order to include those additional cases, we introduce $p_{\rm IF}$ and $p_{\rm IN}$, which represent the number of interface and inner layers (or unit cells), respectively [290]. Then, the corresponding components of the dielectric tensor for our superlattices will be given by:

$$\left(\varepsilon_{\rm IN(IF)}\right)_{jj} = \left(1 \mp p_{\rm IF(IN)}\beta\right)\varepsilon^{jj} \pm p_{\rm IF(IN)}\beta\,\varepsilon_{\rm cubic} \tag{4.4}$$

where the total amount of dichroism is kept fixed and equal to the measured spectra. Here, β serves as the parameter that redistributed the linear dichroism between the two groups



Figure 4.21: Fittings of the reflectivity at constant- q_z energy scans for the a) NNO_{2+ δ}/STO₃, b) LNO_{2+ δ}/STO₃ and c) LNO_{2+ δ}/LGO₃ superlattices using the cluster calculations optical constants of Ni¹⁺ and Ni²⁺.

of layers in a similar way as α with certain differences. For example, a value of $\alpha = -1$ in Eq. 4.3 will correspond to $\beta = -1/p_{\text{IN}}$ in Eq. 4.4. In addition, values of β below $-1/p_{\text{IN}}$ (or $\alpha < -1$) will lead to small negative dichroism at the interface layers and positive dichroism in the inner layers, larger than the average dichroic signal obtained from the experiment. Our fitting results agree with those of Refs. 91,92 for the case of the pristine samples, where a positive α was found with a preferential hole occupation of $d_{3z^2-r^2}$ that is higher in the interface layers as compared to the inner layers of the nickelate stack. For all reduced samples, we obtained negative values of β , which suggest an averaged preferential hole occupation of the $d_{3z^2-r^2}$ orbitals in the interface layers, whereas a large hole occupation at the $d_{x^2-y^2}$ orbitals is observed for the inner layers. For completeness, various negative and positive values of β were tested to fit the reflectivity profiles of the reduced samples, and a single solution was found for each case (see Appendix H.2). The results obtained using this method (solid black and grey lines) and the corresponding values of β are presented in Figs. 4.20 d, e, f. Surprisingly, the values of β are similar for all three superlattices, indicating that the reduction process yields comparable results.

For the second method, we used two optical constants obtained from the cluster calculations with the program Quanty [291, 292]. Here, instead of redistributing the averaged optical constants taken from the XAS measurement as in the previous method, we assign a valence state of Ni²⁺ to the interface layers and Ni¹⁺ to the inner ones (see Appendix F.2). It is important to mention that the crystal and ligand fields are also different. The ligand field parameters were obtained from a tight-binding model fit to the layer-resolved DFT band structure obtained for LNO/LGO as described in Sec. 4.3 and Ref 273. Then, we use a similar formula as Eq. 4.4 but with a modified cubic tensor

$$\varepsilon_{\rm cubic}' = (p_{\rm IF} \varepsilon_{\rm cubic}^{2+} + p_{\rm IN} \varepsilon_{\rm cubic}^{1+}) / (p_{\rm IF} + p_{\rm IN})$$

$$(4.5)$$

where ε_{cubic}^{1+} and ε_{cubic}^{2+} are the cubic scattering factors of Ni¹⁺ and Ni²⁺, respectively. This definition is made to keep the total dichroism produced by the two valence states constant and as close as possible to the dichroism observed in XAS. In addition, to improve the fittings we added small spectral weight at the Ni- $L_{2,3}$ edges for the π -polarization of the Ni¹⁺ spectra to simulate a more realistic scenario as observed in the experimental data (see I_z(E)_{IN} in the second row of Fig. 4.18). This additional spectral weight can be regarded as the effect produced by small amounts of impurities or by a-axis oriented regions as discussed in section 4.2. The results of the fits are shown in Fig. 4.21, and they



Figure 4.22: First Row: Layer resolved XAS at the Ni- $L_{2,3}$ edges for three types of superlattices: a) NNO_{2+ δ}/STO₃, b) LNO_{2+ δ}/STO₃ and c) LNO_{2+ δ}/LGO₃. The curves in the upper panels show the XAS spectra for the inner layers, the curves in the middle panels correspond to the interface layers, and the bottom panels correspond to the dichroism of both inner and interface layers. The curves were obtained following a similar procedure (α) as the one used in Ref. 91. Second Row: Layer resolved XAS at the Ni- $L_{2,3}$ edges for the same type of superlattices: d) NNO_{2+ δ}/STO₃, e) LNO_{2+ δ}/STO₃ and f) LNO_{2+ δ}/LGO₃ obtained using the cluster calculations optical constants of Ni¹⁺ and Ni²⁺.

are in good agreement with the experimental results. Moreover, the fittings performed using separated Ni^{2+}/Ni^{1+} seem to adjust better to the experimental data than those obtained by redistributing the total linear dichroism. Therefore, based on the similarities between the experimental and calculated q_z -fixed reflectivity curves, we conclude that in the reduced samples, the charge redistributes between values close to Ni^{2+} at the interface and Ni^{1+} in the inner layers among the nickelate slabs.

In addition, for this second method, we performed two tests to demonstrate the accuracy and uniqueness of our modeling. In the first test, we created interfacial and inner optical constants with a homogeneous distribution of charge, i.e., $Ni^{1.25+}$ but the fittings were not adequate, suggesting that the superlattices do not consist of a homogeneous mixture of Ni¹⁺ in all inner layers and Ni²⁺ in one interfacial unit cell thick layer (see Appendix G.1). For completeness, we have also tried to use only Ni¹⁺ to fit the Ni profiles in all reflectivity data, but the results were also not satisfactory (see Appendix G.2). Although the optical constants used in both methods are obtained differently, only minimal modifications had to be performed to the structural model for this second method (see Appendix E.2), which underpins the robustness of the structural model.



Figure 4.23: a) Layer-resolved X_{AV} for the NNO/STO (red), LNO/LGO (green) and LNO/STO (blue) superlattices with interface (dark solid lines) and inner (light dashed lines) layers, using optical constants from averaged XAS (purple) and cluster calculations (orange). Proposed structural configuration of the infinite-layer nickelate superlattices for the cases b) LNO/LGO and c) (L,N)NO/STO, based on the results from the orbital reflectometry analysis. The valence state of Ni at the interface layers correspond to (orange) one and 1.5 (green) unit cells for the LNO/LGO and (L,N)NO superlattices respectively.

Layer-resolved configuration of the reduced superlattices

The XAS spectra and XLD profiles, derived from the imaginary parts of the modeled scattering factors $f_{\rm IN}$ and $f_{\rm IF}$ are shown in Fig. 4.22. Although the results in rows one and two were obtained with two different approaches, the dichroic data match very well for each sample. A more surprising result is the opposite dichroism observed between interface and inner layers, the former being slightly negative. The linear dichroism observed in Figs. 4.22 a, b, c coincides with the lineshape of Ni¹⁺ (purple) and Ni²⁺ (coffee) in Figs. 4.22 d, e, f. These results strengthen the idea that reduced $R \text{NiO}_{2+\delta}/\text{ABO}_3$ form a nickelate sublattice composed of interfacial pyramidal Ni²⁺ and inner square-planar Ni¹⁺ layers. These results also reveal that the orbital polarization of NNO/STO in both inner and interfacial layers is larger than in the samples with LNO. This behaviour could be directly related to the electronic response observed in the transport measurements (see Fig. 4.14 d and Fig. 4.8 c) where NNO/STO is the superlattice with the highest conductivity.

In contrast to similar studies using the same technique on pristine superlattices [91, 92, 197, 219], here it is not possible to compare the orbital polarization P (see Eq. 3.28) corresponding to the interface and inner layers of the reduced samples because each layer group is assumed to have a distinct 3d-filling and crystal field (C_{4v}/D_{4h}) environment (see Fig. 4.18 a). In the same line, the hole ratio X_{av} is a better value to compare as it is the integral of the spectra across the Ni- $L_{2,3}$ region. However, its estimation using Eq. 3.27 does not yield a good agreement between the two methods used above, possibly because the calculated optical constants do not account for the small but significant spectral weight appearing between the Ni- $L_{2,3}$ edges in the measured XAS data. Nevertheless, both approaches have a qualitative agreement where values of $X_{av} \approx 1$ and $X_{av} \ll 1$ are obtained for the interfacial and inner layers, respectively (see Fig. 4.23 a).

The results for both methods discussed above were tested for different combina-

tions $(p_{\rm IF} + p_{\rm IN} = 8)$ of interface an inner layers (see Appendix H.1). In both approaches we find that the best results are obtained when $(p_{\rm IF}/p_{\rm IN})_{\rm LNO/LGO} = 2/6$ and $(p_{\rm IF}/p_{\rm IN})_{\rm LNO/STO} = (p_{\rm IF}/p_{\rm IN})_{\rm NNO/STO} = 3/5$. These results indicate that the additional charge stemming from the remaining apical oxygen at the interface is fully accommodated in the interface Ni atoms, in agreement with the DFT+DMFT results (see Sec. 4.3). Therefore, the LNO/LGO superlattice can be described as in Fig. 4.23 b where the oxygen in the Ni-O-Ga bond remains upon reduction. On the other hand, for NNO/STO and LNO/STO, the interface layers account for 3 unit cells. This value of 3 u.c. can be interpreted as a homogeneous distribution of two and one unit cells originating from the mixed termination across the superlattice. In this regard, we tested three combinations of IF-IN-IF layers, namely 2-5-1, 1-5-2, and 1.5-5-1.5, all resulting in very similar fittings (see Appendix H.1). These different results observed for the heterostructures with $SrTiO_3$ can be associated with diverse sources such as spatial confinement, strain, structural distortions, electronic reconstruction, and intermixing effects. The first two effects seem less likely given that all superlattices have the same stacking (8/4) and are grown on the same substrate. However, one will expect fewer structural distortions in the LNO/LGO superlattices compared to LNO/STO or NNO/STO, given that the former one has an invariant A-cation. Moreover, A polar/non-polar interface such as (L,N)NO/STO is expected to reconstruct according to electrostatic considerations, which can explain the unexpected value of three interfacial layers. STEM investigations performed by collaborator C. Yang strongly suggest the presence of mixed (Sr,Nd)O atomic layers at the interface and no apical oxygen removal in these atomic layers [293]. This scenario is depicted in Fig. 4.23 c, where the reconstruction process counteracts the polar discontinuity through a change in the valence of the 3d-material. From this picture, two possibilities are probable: The first one, with no Ti valence change, will lead to an averaged valence state for the interface layers of Ni^{1.67+}. The second, which involves a small decrease in the Ti oxidation state, will result in a valence of $Ni^{1.83+}$. Given that no significant changes between the pristine and reduced samples have been observed in the Ti- $L_{2,3}$ edges (see Appendix C.2), we suggest that the former case is the most likely scenario.

Our quantitative x-ray absorption and reflectivity study on various reduced superlattices allowed us to understand the results of the reduction process in the nickelate part of the heterostructures and at their corresponding interfaces with the buffer layers. As a first observation, we see a clear tendency of the hole ratio X_{AV} which decreases proportionally as the c-axis lattice constant of the reduced samples becomes smaller than the prisitine ones. The average polarization measured in XAS shows an overall, preferential electron occupation of the $d_{3z^2-\mathbf{r}^2}$, however, the RXR results reveal that a redistribution of the charge with Ni²⁺ at the layers close to the interfaces and Ni¹⁺ in the rest of nickelate layers is realized. The layer-resolved XAS spectra produced from the fitting of the q_z -fixed reflectivity scans show that the averaged occupation of the $d_{3z^2-\mathbf{r}^2}$ and $d_{x^2-y^2}$ orbitals in the interface with the buffer layers is substantially different compared to the central part of the nickelate layers (see Fig. 4.18b). This difference is related to the different fillings, Ni¹⁺ with one hole in the $d_{x^2-y^2}$, and Ni²⁺ with one hole in each of the e_g orbitals (Hund's coupled S = 1). In the latter case, the energy integral over the dichroism should vanish or be close to zero. The experimental results for the LNO/LGO agree with the model and theoretical predictions established in Sec. 4.3 where exactly one layer, which is not square planar, sits next to the interface. Finally, the reflectivity analysis on the LNO/STO and NNO/STO superlattice indicates a strong effect of the electronic reconstruction at the polar interfaces with the possibility of intermixing at the Sr-Nd-O layers.

4.6 Comparative study of infinite-layer nickelate superlattices

In this section, we summarize and compare the results from spectroscopic experiments on superlattices with various compositions $[(La,Nd)NiO_{2+\delta}]_8/[ABO_3]_4$, but with the same stacking. We begin with observing the spectral region around the Ni- $L_{2,3}$ edges, which gives information about the electronic configuration. Then, we analyze the x-ray absorption data of the O-K edge in detail, which allows the study of the Ni-O hybridized states. In previous sections, we studied numerous superlattice combinations and sequences, intending to find a configuration that leads to a superconducting state. Although no signs of superconductivity were found, our investigation granted us a better understanding of the electronic and structural properties of the infinite-layer nickelate heterostructures. Our diffraction measurements indicate that superlattices with a nominal stacking of eight nickelate unit cells (u.c.) and four u.c. of the blocking layers show good crystallinity. Therefore, we decided to keep these numbers fixed and study the blocking layer composition dependence. Our main goal here is to understand how different blocking layers affect the electronic structure of nickelates and the environment at the interface between the two materials.

In Fig. 4.24, we compare a series of x-ray absorption spectra at the Ni- $L_{2,3}$ edge, measured in TEY mode. The measurements were performed on a series of reduced (La,Nd)NiO_{2+ δ}/ABO₃ superlattices with the insulating buffer layers ABO₃ = LaGaO₃ (LGO), LaAlO₃ (LAO), DyScO₃ (DSO), GdScO₃ (GSO), and SrTiO₃ (STO). All samples were grown on the same substrate as the insulating buffer layer, except for LNO/LGO and LNO/LAO, which were grown on STO and LSAT, respectively. We followed the same procedure for each composition, where pristine and reduced samples were cut out from the same piece. All superlattices are grown so that we start with a nickelate slab next to the substrate and end with a blocking layer. The oxide bilayer composed of the nickelate slab and the buffer layers is repeated at least eight times for all superlattices.

Fig. 4.24 a, shows the compared spectra of all LaNiO_{2+ δ} superlattices together with their corresponding normalized linear dichroism. This set of data allows us to make various important observations. For example, LNO/LAO is the superlattice with the least orbital polarization, followed by LNO/LGO. Although La(Al,Ga)O₃ was used to produce minimal changes at the interfaces and thus avoid structural distortions, the absorption measurements indicate that they have a minor contribution to the preferential occupation of orbitals compared with the rest of heterostructures. On the other hand, the sample with the larger orbital polarization is LNO/DSO, followed very closely by LNO/STO and LNO/GSO, where the substrate exerts tensile strain. Moreover, the linear dichroism in the latter heterostructures falls almost on top of each other, although LNO/STO has more negative dichroism in the region between the two Ni absorption edges. This similarity in the linear dichroism is surprising given the differences between heterostructures substrates and blocking layers. The calculated hole ratio of each superlattice seems to decrease as a function of strain, suggesting that the substrate's choice might influence the observed orbital polarization. However, a comparison between LNO/STO and LNO/LGO (both grown on STO) displays a significant difference in the linear dichroism, indicating that the major contribution to the orbital polarization originates mainly from the nickelate/bufferlayer interaction and not from the choice of the substrate. This result agrees with the transport measurements where both LNO superlattices grown on STO show different transport properties. Furthermore, a change from LNO to NNO also increases the prefer-



Figure 4.24: X-ray absorption measurements at the Ni- $L_{2,3}$ edges for a group of a) LaNiO_{2+ δ} and b) NdNiO_{2+ δ} superlattices with eight nickelate and four blocking layers. The curves in the top panels have been vertically translated for clarity. The bottom panels contain data that has been normalized according to Eq. 3.22. X_{av} is the hole ratio calculated according to Eq. 3.27.

ential orbital occupation, as can be seen in the NNO/STO sample (Fig. 4.24 b). Finally, a comparison between Fig. 4.24 and the transport data presented in previous sections yields a direct correlation between the hole ratio and the conductivity in all heterostructures. More specifically, reduced samples with a hole ratio lower than one at the Ni absorption edges are metallic, whereas those with a hole ratio closer to one are semiconducting or insulating. In other words, one can establish a numerical threshold between the metallic and insulating states in the following way: Samples with $X_{av} \leq 0.75$ are metallic, whereas that the obtained numerical boundary only estimates the observed results and is not intended to be a general rule for infinite-layer nickelate superlattices.

Oxygen hole character in reduced nickelate superlattices

In Fig. 4.25 a, we compare a series of x-ray absorption spectra at the O-K edge performed on the same group of samples as in Fig. 4.24 together with their pristine counterparts. Previous results from x-ray diffraction and x-ray absorption have confirmed the layer-selective nature of the reduction process in LNO/DSO, LNO/GSO, LNO/LGO, LNO/STO, and NNO/STO (see Sec. 4.3). Our spectroscopy experiments at the O-K edge region show that the major loss of spectral weight occurs in all spectra at the pre-peak A at 528.3 eV, which is associated with the Ni³⁺-O hybridized states. In Fig. 4.25 b we compare pairwise the difference spectra of reduced and pristine samples obtained from Fig. 4.25 a. The top panel compares all samples with scandates as blocking layers (NNO/DSO, LNO/DSO, and LNO/GSO), while the second panel compares those superlattices with no A-cation change between interfaces (LNO/LGO and LNO/LAO). The third panel compares the polar superlattices with SrTiO₃ as the blocking layer. Finally, the bottom panel compares the Nd-based nickelate heterostructures together with results from a superconducting



Figure 4.25: a) Averaged XAS spectra at the O-K edge for a group of pristine (P) and reduced (R) (La,Nd)NiO_{2+ δ}/ABO₃ superlattices with eight nickelate and four blocking layers. b) The intensity difference between pristine and reduced superlattices of a). The panels (top to bottom) separate the samples by Sc-, La-, Ti-, and Nd-based superlattices. The two regions with spectral weight loss (A, C) are marked in orange, and the two regions with spectral weight gain (B, D) are depicted in light blue. Data from sample NSNO (Nd_{0.8}Sr_{0.2}NiO₂) was adapted from Ref. 294.

 $Nd_{0.8}Sr_{0.2}NiO_2$ thin film reported in Ref. 294.

The first observations we can make from Fig. 4.25 b are that spectral weight is redistributed and that the fine structure shows a strong resemblance. Further inspection allows us to identify various regions, i.e., A, C, and D, which have similar lineshapes and peak structures, independently of the blocking layer used. On the other hand, region Bis the zone where most differences occur, indicating a substantial change in the cationoxygen correlations. Since, in this range, contributions from all elements other than Ni which hybridize with oxygen are expected, we attempted to disentangle those by pairwise comparing the difference spectra of samples with different compositions (Fig. 4.25 b). In Sec. 4.3 we found that while in the inner part of the LNO layer stack, an infinite-layer structure is realized, the interfacial Ni layers have pyramidal oxygen coordination. The hybridization of Al or Ga with this interfacial oxygen of the pyramid is expected to be slightly different only because of the different ionic radii. Except for this distinction between Al and Ga, the difference spectra LNO/LAO and LNO/LGO superlattices fall almost on top of each other. A similar observation is made on the top panel, where all curves coincide in the A, B and C regions, while DSO-based structures significantly differ from the GSO-based ones at B. Furthermore, Although the dichroic data for the Ni- $L_{2,3}$ edges shows significant differences between NNO/STO and NNO/DSO superlattices, the O-K edge spectra show very similar curves, especially above 535 eV. We take these observations as evidence that the loss of spectral weight up to 530 eV and between 542 and 547 eV, together with the spectral weight gain between 530 and 540 eV and around 550 eV can be mainly attributed to the reduction of Ni^{3+} in (La,Nd)NiO₃ (pristine samples) to Ni^{1+} and Ni^{2+} in (La,Nd) $NiO_{2+\delta}$ (reduced samples). However, as the La-O and Nd-O distances change in the nickelate slabs upon reduction, we also expect small features associated with these elements.

As it was pointed out by Abbate et. al. in a previous work, various energy regions

	Energy (eV)	Associated with	Transition	Proposed origin
A_1	528.3	Ni ³⁺	$3d^{8}\underline{L} \rightarrow \underline{c}3d^{8}$	Ni ³⁺ : O_h , (e.g. LaNiO ₃) †
B_1	530.0	Ni^{3+}	$3d^{8}\underline{L} \rightarrow \underline{c}3d^{8}$	Ni ³⁺ : D_{4h} , (e.g. LaNiO ₃) †
B_2	531.7	Ni^{2+}	$3d^9\underline{L} \rightarrow \underline{c}3d^9$	Ni ²⁺ : O_h , (e.g. NiO) †
B_3	532.5	Ni^{2+}	$3d^9\underline{L} \rightarrow \underline{c}3d^9$	Ni ²⁺ : C _{4v} , (e.g. NiO)
B_4	533.8	Ni^{2+}	$3d^9\underline{L} \rightarrow \underline{c}3d^9$	$Ni^{2+}: D_{4h}, (e.g. La_2Ni_2O_5) \dagger$
B_5	535.2	$\mathrm{Sr} \to \mathrm{Sr}\text{-}\mathrm{O}$	4d	Proposed ‡
B_6	536.0	$\text{La-O} \to \text{La}$	5d	Proposed †
B_7	537.4	Ni^{1+}	$3d^{10}\underline{L} \rightarrow \underline{c}3d^{10}$	Proposed ‡
B_8	538.6	$\mathrm{Nd}\text{-}\mathrm{O}\to\mathrm{Nd}$	5d	Proposed ‡
B_9	539.6	Ni^{1+}	$3d^{10}\underline{L} \rightarrow \underline{c}3d^{10}$	Proposed ‡
C_1	540.8	Ni^{3+}	4sp	Assigned in Ref. 295
C_2	543.5	Ni^{2+}	4sp	Assigned in Ref. 295
D_1	550.0	Ni^{1+}	4sp	Proposed †

Table 4.1: Assignment of absorption features in the O-K spectra region. \underline{L} represents a O-2p ligand hole and \underline{c} an O-1s core hole. \dagger and \ddagger : peaks assigned or proposed based on comparisons with data from Refs 295 and 294, respectively.

can also be identified, consistent with analysis performed on different perovskite materials. For example, peaks appearing in the region between 527 and 535 eV correspond to transitions in the Ni 3d band. The small but clear peak around 536 eV can be directly attributed to the La-5d band region as it is not present in the Nd-based superlattices panel. The bumps in C can be assigned to the Ni 4sp band region [295]. Furthermore, the small feature at the intersection between regions A and B occurs prominently in the LNO/L(Al,Ga)O superlattices and is attributed to the self-doped holes that get trapped at the interfacial pyramidal coordinated nickel ions with electron configuration dominated by $3d^9\underline{L}$. Table 4.1 shows a resume of all features identified in Fig. 4.25 b. The peak identification was made by direct contrast between the spectra of all superlattices and with previous experimental works performed on similar samples (Ref. 295, Ref. 294 and Ref. 244).

Understanding the O-K spectra

The nickel ground state configuration in ligand-field theory is given by

$$|\Psi_0\rangle = \sum_i c_i |d^{n+i}\underline{L}^i\rangle, \qquad (4.6)$$

where $\sum_{i} c_{i}^{2} = 1$ with c_{i} being the weight of configuration *i*.

For $RENiO_3$ there are four terms (similarly as in Eq. 1.1):

$$|\Psi_{RENiO_3}\rangle = c_0 |\text{Ni}\,3d^7\rangle + c_1 |\text{Ni}\,3d^8\underline{L}\rangle + c_2 |\text{Ni}\,3d^9\underline{L}^2\rangle + c_3 |\text{Ni}\,3d^{10}\underline{L}^3\rangle \tag{4.7}$$

For $RENiO_3$, which is a negative charge transfer system, values of $(c_1)^2 = 0.25$, $(c_2)^2 = 0.57$, $(c_3)^2 = 0.17$, and $(c_4)^2 = 0.03$ have been reported [5] (single cluster, interacting approximation), indicating that the leading configuration is $3d^8\underline{L}$. Here, we will neglect the $|Ni 3d^{10}\underline{L}^3\rangle$ term because it is probably situated a very high energies and mainly due

to the low value of the c_4 in comparison with the rest of parameters. For the other two terms, a small but negative effective charge transfer energy from d^7 to $d^8\underline{L}$ of about 2 eV [46], and the $3d^9\underline{L}^2$ state being about 2 or 3 eV higher in energy than the $3d^8\underline{L}$ state, have been observed. Therefore $3d^8\underline{L}$ is the lowest energy state and $3d^9\underline{L}^2$ and d^7 both mix with $3d^8\underline{L}$ via the pd hopping which are 2 or 3 eV higher in energy, and $c_2 > c_1 \sim c_3$. We also know that in the O-K XAS, the broad band part of the spectrum is determined by the O p hybridizing with the broad bands formed by O-3p, Ni-4s, 4p and RE-5d, 6s. However, theses broad bands are rather high in energy and well separated from the local O 1s - 2p transitions.

For $RENiO_2$, the ground state configuration to begin with is closer to that of the cuprates:

$$|\Psi_{RENiO_2}\rangle = c_1'' |Ni \, 3d^9\rangle + c_2'' |Ni \, 3d^{10} \underline{L}\rangle, \qquad (4.8)$$

but the energies of the d^{10} state in Ni¹⁺ would be about 5 eV higher in energy than the d^{10} state of Cu²⁺ because of the more significant nuclear charge of Cu [150]. In O-K XAS, we can reach only the final d^{10} state, which is very high in energy and well inside the broad continuum. So it is possible that the associated transition cannot be detected in NdNiO₂ or LaNiO₂. This energy difference suggests that Ni $3d^9$ is the dominant configuration.

Reduced superlattices have an additional complexity due to the interfacial reconstructions that, depending on the buffer material composition (DSO, GSO, LAO, LGO, or STO), introduce a Ni²⁺-type configuration, i.e., we have to distinguish interface layers L1with

$$|\Psi_{RENiO_{2+\delta}(L1)}\rangle = c_1' |Ni \, 3d^8\rangle + c_2' |Ni \, 3d^9 \underline{L}\rangle + c_3' |Ni \, 3d^{10} \underline{L}^2\rangle \tag{4.9}$$

from infinite-layer-type inner layers L2 - 4 with

$$|\Psi_{RENiO_{2+\delta}(L2-4)}\rangle = c_1'' |Ni \, 3d^9\rangle + c_2'' |Ni \, 3d^{10}\underline{L}\rangle \tag{4.10}$$

Assuming the L1 layers have a pure Ni²⁺ configuration, one can compare the weight of each configuration with materials with a similar valence state, such as NiO. For NiO with a positive charge-transfer nature of the gap (band gap about ~ 4 eV) values of $(c'_1)^2 \approx 0.82$, $(c'_2)^2 \approx 0.18$ and $(c'_3)^2 \approx 0.0$ have been found, with Ni $3d^8$ being the leading configuration [296]. This result is in clear contrast to calculations made by collaborators where the $3d^9L$ was the prevailing configuration [273]. Then, we can use the same reasoning as in Eq. 4.8 for layers L2-4 where c''_1 was the dominant configuration. Finally, the ground state configuration observed in the XAS measurements will be a combination of Eq. 4.9 and Eq. 4.10. The terms discussed above are present in the O-K edge spectra in the form of small peaks in the energy region between 530 and 540 eV.

Chapter 5

Polycrystalline infinite-layer nickelates

In this chapter, we focus on the study of polycrystalline infinite-layer nickelates obtained from their perovskite pristine compounds (La,Nd)NiO₃. In comparison with the films and heterostructures analyzed in the previous chapter, the study of polycrystalline samples has significant differences. For example, in contrast to PLD growth which requires a couple of hours, the citrate-nitrate method used for synthesizing powder perovskite samples needs several days. When characterizing, the powder X-ray diffraction (PXRD) experiment can record simultaneously various crystallographic reflections in polycrystals, whereas for films, it measures Bragg peaks along with a specific lattice orientation. In addition, the amount of material provided in powder form is significantly larger than in thin films (various orders of magnitude), making the polycrystalline samples more suitable for certain experiments such as neutron scattering and muon spin rotation. On the other hand, while electrical transport measurements performed on infinite-layer nickelate films show a metallic behavior, powder measurements display a semiconducting or insulating trend which is most likely due to extrinsic effects such as planar anisotropy, and the lack of contact between grain boundaries [119, 297].

Early studies of the infinite-layer phase include the characterization with x-ray diffraction and neutron powder diffraction performed by Crespin and coworkers [118]. Further studies comprise magnetic susceptibility and magnetization measurements done by Hayward et. al., who found no long-range antiferromagnetic order but instead a paramagnetic trend. The authors also performed resistivity measurements which were orders of magnitude higher than those on the pristine samples [119, 121], a result that was in contrast with subsequent studies on thin films [297]. More recently, motivated by the discovery of superconductivity in Sr-doped NdNiO₂ epitaxial films, experimental works have been performed on doped infinite-layer nickelates polycrystals in an attempt to reproduce similar results in the bulk [132, 133], however, no signs of superconductivity have been found in powder samples so far. Possible explanations for this could be the interference of metallic nickel impurities as well as the lack of polycrystalline compaction. Along these lines, Li et. al., performed resistivity measurements on $Nd_{1-x}Sr_xNiO_2$ (x = 0, 0.2, 0.4) under high pressure to improve the grain compaction, and they observed and substantial suppression of the insulating behavior detected at ambient pressure but no clear metallic or superconducting trends. In addition, Wang et. al., performed in situ synchrotron x-ray diffraction during the reduction process to track the changes in the structure of the treated nickelate samples. The authors concluded that the addition of Sr makes the pristine samples metallic and facilitates the achievement of the infinite-layer phase, although they become semiconducting without doping [133]. We will focus our study on the parent compounds



Figure 5.1: Powder x-ray diffraction (PXRD) measurements of various treated a) LaNiO_{2+ δ} and b) NdNiO_{2+ δ} polycrystalline samples. Samples in black represent the untreated samples ($\delta = 1$). The circles enclose peaks corresponding to La₂O₃ and Ni.

 $(La,Nd)NiO_{2+\delta}$, given that many of their properties are still not well understood. Moreover, it is worth mentioning that superconductivity has also been observed in pure LaNiO₂ thin films, and some insights into this enigmatic behavior could be found in the powder counterpart [127]. In the next sections, we will first study the optimization process for obtaining high-quality infinite-layer powder samples and, second, the magnetic correlations in these compounds by means of various experimental techniques.

5.1 LaNiO_{2+ δ} and NdNiO_{2+ δ} samples

Polycrystalline LaNiO₃ powder was synthesized via the citrate-nitrate method by R. Merkle and A. Fuchs. The synthesis process can be described as follows: aqueous solutions of the metal-nitrides Ni(NO₃)₂ and La(NO₃)₃ were mixed with an aqueous solution of citric acid to obtain a mixture of the nickel-oxides. Then, the resulting material was heated to 500 °C, and various steps of grinding and calcination at 750 °C for at least 12 h were performed. Finally, the powder was treated in an autoclave with 400 bar O₂ pressure at 450 °C to guarantee phase purity and complete oxygenation. A similar procedure as the one described above was conducted for NdNiO₃.

We obtained the (La,Nd)NiO₂ infinite-layer phase through topotactic reduction of the (La,Nd)NiO₃ perovskite phase using CaH₂ as a reducing agent. Batches of 50 to 200 mg of (La,Nd)NiO₃ powder were wrapped in aluminum foil with an opening at one end and loaded into quartz tubes with approximately 250 mg CaH₂ powder. To prevent the CaH₂ from reacting with air, the procedure was performed in an Ar-filled glove box, and the quartz tubes were sealed under vacuum ($\approx 10^{-7}$ mbar). After sealing, the tubes were heated in a furnace with a ramp rate of 10 °C/min and kept at 280 °C for LaNiO₃ and 260 °C for NdNiO₃ at various times. Finally, the samples were cooled at a similar rate, and the reduced powder was extracted. During the entire process, the nickelate and CaH₂ powder have not been in direct contact. The high quality of pristine and reduced powder samples was corroborated by powder x-ray diffraction measurements. This experimental technique was also used to characterize the results from the different reduction phases.

Fig. 5.1 a shows various LaNiO_{2+ δ} samples reduced at different times. The black and

grey curves correspond to LaNiO₃ and LaNiO_{2.5}. We see that LaNiO_{2.5} can be obtained after a relatively short reduction time $t \leq 96$ h whereas it requires more than double of time to obtain highly pure LaNiO₂. Moreover, after a certain reduction time ($t \geq 348$ h), the treatment process starts to generate impurity phases like La₂O₃ and Ni metal, which can be identified by small peaks around 30° and 40° respectively.

While optimizing our process, we found various aspects that are worth mentioning. Given that there are several variables that influence the final results of the reduction process, namely time, pressure, temperature, the amount of CaH₂ and the amount of (La,Nd)NiO₃, we decided to keep the first two parameters fixed to reduce the number of variables (T = 280 K and $p = 1 \times 10^{-7}$ mbar). In addition, we observed that for our setup, when large amounts of material were reduced (≥ 200 mg), the final product presented impurity phases such as La₂O₃ and Ni, indicating that the topochemical process with CaH₂ was not homogeneous and it decomposed certain regions of the sample while it partially reduced other zones. Therefore we decided to keep the amount of material below 150 mg to improve sample homogeneity. Moreover, we found that a stoichiometric excess of CaH₂ greater than 2.5:1 is required to obtain a reduced material with good diffraction patterns and crystallinity. With all previous parameters fixed, this leaves the reduction time t as the most important variable for optimizing the reduction mechanism (Fig. 5.1).

Fig. 5.1 b shows a systematic study of the different reduction stages for NdNiO_{2+ δ}. According to data obtained from the refinement process, a single-phase NdNiO₂ was not achieved probably because the reduction conditions (temperature and time) have not been completely optimized. However, the graphs plotted as a function of time indicate a clear formation of a pair of asymmetric Bragg peaks around 33° which are well separated in the LaNiO₂ counterpart and that represent a qualitative indication of the reduction stage. As stated by Wang *et. al.*, the transition between NdNiO₃ and the intermediate state can be achieved at relatively low temperatures (200 °C) but the change from Nd₃Ni₃O₇ to pure NdNiO₂ required temperatures higher than 260 °C [133]. Our PXRD results suggest that the obtained powders have mainly the Nd₃Ni₃O₇ phase in qualitative agreement with previous experimental results [133, 266, 270]. In terms of oxygen stoichiometry, it makes sense that La₂Ni₂O₅ requires less reduction time than Nd₃Ni₃O₇ as their structures have different square-planar/octahedral configuration ratios (1 : 1 and 2 : 1 respectively). This difference in stoichiometry could be the reason why NdNiO₂ requires substantially different reduction times and temperatures compared with LaNiO₃ to reach the infinite-layer phase.

Finally, we would like to point out that the optimized times found in this section might vary slightly depending on the sample preparation conditions, the synthesis of the precursor phase, and, naturally, from the variables mentioned above. Therefore, we propose a basic procedure for obtaining the infinite-layer phase for nickelate polycrystals: After a proper synthesis and characterization of the perovskite phase, we separate the powder into two batches. The first batch, which accounts for less than 20% of the whole powder, will serve as a "dummy" portion for a trial reduction. A good starting point for this trial reduction is to use the optimized values we have found in this section ($t \approx 316$ h). Once the results are satisfactory, we proceed with the reduction of the rest of the powder. This way, we ensure an optimal procedure to obtain large amounts of high-quality infinite-layer polycrystals without the loss of material due to the presence of undesired impurity phases, which are prompt to appear in each new sample. In the next section, we investigate the magnetic correlations in our optimally reduced LaNiO₂ samples by performing various measurements such as specific heat, muon-spin rotation, and susceptibility.

5.2 Magnetic correlations in bulk infinite-layer nickelates

One of the current challenges in condensed matter physics is to understand the pairing mechanism of unconventional superconductors. In cuprates and iron pnictides, the weak coupling of antiferromagnetic paramagnons seems to be the most likely scenario [298–301]. However, in the newly discovered nickelate superconductors, there is still debate regarding the possible mechanism. From the theoretical point of view, the appearance of spin fluctuations has been predicted in infinite-layer nickelates [141,142,156,162,164,165,238]. On the experimental side, a long-range magnetic order (which is clearly visible in undoped cuprates) has not been observed in bulk [118,119,121]. Nevertheless, very recently, undoped and Sr-doped NdNiO₂ thin films were found to display magnetic excitations [139] and intrinsic magnetism [269] respectively. Then, based on the new developments and previous results, a combined study between theory and experiment regarding the magnetic correlations in infinite-layer nickelates is highly desired. Moreover, a thorough comparison between the properties of the parent compounds of nickelates and cuprates needs to be addressed.

In this section, we describe the study of magnetic correlations in bulk polycrystals of LaNiO₂. This material is one of the parent compounds of the infinite-layer nickelate superconductor family recently discovered in thin-film form [135]. The comprehensive study includes a collection of experimental and theoretical methods performed in collaboration with partner research groups. Our optimally reduced polycrystalline samples analyzed in the previous section were used for specific heat (c_p) , muon-spin rotation (μSR) , and magnetic susceptibility (χ) experiments.

Characterization and refinement

The infinite-layer phase LaNiO₂ was obtained following the optimized procedure described in the previous section, which yielded high-quality samples within a time of approximately 316 h. Fig. 5.2 shows the PXRD measurements of pristine $LaNiO_3$ and reduced $LaNiO_2$ together with the fitted data and their corresponding difference. The experiments needed for characterization of the samples were conducted by C. Stefani at room temperature using a Rigaku Miniflex diffractometer equipped with Cu K_{α} radiation and in a range of $20^{\circ} < 2\Theta < 90^{\circ}$. To fit the samples, Rietveld refinements were performed by P. Puphal using the FullProf software suite [302]. While the refinement process corresponds to a rhombohedral space group $R\bar{3}c$ for LaNiO₃, it required a tetragonal P4/mmm configuration for LaNiO₂ to ensure a good fit. Moreover, fits done with other space groups yielded less agreement with the experimental data. The refinement of $LaNiO_3$ (Fig. 5.2 a) indicates that the synthesis method yields highly pure powders without traceable secondary phases, such as the Ruddlesden Popper structure. On the other hand, the reduced samples were refined assuming a single phase of infinite-layer $LaNiO_2$ given that no visible traces of phases such as NiO, La_2O_3 or $LaNiO_{2.5}$ were found (Fig. 5.2 b). The resulting parameters provided by the refinement process (Tab. 5.1) are in good agreement with previous experimental reports [37, 119, 120]. Although no impurity phases were detected in the PXRD data, less than 2 wt% of ferromagnetic Ni inclusions are believed to be present in the $LaNiO_2$ powders, which could originate from the reduction process.



Figure 5.2: Powder X-ray diffraction measurements of a) LaNiO₃ and b) LaNiO₂. The black and grey lines correspond to the fittings obtained from the Rietveld refinement and the difference between experimental and calculated intensities respectively. The vertical bars indicate the calculated Bragg peak positions. [189].

Table 5.1: The refined atomic positions of a) LaNiO₃ with rhombohedral space group $R\bar{3}c$ and b) LaNiO₂ in tetragonal space group P4/mmm extracted from fittings of the powder X-ray diffraction measurements [189].

Experiments regarding the magnetic properties

After performing a proper characterization to determine the quality of our samples, we continue our study by exploring the magnetic correlations in $LaNiO_2$ by gathering information from a series of experiments dedicated to this end. Together with P. Puphal and M. Hepting, we determine the temperature dependence of the specific heat (c_p) in both pristine and reduced samples (Fig. $5.3 \,\mathrm{a}$). Both curves increase monotonically and smoothly in the temperature range from 2 to 300 K. Since there are no spikes or discontinuities (called λ -anomalies) that would be indicative of structural or magnetic transitions, we conclude that there is no long-range magnetic order nor symmetry change in these samples as a function of temperature. These results are in agreement with neutron diffraction experiments on polycrystalline $LaNiO_2$ and $NdNiO_2$, which found no evidence of magnetic Bragg reflections [119, 121]. In addition, a comparison between pristine LaNiO₃ and reduced LaNiO₂ samples yields some insights into the changes in the structural properties upon reduction. For example, in the region between 2 and 120 K, the specific heat of both materials is very similar. Given that at low temperatures, the main contribution to c_p originates from the lattice configuration, we conclude that this resemblance is due to the La-Ni sublattice, which is expected to be the one that remains almost unaltered after the treatment. On the other hand, above 120 K the curves start to deviate from each other with $c_p(\text{LaNiO}_3) > c_p(\text{LaNiO}_2)$. At high temperatures, phonons (associated with the oxygen sublattice) start to play an important role in the value of c_p . Then, since the reduction process subtracts oxygen atoms from the sample, it is expected to have a lower



Figure 5.3: a) Specific heat C_p of a pair of polycrystalline pristine LaNiO₃ (blue) and reduced LaNiO₂ (orange) samples from 2 to 300 K. b) Zero-field μ SR spectra of LaNiO₂ at various temperatures. The solid black lines represent the fits of polarization according to $P(t) = P_0 e^{(\lambda_{Dyn}t)^{\beta}}$, T > 75 K and $P(t) = \frac{1}{3} e^{-\lambda_L t} + \frac{2}{3} \cos(2\pi\nu t) e^{(\lambda_T t)^{\beta}}$, T < 75 K [189].

 c_p in LaNiO₂ as observed in Fig. 5.3 a at high temperatures.

Next, we turn to the muon spin rotation (μ SR) measurements, which give information about the quasi-static and dynamical magnetic processes. In this type of experiment, spinpolarized positive muons (μ^+) are fired into the sample and implanted at the interstitial lattice sites, where they stop momentarily and acquire information about the magnetic environment. Then, the muons become a sensitive local probe for small internal magnetic fields by quantifying the polarization P(t). The μ SR measurements were performed by F. Hotz, R. Khasanov, and H. Luetkens with the General Purpose Surface-Muon Instrument (GPS) [303] at the Paul Scherrer Institute (PSI) in Switzerland. The data analysis was carried out employing the free software package must fit [304]. Figure 5.3 b shows the measured polarization P(t) of LaNiO₂ as function of time for various temperatures ranging from 5 to 290 K. Since there are no persistent oscillations in the spectra, we conclude that long-range magnetic ordering is absent within the temperature range. This conclusion is in agreement with our previous results regarding the specific heat measurements. Although infinite-layer nickelates seem not to show macroscopic magnetism, long-range magnetic order has been observed with μ SR in AFM trilayer nickelate La₄Ni₃O₈ [305]. A close inspection of Fig. 5.3 b shows a strongly damped oscillation in the spectra of 5 K. This oscillation, which presents a local minimum around $t \approx 0.25 \,\mu s$ is an indication of shortrange order at this temperature. In addition, at longer times, the 5 K spectra shows a tail with polarization values close to 1/3 of the initial polarization (i.e. $P_{t\to\infty}(5 \text{ K}) \approx 1/3P_0(T)$). This behavior suggests a quasi-static magnetism such as the one associated with spin glasses below a freezing temperature (T_f) [306]. Moreover, further analysis of the μ SR data indicates that the spin glass behavior, if present, is arising from the bulk of the sample (see Ref. 189 for more details).

Besides c_p and μ SR experiments, we analyzed the static magnetic susceptibility of LaNiO₂. The low-temperature dc susceptibility measurements were performed using a vibrating sample magnetometer (MPMS VSM SQUID, Quantum Design) by collaborators P. Puphal and M. Hepting. Figure 5.4 a shows $\chi(T)$ of LaNiO₂ measured in a small external field of 0.1 T. The magnetization curve shows no signs of long-range magnetic



Figure 5.4: Static susceptibility χ of LaNiO₂ measured as function of temperature for two modes: zero-field cooling (ZFC, solid line) and field-cooling (FC, dashed line), in external fields of a) $\mu_0 H = 0.1 \text{ T}$ and b) $\mu_0 H = 7.0 \text{ T}$. c) Isothermal magnetization of LaNiO₂ measured between 0 T and 7 T at various temperatures from 2 K and 650 K. The gray area represents the region where the ferromagnetic Ni signal is assumed to be saturated and where the linear fits for the Honda-Owen method are performed (5 - 7 T) d) Paramagnetic susceptibility of LaNiO₃ (blue triangles) and LaNiO₂ (orange circles) obtained from measurements and the Honda-Owen method respectively [189].

order between 4 and 300 K in good agreement with our c_p and μ SR measurements and with previous experiments [118–121, 153]. In addition, we observed the irreversibility of the magnetization curves measured with the zero-field cooled and field-cooled modes at low temperatures (< 20 K). When the sample is cooled under a small magnetic field (FC), its magnetization increases following Curie's Law. However, when the sample is first cooled and then warmed up under a small magnetic field (ZFC), its magnetization increases up to a maximum value and then follows a paramagnetic trend. This behavior is characteristic of a spin glass with the spin freezing temperature ($T_f \approx 17$ K) corresponding to the maxima of the ZFC curve. A similar response of the magnetization in the ZFC-FC curves has been also reported in recent studies on RENiO₂ and Pr₄Ni₃O₈ polycrystals [307, 308] as well as La_{1-x}Ca_xNi_{2+ $\delta}} single crystals [134].</sub>$

In principle, the origin of the observed spin glass state could be an intrinsic property of the material, or it could arise due to the existence of impurities or secondary phases. To address this issue, we performed two types of experiments, i.e., a susceptibility measurement at high magnetic fields and a magnetization versus field measurement at various temperatures (see Figs. 5.4 b,c). From the χ measured at high magnetic fields (Fig. 5.4 b) is possible to see that the spin glass behavior does not dominate in this regime, but it has been suppressed. Moreover, the ZFC-FC curves have features, such as the slight upturn at low temperatures and a $\partial \chi / \partial T > 0$ behavior that is not seen in the χ obtained under small magnetic fields. These results suggest that the observed spin glass behavior is not an intrinsic property of the system but that it arises from other sources. In addition, it seems improbable that an intrinsic square planar spin glass system could be realized in nickelates due to the precise fine-tuning required for the nearest and next-nearest neighbors exchange to realize such a frustration.

Figure 5.4 c shows the isothermal magnetization-field measurements at various temperatures. The curves show a clear non-linearity between the low-field and high-field regions that vanishes for 650 K and higher temperatures. Given that the Curie temperature of Ni is $T_c \approx 620$ K, we attribute the observed non-linearity to the presence of a small amount of Ni impurities. However, according to Refs. 307, 308 and our μ SR results, the appearance of a spin glass state in nickelates due to a dilute distribution of Ni impurities is unlikely. Moreover, a more likely scenario for the origin of the spin glass state is the presence of local oxygen disorder in the form of remaining apical oxygen after the reduction process. In this scheme, the effective moment is produced by Ni²⁺ atoms sitting in regions with an excess of oxygen. Here, it is important to point out that although the previous scenario is possible in our system, there are other possible sources for magnetic clusters, such as remaining LaNiO_{2.5} inclusions or domain walls separating regions with different NiO₂ plane orientations. Therefore, further work is necessary to conclusively determine the source of the spin glass state in LaNiO₂ polycrystals.

The susceptibility observed in Fig. 5.4 b seems to be the result of collective effects, including the intrinsic properties of the sample and the Ni impurities; however, the latter can be corrected by employing the Honda-Owen method, which subtracts the intrinsic susceptibility from an isothermal magnetization-field measurement (see Fig. 5.4 c) provided it can be expressed as

$$\frac{M}{H} = \chi_{\rm corr} + C_{\rm sat} \frac{M_{\rm sat}}{H}, \qquad \rightarrow \qquad \lim_{H \to \infty} \frac{M}{H} = \chi_{corr} \tag{5.1}$$

where M is the measured magnetization, H is the applied magnetic field, χ_{corr} the corrected, intrinsic susceptibility, C_{sat} the presumed magnetic impurity content and M_{sat} its saturation magnetization. In other words, the magnetization signal of magnetic impurities is expected to saturate in sufficiently strong fields, resulting in a constant contribution above a certain threshold value of the magnetic field [119].

Figure 5.4 d shows the temperature dependence of χ for LaNiO₃ and of the χ_{corr} for LaNiO₂ obtained using Eq. 5.1, which is different from $\chi(T)$ in Fig. 5.4 a. For LaNiO₃, χ shows a characteristic Curie-Weiss behavior in agreement with previous results [309,310]. However, for LaNiO₂, $\chi_{corr}(T)$ presents a minimum value around 65 K, and then, it has a roughly linear increase towards room temperature and above, indicating a clear non-Curie-Weiss behavior. This trend is also observed in the magnetic Knight shift of a ¹³⁹La nuclear magnetic resonance (NMR) measurement performed on LaNiO₂ polycrystals [311]. This result also confirms that the $\chi_{corr}(T)$ signal is intrinsic and not affected by the presence of Ni impurities since they were removed by the Honda-Owen method. The behavior observed in Fig. 5.4 d for LaNiO₂ is in contrast to previous studies on similar polycrystals where a paramagnetic Curie-Weiss comportment was reported in the same temperature range [119]. Moreover, the authors identified two Curie-Weiss regions divided by a boundary around 150 K, which could be linked to distinct impurity phases in their samples. This discrepancy in the susceptibility can be related to the reduction process itself, given that we employed CaH₂ instead of NaH as a reducing agent and our powders were not in direct contact as in the NaH-LaNiO₃ chemical process. Since we determine a shorter *c*-axis lattice parameter for our LaNiO₂ powders (see Tab. 5.1 b) and we apply longer reduction times in our treatment process, we conclude that our samples possess less apical oxygen remnants. Despite the differences observed, it is important to notice that the extracted absolute value of χ_{corr} at room temperature is comparable in the two groups of samples (CaH₂- and NaH-treated) and also in the same order of magnitude as the susceptibility of perovskite LaNiO₃ (see Fig. 5.4 d).

The behavior of $\chi_{corr}(T)$ obtained for LaNiO₂ has also been observed in polycrystalline cuprates. For example, La_{2-x}Sr_xCuO₄ with $x \ge 0.04$ show an almost linear increase of the susceptibility as a function of temperature after a local minimum, which changes as a function of doping concentration [312]. Moreover, the analogy between bulk nickelates and cuprates can be extended even further as materials such as La_{2-x}Sr_xCuO₄ show a spin glass state for doping concentrations between 0.02 < x < 0.06, which is the region between the AFM and superconducting phases [313, 314]. In cuprates, the spin glass state is believed to arise due to the charge segregation into hole-rich, and hole-poor regions, which generates AFM clusters [315]. This observation seems to be in contrast with nickelates, although the charge separation scenario cannot be entirely ruled out from our experiments.

Finally, our collaborators studied the same LaNiO₂ system from the theoretical point of view. M. Klett, P. Hansmann, and T. Schäfer applied theory calculations within the framework of D\GammaA, a diagrammatic extension of DMFT customized to include systematically spatial correlations on all length scales. The calculated susceptibility from DΓA qualitatively resembles the obtained susceptibility $\chi_{corr}(T)$ shown in Fig. 5.4 d. In addition, the calculated χ was obtained without the appearance of long-range magnetic order but with the presence of a maximum centered around $T_*^{D\Gamma A} \approx 900$ K below which a Curie-Weiss behavior is observed. These results support the concept that strong magnetic fluctuations quench the possible ordering in parent infinite-layer nickelates and hinder the appearance of long-range magnetic order at any measurable temperature. Moreover, the similarities between calculated and measured susceptibilities strengthen the idea that infinite-layer nickelates are a close realization of the single-band Hubbard model (see Ref. 189 for more details).

Chapter 6

Summary and outlook

In this thesis, we have employed various methods and techniques to gain insights into the microscopic and macroscopic properties of a well-known group of TMOs, i.e., the rareearth nickelates. We focused on two $RENiO_{2+\delta}$ sample types, i.e., the superlattice and polycrystalline forms. We obtained the infinite-layer phase departing from the perovskite phase in both systems, which underwent a topotactic chemical treatment. Our samples passed through a characterization procedure to trace the quality of the synthesis and the outcome of the treatment process. In addition, we obtained valuable information about our samples' properties using modern spectroscopic techniques, such as resonant x-ray scattering, absorption, and reflectivity, together with theoretical models and calculations. Therefore, we evidence the versatility of light scattering in probing the nickelates' structural, electronic, and magnetic properties in their various forms. This section summarizes the most important findings of this thesis and compares them with current research topics regarding similar methods and compounds. In addition, we also discuss the possible directions to follow in the future concerning TMOs heterostructures as promising quantum materials.

Chapter 4 has been dedicated to studying the structural and electronic properties of various rare-earth nickelate superlattices. Our main goal was to create a new superconductor by combining two materials with various properties present in well-known superconducting materials, such as cuprates. We succeeded in synthesizing a new type of superlattice fabricated by heterostructuring two oxide materials together and subsequently chemically treating the resultant compound to selectively remove oxygen ions from one of its constituents. The oxide materials were chosen such that one of them is prompt to lose oxygen (i.e., the nickelate), whereas the other is very stable against oxygen removal (i.e., the band-gap insulator). Our material of interest is the nickelate, which was recently found to exhibit superconductivity upon chemical doping and reduction. Oxygen anions can be removed from nickelate materials, yielding new properties without severely altering the structural frame. On the other hand, we selected various band-gap insulators to form the buffer layers (also called blocking layers). These materials can either confine the nickelate layers or act as charge reservoirs and a doping source.

In section 4.2, we study our first group of superlattices composed of nickelates and scandates. Our analysis of the diffraction intensity patterns in the LaNiO_{2+ δ}/(Dy,Gd)ScO₃ superlattices allowed us to extract the averaged lattice constant $\bar{c}_{\rm SL}$, which suggests that only a part of the nickelate layers achieve the square-planar phase after the reduction process. Since it is not possible to achieve reductions where the lattice constant of the nickelate slabs matches that of the thin films and bulk samples [118, 119, 122, 124], we

conclude that it is not possible to achieve a "full" transformation of the nickelate slabs into the square planar configuration. The explanation for this is straightforward; the buffer layers prevent the removal of oxygen at and close to the interfaces. Moreover, we have also estimated our reduced samples' valence state and chemical composition from lattice constants considerations. Compared to similar structures such as the superconducting self-doped T'-type phase [115], and the chemically doped infinite-layer nickelate thin films [110], our samples have a higher averaged valence state, which situates them in the overdoped regime. The transport measurements indicate that the pristine samples follow a non-Fermi liquid behavior at high temperatures, with 3D quantum corrections influencing the low-temperature regime. These results are in good agreement with measurements performed on perovskite nickelate thin films. The reduced samples show a similar non-Fermi liquid trend (although with a lower exponent) as the untreated samples for high temperatures. However, a 2D model with weak localization effects and electron-electron interactions best fits the curves at low temperatures. Our spectroscopic experiments indicate that the reduced samples have valence states close to the Ni¹⁺ and that no traces of Ni³⁺ are detected. In addition, our XAS measurements suggest that the reduction process is layer selective as the valence state of the A- and B-cations in the blocking layers do not change within the experimental energy resolution. The spectroscopic measurements also show that there are significant changes in the Ni valence when the amount of buffer layers increases from two to four and higher. In contrast, a substituting the A-cation in the buffer layers yields no considerable alterations in the electronic structure of the Ni ions.

We also studied nickelate/scandate samples where a magnetic ordering is expected to originate from the nickelate part of the superlattice, i.e., $NdNiO_{2+\delta}/DyScO_3$. Resonant scattering measurements on the pristine sample yielded a small but clear peak appearing around the momentum transfer $\vec{q} = (1/4, 1/4, 1/4)$. This \vec{q} is widely known as the vector representing the magnetic Bragg reflection corresponding to the antiferromagnetic ordering observed in nickelates. Surprisingly, the reduced sample shows a very intense peak around the same value $\vec{q} = (1/4, 1/4, \approx 1/4)$, indicating that this peak might have the same origin as the one observed in the pristine samples. Moreover, the reduced sample's resonant peak is higher in intensity and persists up to room temperature. Altogether, our measurements suggest that the resonant Bragg reflection might originate from intermediate states of the reduced NdNiO_{2+ δ} such as Nd₃Ni₃O₇ although additional measurements will be needed to reach a definitive conclusion.

Section 4.3 describes two types of superlattices where the blocking layer was chosen such that the A-cation site is the same as in the nickelate mataerial. Similarly, as for the nickelate/scandate superlattices, the XRD measurements performed on the LaNiO_{2+ δ}/La(Ga,Al)O₃ superlattices yielded crystalline samples for both pristine and reduced heterostructures. However, the transport measurements show a semiconducting behavior for the reduced samples in contrast to the metallic behavior of the nickelate/scandate samples. Furthermore, our results show that the reduction process is reversible as the reduced samples can be reoxidized to display similar properties as the pristine samples. A close analysis of the diffraction data of LaNiO_{2+ δ}/LaGaO₃ allowed us to identify the structure in the reduced superlattices. The fitting process indicates that the nickelate part of the superlattices is composed of an infinite-layer core surrounded by interfacial pyramidal coordinated layers. Except for a small translation due to the different lattice constants, the configuration is consistently reproduced in various samples, even for heterostructures where the A-cation has been changed in both oxide materials. The spectroscopic measurements confirmed that the reduction process is layer selective, as the valence spectra of the blocking layers seem to be not affected by the treatment process. Finally, collaborators who performed theory calculations on the reduced structures concluded that adding extra holes to the system would lead to charge segregation as the holes are not evenly distributed within the nickelate slabs but are stock at the interface. On the contrary, doping the system with electrons yields a homogeneous charge distribution across the whole nickelate slab.

In section 4.4, we present the study of the third group of superlattices analyzed in this thesis, namely the nickelate/ $SrTiO_3$ superlattices. The transport measurements show a consistent conductivity increase as a function of the number of nickelate layers, the amount of SrTiO₃ layers, and the A-cation element. While samples with $m \leq 6$ and n = 2 show a semiconducting behavior, samples with more nickelate layers are metallic. In contrast, all samples studied with n = 4 are metallic with small upturns at low temperatures. Moreover, Nd-based samples have a higher conductivity than the La-based superlattices. This result is also consistent with a higher orbital polarization observed by XAS in NdNiO_{2+ δ}/SrTiO₃ with respect to LaNiO_{2+ δ}/SrTiO₃. The spectroscopic results obtained for n = 2, 4 agree with those obtained for the nickelate/scandate superlattices, accentuating the strong differences between samples with n = 2 and n = 4 blocking layers. A comparison between XAS spectra of the infinite-layer nickelate superlattices and the cuprate superconductors yields a puzzling result; the normalized intensity of the linear dichroism produced by the cuprates is at least four times larger than the one of nickelate superlattices, even though they have the same $3d^9$ electronic configuration. A possible explanation for this result is that the reduction process and the interfacial regions are responsible for this difference. For example, the reduction process might leave regions with an excess of oxygen which could generate less orbital polarization. In addition, the orbital occupation on the layers near the interface with the band-gap insulator might be different to the one produced by the $3d^9$ system at the Ni- $L_{2,3}$ edges.

In section 4.5, we studied the layer resolved orbital polarization and valence state profiles in various nickelate superlattices employing resonant x-ray reflectivity. Our results indicate that within the nickelate slabs, the interface layers have a small but significant hole occupation in the $d_{z^2-r^2}$ orbitals. In contrast, the holes largely occupy the $d_{x^2-y^2}$ orbitals in the inner layers. Further calculations also indicate that the same system can be consistently reproduced by assigning a valence state of Ni²⁺ to the interface layers and a valence state of Ni¹⁺ to the inner layers. These results agree with the proposed behavior obtained from theory calculations, where additional dopants will separate or distribute evenly within the nickelate slabs, depending on their charge. More specifically, for the case of hole-doping, the electronic structure will be composed of Ni²⁺ layers at the interfaces and Ni¹⁺ layers in the center of the nickelate block.

In section 4.6 we performed a comparison of various reduced nickelate superlattices with the same stacking (i.e., m = 8/n = 4) and the exact repetition (i.e., x8) but with different buffer layers. The results indicate that the hole occupation in the e_g orbitals increases as a function of strain. However, comparing samples grown on the same substrate yields significant differences between their corresponding orbital occupations. This result indicates that the buffer layer contributes more than strain in enhancing the hole occupation. In addition, in this section, we analyzed in detail the oxygen-nickel hybridization and identified all the features present around the O K-edge.

In chapter 5 we focused on studying the parent compound of the superconducting infinite-layer nickelates $RENiO_2$. More specifically, we studied the bulk form of these

materials to learn about the magnetic environment of the Ni ions in the square planar configuration and to gain some insights into why this form of synthesis does not show superconductivity in contrast with their thin film counterparts. Before performing magnetic measurements, we optimized the reduction process for the bulk samples by treating multiple groups of powders. This optimization was straightforward for $LaNiO_2$ $(0 \leq \delta \leq 1)$, probably because the material has very stable intermediate states, establishing the boundaries for the respective reduction times. Once high-quality $LaNiO_2$ was obtained, we performed various measurements to characterize the samples in collaboration with partner institutions. Our results on specific heat, muon-spin rotation, and susceptibility experiments strongly indicate the absence of long-range magnetic order in the powder samples. In addition, the susceptibility and muon-spin rotation measurements signal a clear spin glass behavior at low temperatures, which is believed to arise from the bulk of the samples, but that it is probably not an intrinsic property of the infinite-layer phase. We suggest that these effects appear due to the reduction process, which can produce small regions with an excess of oxygen. Although our samples were not impurity-free, we obtained the intrinsic susceptibility of the system, which resembles the susceptibility observed in cuprates in the underdoped regime. Therefore, cuprates and infinite-layer nickelates show similar features such as a spin 1/2 state, a $3d^9$ electronic configuration, magnetic excitations, and a spin glass state and non-Curie-Weiss behavior of the susceptibility when underdoped. These analogies might serve as essential information for solving both compounds' unconventional superconductivity paradigms.

Based on our experimental results and the outcome of related studies, we believe that the realization of superconductivity in nickelates through heterostructuring is feasible. A similar scenario occurs in various cuprate superlattices, where superconductivity appears without chemical doping. In this regard, Balestrino et. al., who studied $(BaCuO_2)_m/(CaCuO_2)_n$ and Di Castro *et. al.*, who analyzed $(CaCuO_2)_m/(SrTiO_3)_n$, observed superconductivity in heterostructures where the number of buffer layers were fixed at 2 u.c. [249, 250]. Along these lines, Ikeda et. al. found superconductivity in a group of $(CaCuO_2)_m/(CaFeO_{2.5})_n$ superlattices for 2 < n < 5 [251]. Interestingly, the authors found that samples with different amounts of layers (n = 2, n = 5) show insulating behavior. This behavior appears in most of our superlattices with two buffer layers, which display a clear semiconducting trend. In contrast, most samples with four buffer layers show a metallic behavior except for the superlattices with no change in the A-cation site. In the future, it will be interesting to investigate different numbers of blocking layers to those studied in this thesis to see if a superconducting state is stabilized. In addition, the CaCuO₂ superlattices studied by previous authors possess superconductivity in combination with metals (i. e. $BaCuO_2$) as well as with insulators (i. e. $SrTiO_3$ and $CaFeO_{2.5}$), which evidences the importance of the choice of the material selected as blocking layer. Therefore, it will be equally interesting to consider different materials together with the nickelates such that the combined system is doped in a way that allows superconductivity to emerge. In this regard, two promising materials are $SrIrO_3$ and $LaMnO_3$ for which charge transfer has been observed when combined with nickelates in the perovskite form [316–318].

A few years ago, nickelates became the new group of materials where unconventional superconductivity takes place, besides their close neighbors' cuprates and iron pnictides. However, the low-temperature onset of the superconducting transition indicates that much work still needs to be done concerning sample quality and system understanding. In this regard, heterostructures can open the doors to new degrees of freedom not accessible in chemically doped thin films, such as reduced dimensionality, spatial confinement, charge transfer, and interfacial reconstruction. One of these properties might help increase the current transition temperature to values comparable to iron-pnictides or even cuprates, their nearest analogs. Moreover, the proximity of Ni to Cu and Fe in the periodic table might be crucial to understanding the origins of the pairing mechanism in these unconventional superconductors with high transition temperatures. The key to understanding the pairing mechanism might be hiding behind their similarities but also their differences. Our experimental results show similarities between our heterostructures and bulk samples and the cuprate materials, which were not reported before. We hope our novel results help the research field to give a step further toward unveiling the superconductivity mystery in both materials.

In addition to the possibility of exploring unconventional superconductivity, nickelates possess a plethora of other exciting properties. More specifically, nickelate heterostructures show various uncommon phases such as the coexistence of antiferromagnetism and the metallic phases, a non-Fermi liquid metallic state, and a non-charge-ordered localized state, which cannot be obtained in single crystals or powder samples. Furthermore, besides superconductivity, nickelates are promising compounds for applications in other areas of physics, which are already being explored. For example, since LaNiO_{3- δ} is a compound with high conductivity, it can be used as an electrode material [319]. Moreover, the various oxygen-deficient stable states of LaNiO_{3- δ} make it ideal for gas sensing [320, 321]. SmNiO₃ and NdNiO₃ have already been proposed as versatile materials for tuning photonics in optoelectronics [322], as fuel cells with high ion-conduction [323] and as Mott transistors for resistance switching [54].

The properties and applications mentioned above make nickelates a very appealing group of materials to create new devices for energy conversion and storage. Based on the studies we have performed over the last years, we are optimistic that these compounds will be crucial for understanding long-time unsolved solid state research problems, such as unconventional superconductivity. In addition, We believe that nickelates will be an essential component of the next-generation materials destined for large-scale applications that help us visualize a better future.

Appendix A Crystal structure factors

Model C: 4 interface layers and 4 inner layers

$$F_{001} = (f_{ABO} - f_{RNO,IN}) \left(\frac{\sqrt{3} + 3}{2}\right) (1+i)$$
(A.1)

$$F_{002} = (f_{ABO} - 2f_{RNO,IF} + f_{RNO,IN})\sqrt{3}i$$
 (A.2)

$$F_{003} = 0$$
 (A.3)

Model D: 6 interface layers and 2 inner layers

$$F_{001} = \left[f_{ABO} \left(\frac{\sqrt{3} + 3}{2} \right) - f_{RNO,IN} \left(\frac{\sqrt{3} + 1}{2} \right) - f_{RNO,IF} \right] (1+i)$$
(A.4)

$$F_{002} = (f_{ABO} - 2f_{RNO,IF} + f_{RNO,IN})\sqrt{3}i$$
 (A.5)

$$F_{003} = (f_{\rm RNO,IN} - f_{\rm RNO,IF})(1-i)$$
(A.6)

Model E: 3 interface layers and 5 inner layers

$$F_{001} = \left[f_{ABO} \left(\frac{\sqrt{3} + 3}{2} \right) - f_{RNO,IN} \left(\frac{3\sqrt{3} + 5}{4} \right) + f_{RNO,IF} \left(\frac{\sqrt{3} - 1}{4} \right) \right] (1+i)$$
(A.7)

$$F_{002} = \left(f_{\rm ABO} - \frac{3}{2}f_{\rm RNO,IF} + \frac{1}{2}f_{\rm RNO,IF}\right)\sqrt{3}\,i\tag{A.8}$$

$$F_{003} = \frac{1}{2} (f_{\text{RNO,IF}} - f_{\text{RNO,IN}})(1-i)$$
(A.9)

Appendix B XAS of pristine nickelate superlattices



Figure B.1: Polarization dependent XAS for a group of pristine a) LNO/DSO and b) LNO/GSO superlattices. The data in the upper panels have been vertically translated for clarity. The bottom panels represent data that has been normalized according to Eq 3.22.



Figure B.2: Polarization dependent XAS for a group of pristine a) NNOX/STO2 and b) NNOX/STO4 superlattices. The data in the upper panels have been vertically translated for clarity. The bottom panels represent data that has been normalized according to Eq 3.22.

Appendix C

XAS at the Gd, Dy, Sc and Ti absorption edges



Figure C.1: Polarization-averaged XAS spectra $(I_{\text{average}} = \frac{1}{3}(2I_{E\perp c} + I_{E\parallel c}))$ of the energy range covering a) Dy- $M_{4,5}$ edges and b) of the Gd- $M_{4,5}$ edges.



Figure C.2: Polarization-averaged XAS spectra $(I_{\text{average}} = \frac{1}{3}(2I_{E\perp c} + I_{E\parallel c}))$ of the energy range covering a) Sc- $L_{2,3}$ edges and b) of the Ti- $L_{2,3}$ edges.
Appendix D

$LaNiO_{2+\delta}/SrTiO_3$ superlattices



Figure D.1: a) XRD of a group of pristine and reduced LNO/STO superlattices. The region comprises the (001) and (002) substrate peaks. b) resistivity of the same group of (top) pristine and (bottom) reduced samples. Data in a) has been vertically translated for clarity.



Figure D.2: Polarization dependent XAS for a group of LNOX-STO4 a) pristine and b) reduced superlattices. The data in the upper panels have been vertically translated for clarity. The bottom panels represent data that has been normalized according to Eq 3.22.

Appendix E

Structural model and fittings from reflectivity

Fit Parameters	Thickness (Å)			Roughness (Å)		
	NNO/STO	LNO/STO	LNO/LGO	NNO/STO	LNO/STO	LNO/LGO
7 layers (Nd, La)NiO _{2+δ}	27.4	23.6	27.6	3.4	4.3	7.6
7 layers of STO_3 (LGO ₃)	15.2	16.8	16.0	3.1	3.6	7.2
STO_3 substrate	∞	∞	∞	2.7	2.7	1.1
(Nd, La)NiO _{2+δ} buffer layer	25.2	30.6	36.8	1.1	3.1	4.8
STO ₃ (LGO ₃) capping layer	13.3	14.8	12.3	4.5	5.8	1.9
7 layers (Nd, La)NiO ₃	29.1	29.5	30.0	5.9	7.4	4.4
7 layers of $STO_3 (LGO)_3$	15.2	15.0	15.7	5.6	6.0	3.9
STO_3 substrate	∞	∞	∞	3.9	3.9	2.1
(Nd, La)NiO ₃ buffer layer	30.9	28.5	28.7	2.1	1.5	1.8
STO_3 (LGO ₃) capping layer	13.5	13.8	17.8	6.7	7.6	2.2

Table E.1: Parameters for the structural model of the reduced (upper row) and pristine (lower row) samples (α method). The corresponding fittings from these values are shown in panels a), b) and c) of figure 4.20.

Fit Parameters	Thickness (Å)			Roughness (Å)		
	NNO/STO	LNO/STO	LNO/LGO	NNO/STO	LNO/STO	LNO/LGO
7 layers (Nd, La)NiO _{2+δ}	27.4	23.6	27.0	1.4	3.8	7.6
7 layers of STO_3 (LGO ₃)	15.2	14.8	16.0	2.1	4.0	7.2
STO_3 substrate	∞	∞	∞	2.7	3.5	1.1
(Nd, La)NiO _{2+δ} buffer layer	25.2	30.6	36.8	1.1	1.6	4.8
STO_3 (LGO ₃) capping layer	13.3	14.8	15.3	4.5	2.8	1.9
7 layers (Nd, La)NiO ₃	29.1	29.5	30.0	5.9	7.4	4.4
7 layers of STO_3 (LGO) ₃	15.2	15.0	15.7	5.6	6.0	3.9
STO_3 substrate	∞	∞	∞	3.9	3.9	2.1
$(Nd, La)NiO_3$ buffer layer	30.9	28.5	28.7	2.1	1.5	1.8
STO_3 (LGO ₃) capping layer	13.5	13.8	17.8	6.7	7.6	2.2

Table E.2: Parameters for the structural model of the reduced (upper row) and pristine (lower row) samples in the cluster calculations method. For this method some values (in bold) had to be slightly adjusted from table E.1.



Figure E.1: Reflectivity as a function of q_z for the pristine a) NNO/STO, b) LNO/STO and c) LNO/LGO superlattices. Each panel shows three curves corresponding to one off-resonant (green) and two resonant (blue and red) measurements at the Ni- $L_{2,3}$ edges. The dashed vertical lines correspond to the position of the (002) and (003) superlattice peaks. Reflectivity constant q_z energy scans for the d) NNO/STO, e) LNO/STO and f) LNO/LGO superlattices. The dashed lines in e) and f) correspond to the position of the La- M_4 line. π^* corresponds to $\pi_{pol} \times (\cos(2\theta)^{-2})$ which is a correction that accounts for the error produced by the proximity of the measurement to the Brewster angle.

Appendix F

Reflectivity preliminary data



Figure F.1: Fittings of the reflectivity at constant- q_z energy scans for the a) NNO_{2+ δ}/STO₃, b) LNO_{2+ δ}/STO₃ and c) LNO_{2+ δ}/LGO₃ superlattices using the optical constants of the averaged XAS spectra.



Figure F.2: Optical constant obtained from cluster calculations for the a) $NNO_{2+\delta}/STO_3$, b) $LNO_{2+\delta}/STO_3$ and c) $LNO_{2+\delta}/LGO_3$ superlattices.

Appendix G

Reflectivity homogeneous charge fits



Figure G.1: Fittings of the reflectivity at constant- q_z energy scans for the a) NNO_{2+ δ}/STO₃, b) LNO_{2+ δ}/STO₃ and c) LNO_{2+ δ}/LGO₃ superlattices using the cluster calculations optical constants of homogeneous Ni^{1.25+}.



Figure G.2: Fittings of the reflectivity at constant- q_z energy scans for the a) NNO_{2+ δ}/STO₃, b) LNO_{2+ δ}/STO₃ and c) LNO_{2+ δ}/LGO₃ superlattices using the cluster calculations optical constants of homogeneous Ni¹⁺.

Appendix H

Reflectivity uniqueness test results



Figure H.1: Polarization dependent reflectivity at constant q_z of the (003) superlattice peak for NdNiO_{2+ δ}/SrTiO₃: a) Tests for various amount of interface and inner layers b) Tests for various distributions of the 3 interface layers.



Figure H.2: Polarization dependent reflectivity at constant q_z of the (003) superlattice peak for: a) alpha test of LaNiO_{2+ δ}/LaGaO₃ and b) alpha test of NdNiO_{2+ δ}/SrTiO₃.

Bibliography

- C. N. R. Rao, "Transition Metal Oxides," Annual Review of Physical Chemistry, vol. 40, no. 1, pp. 291–326, 1989.
- [2] S. Middey, J. Chakhalian, P. Mahadevan, J. Freeland, A. Millis, and D. D. Sarma, "Physics of Ultrathin Films and Heterostructures of Rare-Earth Nickelates," *Annual Review of Materials Research*, vol. 46, no. 1, pp. 305–334, 2016.
- [3] S. Catalano, M. Gibert, J. Fowlie, J. Íñiguez, J.-M. Triscone, and J. Kreisel, "Rareearth nickelates RNiO₃: thin films and heterostructures," *Reports on Progress in Physics*, vol. 81, p. 046501, feb 2018.
- [4] V. M. Goldschmidt, "Die Gesetze der Krystallochemie," Naturwissenschaften, vol. 14, pp. 477–485, May 1926.
- [5] R. J. Green, M. W. Haverkort, and G. A. Sawatzky, "Bond disproportionation and dynamical charge fluctuations in the perovskite rare-earth nickelates," *Phys. Rev. B*, vol. 94, p. 195127, Nov 2016.
- [6] J. L. García-Muñoz, J. Rodríguez-Carvajal, P. Lacorre, and J. B. Torrance, "Neutron-diffraction study of RNiO₃ (R = La, Pr, Nd, Sm): Electronically induced structural changes across the metal-insulator transition," *Phys. Rev. B*, vol. 46, pp. 4414–4425, Aug 1992.
- [7] K. Momma and F. Izumi, "VESTA3 for three-dimensional visualization of crystal, volumetric and morphology data," Journal of Applied Crystallography, vol. 44, pp. 1272–1276, Dec 2011.
- [8] A. Awan, H. Truong, and R. J. Lancashire, "Crystal Field Theory," sep 5 2021. [Online; accessed 2022-01-25].
- [9] D. I. Khomskii, *Transition Metal Compounds*. Cambridge University Press, 2014.
- [10] N. F. Mott, "The Basis of the Electron Theory of Metals, with Special Reference to the Transition Metals," *Proceedings of the Physical Society. Section A*, vol. 62, pp. 416–422, jul 1949.
- [11] N. F. Mott, "Metal-Insulator Transition," Rev. Mod. Phys., vol. 40, pp. 677–683, Oct 1968.
- [12] J. Hubbard and B. H. Flowers, "Electron correlations in narrow energy bands," Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences, vol. 276, no. 1365, pp. 238–257, 1963.

- [13] J. Hubbard and B. H. Flowers, "Electron correlations in narrow energy bands. II. The degenerate band case," *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, vol. 277, no. 1369, pp. 237–259, 1964.
- [14] N. Li, D. K. Bediako, R. G. Hadt, D. Hayes, T. J. Kempa, F. von Cube, D. C. Bell, L. X. Chen, and D. G. Nocera, "Influence of iron doping on tetravalent nickel content in catalytic oxygen evolving films," *Proceedings of the National Academy of Sciences*, vol. 114, no. 7, pp. 1486–1491, 2017.
- [15] A. Fujimori and F. Minami, "Valence-band photoemission and optical absorption in nickel compounds," *Phys. Rev. B*, vol. 30, pp. 957–971, Jul 1984.
- [16] J. Zaanen, G. A. Sawatzky, and J. W. Allen, "Band gaps and electronic structure of transition-metal compounds," *Phys. Rev. Lett.*, vol. 55, pp. 418–421, Jul 1985.
- [17] T. Bandyopadhyay and D. D. Sarma, "Calculation of Coulomb interaction strengths for 3d transition metals and actinides," *Phys. Rev. B*, vol. 39, pp. 3517–3521, Feb 1989.
- [18] P. Mahadevan, N. Shanthi, and D. D. Sarma, "Estimates of electronic interaction parameters for LaMO₃ compounds (M = Ti - Ni) from ab initio approaches," *Phys. Rev. B*, vol. 54, pp. 11199–11206, Oct 1996.
- [19] D. D. Sarma, "Electronic structure of transition metal compounds: Photoemission experiments and model Hamiltonian calculations," *Journal of Solid State Chemistry*, vol. 88, no. 1, pp. 45–52, 1990.
- [20] S. Nimkar, D. D. Sarma, and H. R. Krishnamurthy, "Electronic structure of NaCuO₂," *Phys. Rev. B*, vol. 47, pp. 10927–10930, Apr 1993.
- [21] T. Mizokawa, A. Fujimori, H. Namatame, K. Akeyama, and N. Kosugi, "Electronic structure of the local-singlet insulator NaCuO₂," *Phys. Rev. B*, vol. 49, pp. 7193– 7204, Mar 1994.
- [22] A. Wold, B. Post, and E. Banks, "Rare Earth Nickel Oxides," Journal of the American Chemical Society, vol. 79, pp. 4911–4913, Sep 1957.
- [23] G. Demazeau, A. Marbeuf, M. Pouchard, and P. Hagenmuller, "Sur une série de composés oxygènes du nickel trivalent derivés de la perovskite," *Journal of Solid State Chemistry*, vol. 3, no. 4, pp. 582–589, 1971.
- [24] J. K. Vassiliou, M. Hornbostel, R. Ziebarth, and F. Disalvo, "Synthesis and properties of NdNiO₃ prepared by low-temperature methods," *Journal of Solid State Chemistry*, vol. 81, no. 2, pp. 208–216, 1989.
- [25] P. Lacorre, J. Torrance, J. Pannetier, A. Nazzal, P. Wang, and T. Huang, "Synthesis, crystal structure, and properties of metallic PrNiO₃: Comparison with metallic NdNiO₃ and semiconducting SmNiO₃," *Journal of Solid State Chemistry*, vol. 91, no. 2, pp. 225–237, 1991.
- [26] J. Alonso, M. Martinez-Lope, and M. Hidalgo, "Hole and Electron Doping of RNiO₃ (R = La, Nd)," Journal of Solid State Chemistry, vol. 116, no. 1, pp. 146–156, 1995.

- [27] M. L. Medarde, "Structural, magnetic and electronic properties of perovskites RNiO₃ (R = rare earth)," Journal of Physics: Condensed Matter, vol. 9, pp. 1679– 1707, feb 1997.
- [28] J. L. García-Muñoz, M. A. G. Aranda, J. A. Alonso, and M. J. Martínez-Lope, "Structure and charge order in the antiferromagnetic band-insulating phase of NdNiO₃," *Phys. Rev. B*, vol. 79, p. 134432, Apr 2009.
- [29] M. Medarde, J. Mesot, S. Rosenkranz, P. Lacorre, W. Marshall, S. Klotz, J. Loveday, G. Hamel, S. Hull, and P. Radaelli, "Pressure-induced orthorhombic-rhombohedral phase transition in NdNiO₃," *Physica B: Condensed Matter*, vol. 234-236, pp. 15–17, 1997. Proceedings of the First European Conference on Neutron Scattering.
- [30] X. Granados, J. Fontcuberta, X. Obradors, and J. B. Torrance, "Metastable metallic state and hysteresis below the metal-insulator transition in PrNiO₃," *Phys. Rev. B*, vol. 46, pp. 15683–15688, Dec 1992.
- [31] X. Granados, J. Fontcuberta, X. Obradors, L. Mañosa, and J. B. Torrance, "Metallic state and the metal-insulator transition of NdNiO₃," *Phys. Rev. B*, vol. 48, pp. 11666–11672, Oct 1993.
- [32] J. A. Alonso, J. L. García-Muñoz, M. T. Fernández-Díaz, M. A. G. Aranda, M. J. Martínez-Lope, and M. T. Casais, "Charge Disproportionation in RNiO₃ Perovskites: Simultaneous Metal-Insulator and Structural Transition in YNiO₃," *Phys. Rev. Lett.*, vol. 82, pp. 3871–3874, May 1999.
- [33] J. Pérez-Cacho, J. Blasco, J. García, M. Castro, and J. Stankiewicz, "Study of the phase transitions in SmNiO₃," *Journal of Physics: Condensed Matter*, vol. 11, pp. 405–415, jan 1999.
- [34] T. Katsufuji, Y. Okimoto, T. Arima, Y. Tokura, and J. B. Torrance, "Optical spectroscopy of the metal-insulator transition in NdNiO₃," *Phys. Rev. B*, vol. 51, pp. 4830–4835, Feb 1995.
- [35] T. Mizokawa, H. Namatame, A. Fujimori, K. Akeyama, H. Kondoh, H. Kuroda, and N. Kosugi, "Origin of the band gap in the negative charge-transfer-energy compound NaCuO₂," *Phys. Rev. Lett.*, vol. 67, pp. 1638–1641, Sep 1991.
- [36] M. Medarde, A. Fontaine, J. L. García-Muñoz, J. Rodríguez-Carvajal, M. de Santis, M. Sacchi, G. Rossi, and P. Lacorre, "RNiO₃ perovskites (R = Pr, Nd): Nickel valence and the metal-insulator transition investigated by x-ray-absorption spectroscopy," *Phys. Rev. B*, vol. 46, pp. 14975–14984, Dec 1992.
- [37] J. L. García-Muñoz, J. Rodríguez-Carvajal, and P. Lacorre, "Sudden Appearance of an Unusual Spin Density Wave At the Metal-Insulator Transition in the Perovskites RNiO₃ (R = Pr, Nd)," *Europhysics Letters (EPL)*, vol. 20, pp. 241–247, oct 1992.
- [38] J. L. García-Muñoz, J. Rodríguez-Carvajal, and P. Lacorre, "Neutron-diffraction study of the magnetic ordering in the insulating regime of the perovskites RNiO₃ (R = PrandNd)," *Phys. Rev. B*, vol. 50, pp. 978–992, Jul 1994.

- [39] J. Rodriguez-Carvajal, S. Rosenkranz, M. Medarde, P. Lacorre, M. T. Fernandez-Diaz, F. Fauth, and V. Trounov, "Neutron diffraction study of the magnetic and orbital ordering in ¹⁵⁴SmNiO₃ and ¹⁵³EuNiO₃," *Phys. Rev. B*, vol. 57, pp. 456–464, Jan 1998.
- [40] J. B. Goodenough and P. M. Raccah, "Complex vs Band Formation in Perovskite Oxides," *Journal of Applied Physics*, vol. 36, no. 3, pp. 1031–1032, 1965.
- [41] W. Koehler and E. Wollan, "Neutron-diffraction study of the magnetic properties of perovskite-like compounds LaBO₃," *Journal of Physics and Chemistry of Solids*, vol. 2, no. 2, pp. 100–106, 1957.
- [42] J. A. Alonso, A. Muñoz, A. Largeteau, and G. Demazeau, "Crystal growth of NdNiO₃ perovskite under high oxygen pressure," *Journal of Physics: Condensed Matter*, vol. 16, pp. S1277–S1281, mar 2004.
- [43] H. Guo, Z. W. Li, L. Zhao, Z. Hu, C. F. Chang, C.-Y. Kuo, W. Schmidt, A. Piovano, T. W. Pi, O. Sobolev, D. I. Khomskii, L. H. Tjeng, and A. C. Komarek, "Antiferromagnetic correlations in the metallic strongly correlated transition metal oxide LaNiO₃," *Nature Communications*, vol. 9, p. 43, Jan 2018.
- [44] J. Zhang, H. Zheng, Y. Ren, and J. F. Mitchell, "High-Pressure Floating-Zone Growth of Perovskite Nickelate LaNiO₃ Single Crystals," *Crystal Growth & Design*, vol. 17, pp. 2730–2735, May 2017.
- [45] T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, "Spin and charge ordering in self-doped Mott insulators," *Phys. Rev. B*, vol. 61, pp. 11263–11266, May 2000.
- [46] S. Johnston, A. Mukherjee, I. Elfimov, M. Berciu, and G. A. Sawatzky, "Charge Disproportionation without Charge Transfer in the Rare-Earth-Element Nickelates as a Possible Mechanism for the Metal-Insulator Transition," *Phys. Rev. Lett.*, vol. 112, p. 106404, Mar 2014.
- [47] V. Bisogni, S. Catalano, R. J. Green, M. Gibert, R. Scherwitzl, Y. Huang, V. N. Strocov, P. Zubko, S. Balandeh, J.-M. Triscone, G. Sawatzky, and T. Schmitt, "Ground-state oxygen holes and the metal-insulator transition in the negative charge-transfer rare-earth nickelates," *Nature Communications*, vol. 7, p. 13017, Oct 2016.
- [48] R. Eguchi, A. Chainani, M. Taguchi, M. Matsunami, Y. Ishida, K. Horiba, Y. Senba, H. Ohashi, and S. Shin, "Fermi surfaces, electron-hole asymmetry, and correlation kink in a three-dimensional Fermi liquid LaNiO₃," *Phys. Rev. B*, vol. 79, p. 115122, Mar 2009.
- [49] P. D. C. King, H. I. Wei, Y. F. Nie, M. Uchida, C. Adamo, S. Zhu, X. He, I. Božović, D. G. Schlom, and K. M. Shen, "Atomic-scale control of competing electronic phases in ultrathin LaNiO₃," *Nature Nanotechnology*, vol. 9, pp. 443–447, Jun 2014.
- [50] R. S. Dhaka, T. Das, N. C. Plumb, Z. Ristic, W. Kong, C. E. Matt, N. Xu, K. Dolui, E. Razzoli, M. Medarde, L. Patthey, M. Shi, M. Radović, and J. Mesot, "Tuning the metal-insulator transition in NdNiO₃ heterostructures via Fermi surface instability and spin fluctuations," *Phys. Rev. B*, vol. 92, p. 035127, Jul 2015.

- [51] N. Gayathri, A. K. Raychaudhuri, X. Q. Xu, J. L. Peng, and R. L. Greene, "Electronic conduction in LaNiO_{3- δ}: the dependence on the oxygen stoichiometry δ ," *Journal of Physics: Condensed Matter*, vol. 10, pp. 1323–1338, feb 1998.
- [52] R. Scherwitzl, P. Zubko, I. G. Lezama, S. Ono, A. F. Morpurgo, G. Catalan, and J.-M. Triscone, "Electric-Field Control of the Metal-Insulator Transition in Ultrathin NdNiO₃ Films," *Advanced Materials*, vol. 22, no. 48, pp. 5517–5520, 2010.
- [53] J. Son, P. Moetakef, J. M. LeBeau, D. Ouellette, L. Balents, S. J. Allen, and S. Stemmer, "Low-dimensional Mott material: Transport in ultrathin epitaxial LaNiO₃ films," *Applied Physics Letters*, vol. 96, no. 6, p. 062114, 2010.
- [54] J. Son, B. Jalan, A. P. Kajdos, L. Balents, S. J. Allen, and S. Stemmer, "Probing the metal-insulator transition of NdNiO₃ by electrostatic doping," *Applied Physics Letters*, vol. 99, no. 19, p. 192107, 2011.
- [55] S. D. H., R. Jaramillo, D. M. Silevitch, F. Schoofs, K. Kerman, J. D. Baniecki, and S. Ramanathan, "Hall effect measurements on epitaxial SmNiO₃ thin films and implications for antiferromagnetism," *Phys. Rev. B*, vol. 87, p. 125150, Mar 2013.
- [56] V. Scagnoli, U. Staub, A. M. Mulders, M. Janousch, G. I. Meijer, G. Hammerl, J. M. Tonnerre, and N. Stojic, "Role of magnetic and orbital ordering at the metalinsulator transition in NdNiO₃," *Phys. Rev. B*, vol. 73, p. 100409, Mar 2006.
- [57] I. I. Mazin, D. I. Khomskii, R. Lengsdorf, J. A. Alonso, W. G. Marshall, R. M. Ibberson, A. Podlesnyak, M. J. Martínez-Lope, and M. M. Abd-Elmeguid, "Charge Ordering as Alternative to Jahn-Teller Distortion," *Phys. Rev. Lett.*, vol. 98, p. 176406, Apr 2007.
- [58] V. Scagnoli, U. Staub, Y. Bodenthin, M. García-Fernández, A. M. Mulders, G. I. Meijer, and G. Hammerl, "Induced noncollinear magnetic order of Nd³⁺ in NdNiO₃ observed by resonant soft x-ray diffraction," *Phys. Rev. B*, vol. 77, p. 115138, Mar 2008.
- [59] H. K. Yoo, S. I. Hyun, L. Moreschini, H.-D. Kim, Y. J. Chang, C. H. Sohn, D. W. Jeong, S. Sinn, Y. S. Kim, A. Bostwick, E. Rotenberg, J. H. Shim, and T. W. Noh, "Latent instabilities in metallic LaNiO₃ films by strain control of Fermi-surface topology," *Scientific Reports*, vol. 5, p. 8746, Mar 2015.
- [60] S. Catalano, M. Gibert, V. Bisogni, O. E. Peil, F. He, R. Sutarto, M. Viret, P. Zubko, R. Scherwitzl, A. Georges, G. A. Sawatzky, T. Schmitt, and J.-M. Triscone, "Electronic transitions in strained SmNiO₃ thin films," *APL Materials*, vol. 2, no. 11, p. 116110, 2014.
- [61] G. Catalan, R. M. Bowman, and J. M. Gregg, "Metal-insulator transitions in NdNiO₃ thin films," *Phys. Rev. B*, vol. 62, pp. 7892–7900, Sep 2000.
- [62] F. Conchon, A. Boulle, R. Guinebretière, C. Girardot, S. Pignard, J. Kreisel, F. Weiss, E. Dooryhée, and J.-L. Hodeau, "Effect of tensile and compressive strains on the transport properties of SmNiO₃ layers epitaxially grown on (001) SrTiO₃ and LaAlO₃ substrates," *Applied Physics Letters*, vol. 91, no. 19, p. 192110, 2007.

- [63] F. Conchon, A. Boulle, R. Guinebretière, E. Dooryhée, J.-L. Hodeau, C. Girardot, S. Pignard, J. Kreisel, and F. Weiss, "The role of strain-induced structural changes in the metal-insulator transition in epitaxial SmNiO₃ films," *Journal of Physics: Condensed Matter*, vol. 20, p. 145216, mar 2008.
- [64] J. Liu, M. Kargarian, M. Kareev, B. Gray, P. J. Ryan, A. Cruz, N. Tahir, Y.-D. Chuang, J. Guo, J. M. Rondinelli, J. W. Freeland, G. A. Fiete, and J. Chakhalian, "Heterointerface engineered electronic and magnetic phases of NdNiO₃ thin films," *Nature Communications*, vol. 4, p. 2714, Nov 2013.
- [65] D. Meyers, S. Middey, M. Kareev, M. van Veenendaal, E. J. Moon, B. A. Gray, J. Liu, J. W. Freeland, and J. Chakhalian, "Strain-modulated Mott transition in EuNiO₃ ultrathin films," *Phys. Rev. B*, vol. 88, p. 075116, Aug 2013.
- [66] F. Y. Bruno, K. Z. Rushchanskii, S. Valencia, Y. Dumont, C. Carrétéro, E. Jacquet, R. Abrudan, S. Blügel, M. Ležaić, M. Bibes, and A. Barthélémy, "Rationalizing strain engineering effects in rare-earth nickelates," *Phys. Rev. B*, vol. 88, p. 195108, Nov 2013.
- [67] P.-H. Xiang, N. Zhong, C.-G. Duan, X. D. Tang, Z. G. Hu, P. X. Yang, Z. Q. Zhu, and J. H. Chu, "Strain controlled metal-insulator transition in epitaxial NdNiO₃ thin films," *Journal of Applied Physics*, vol. 114, no. 24, p. 243713, 2013.
- [68] T. Liu, H. Wu, T. Jia, X. Zhang, Z. Zeng, H. Q. Lin, and X. G. Li, "Dimensionalityinduced insulator-metal crossover in layered nickelates $La_{n+1}Ni_nO_{2n+2}$ $(n = 2, 3, and \infty)$," *AIP Advances*, vol. 4, no. 4, p. 047132, 2014.
- [69] S. Catalano, M. Gibert, V. Bisogni, F. He, R. Sutarto, M. Viret, P. Zubko, R. Scherwitzl, G. A. Sawatzky, T. Schmitt, and J.-M. Triscone, "Tailoring the electronic transitions of NdNiO₃ films through (111)_{pc} oriented interfaces," *APL Materials*, vol. 3, no. 6, p. 062506, 2015.
- [70] J. Y. Zhang, H. Kim, E. Mikheev, A. J. Hauser, and S. Stemmer, "Key role of lattice symmetry in the metal-insulator transition of NdNiO₃ films," *Scientific Reports*, vol. 6, p. 23652, Apr 2016.
- [71] X. K. Lian, F. Chen, X. L. Tan, P. F. Chen, L. F. Wang, G. Y. Gao, S. W. Jin, and W. B. Wu, "Anisotropic-strain-controlled metal-insulator transition in epitaxial NdNiO₃ films grown on orthorhombic NdGaO₃ substrates," *Applied Physics Letters*, vol. 103, no. 17, p. 172110, 2013.
- [72] T. H. Kim, D. Puggioni, Y. Yuan, L. Xie, H. Zhou, N. Campbell, P. J. Ryan, Y. Choi, J.-W. Kim, J. R. Patzner, S. Ryu, J. P. Podkaminer, J. Irwin, Y. Ma, C. J. Fennie, M. S. Rzchowski, X. Q. Pan, V. Gopalan, J. M. Rondinelli, and C. B. Eom, "Polar metals by geometric design," *Nature*, vol. 533, pp. 68–72, May 2016.
- [73] S. Middey, D. Meyers, D. Doennig, M. Kareev, X. Liu, Y. Cao, Z. Yang, J. Shi, L. Gu, P. J. Ryan, R. Pentcheva, J. W. Freeland, and J. Chakhalian, "Mott Electrons in an Artificial Graphenelike Crystal of Rare-Earth Nickelate," *Phys. Rev. Lett.*, vol. 116, p. 056801, Feb 2016.

- [74] R. Scherwitzl, S. Gariglio, M. Gabay, P. Zubko, M. Gibert, and J.-M. Triscone, "Metal-Insulator Transition in Ultrathin LaNiO₃ Films," *Phys. Rev. Lett.*, vol. 106, p. 246403, Jun 2011.
- [75] M. Sakai, E.and Tamamitsu, K. Yoshimatsu, S. Okamoto, K. Horiba, M. Oshima, and H. Kumigashira, "Gradual localization of Ni 3d states in LaNiO₃ ultrathin films induced by dimensional crossover," *Phys. Rev. B*, vol. 87, p. 075132, Feb 2013.
- [76] D. P. Kumah, A. S. Disa, J. H. Ngai, H. Chen, A. Malashevich, J. W. Reiner, S. Ismail-Beigi, F. J. Walker, and C. H. Ahn, "Tuning the Structure of Nickelates to Achieve Two-Dimensional Electron Conduction," *Advanced Materials*, vol. 26, no. 12, pp. 1935–1940, 2014.
- [77] H. K. Yoo, S. I. Hyun, Y. J. Chang, L. Moreschini, C. H. Sohn, H.-D. Kim, A. Bostwick, E. Rotenberg, J. H. Shim, and T. W. Noh, "Thickness-dependent electronic structure in ultrathin LaNiO₃ films under tensile strain," *Phys. Rev. B*, vol. 93, p. 035141, Jan 2016.
- [78] J. Fowlie, M. Gibert, G. Tieri, A. Gloter, J. Íñiguez, A. Filippetti, S. Catalano, S. Gariglio, A. Schober, M. Guennou, J. Kreisel, O. Stéphan, and J.-M. Triscone, "Conductivity and Local Structure of LaNiO₃ Thin Films," *Advanced Materials*, vol. 29, no. 18, p. 1605197, 2017.
- [79] M. M. Kane, A. Vailionis, L. J. Riddiford, A. Mehta, A. T. N'Diaye, C. Klewe, P. Shafer, E. Arenholz, and Y. Suzuki, "Emergent long-range magnetic order in ultrathin (111)-oriented LaNiO₃ films," *npj Quantum Materials*, vol. 6, p. 44, May 2021.
- [80] T. Asaba, Z. Xiang, T. H. Kim, M. S. Rzchowski, C. B. Eom, and L. Li, "Unconventional ferromagnetism in epitaxial (111) LaNiO₃," *Phys. Rev. B*, vol. 98, p. 121105, Sep 2018.
- [81] S. J. May, T. S. Santos, and A. Bhattacharya, "Onset of metallic behavior in strained (LaNiO₃)_n/(SrMnO₃)₂ superlattices," *Phys. Rev. B*, vol. 79, p. 115127, Mar 2009.
- [82] J. Liu, S. Okamoto, M. van Veenendaal, M. Kareev, B. Gray, P. Ryan, J. W. Freeland, and J. Chakhalian, "Quantum confinement of Mott electrons in ultrathin LaNiO₃/LaAlO₃ superlattices," *Phys. Rev. B*, vol. 83, p. 161102, Apr 2011.
- [83] A. V. Boris, Y. Matiks, E. Benckiser, A. Frano, P. Popovich, V. Hinkov, P. Wochner, M. Castro-Colin, E. Detemple, V. K. Malik, C. Bernhard, T. Prokscha, A. Suter, Z. Salman, E. Morenzoni, G. Cristiani, H.-U. Habermeier, and B. Keimer, "Dimensionality Control of Electronic Phase Transitions in Nickel-Oxide Superlattices," *Science*, vol. 332, no. 6032, pp. 937–940, 2011.
- [84] A. Frano, E. Schierle, M. W. Haverkort, Y. Lu, M. Wu, S. Blanco-Canosa, U. Nwankwo, A. V. Boris, P. Wochner, G. Cristiani, H. U. Habermeier, G. Logvenov, V. Hinkov, E. Benckiser, E. Weschke, and B. Keimer, "Orbital Control of Noncollinear Magnetic Order in Nickel Oxide Heterostructures," *Phys. Rev. Lett.*, vol. 111, p. 106804, Sep 2013.

- [85] G. Berner, M. Sing, F. Pfaff, E. Benckiser, M. Wu, G. Christiani, G. Logvenov, H.-U. Habermeier, M. Kobayashi, V. N. Strocov, T. Schmitt, H. Fujiwara, S. Suga, A. Sekiyama, B. Keimer, and R. Claessen, "Dimensionality-tuned electronic structure of nickelate superlattices explored by soft-x-ray angle-resolved photoelectron spectroscopy," *Phys. Rev. B*, vol. 92, p. 125130, Sep 2015.
- [86] Y. Lu, Z. Zhong, M. W. Haverkort, and P. Hansmann, "Origins of bond and spin order in rare-earth nickelate bulk and heterostructures," *Phys. Rev. B*, vol. 95, p. 195117, May 2017.
- [87] J. r. Chaloupka and G. Khaliullin, "Orbital Order and Possible Superconductivity in LaNiO₃/LaMO₃ Superlattices," *Phys. Rev. Lett.*, vol. 100, p. 016404, Jan 2008.
- [88] P. Hansmann, X. Yang, A. Toschi, G. Khaliullin, O. K. Andersen, and K. Held, "Turning a Nickelate Fermi Surface into a Cupratelike One through Heterostructuring," *Phys. Rev. Lett.*, vol. 103, p. 016401, Jun 2009.
- [89] A. Jang, S. Seung, K. Choi, and J. Song, "Epitaxial growth and electrical transport property of artificial LaNiO₃/LaAlO₃ superlattices," *Ceramics International*, vol. 38, pp. S627–S630, 2012. The 7th Asian Meeting on Electroceramics (AMEC-7) in conjunction with the 7th Asian Meeting on Ferroelectricity (AMF-7).
- [90] J. W. Freeland, J. Liu, M. Kareev, B. Gray, J. W. Kim, P. Ryan, R. Pentcheva, and J. Chakhalian, "Orbital control in strained ultra-thin LaNiO₃/LaAlO₃ superlattices," *EPL (Europhysics Letters)*, vol. 96, p. 57004, nov 2011.
- [91] E. Benckiser, M. W. Haverkort, S. Brück, E. Goering, S. Macke, A. Frañó, X. Yang, O. K. Andersen, G. Cristiani, H.-U. Habermeier, A. V. Boris, I. Zegkinoglou, P. Wochner, H.-J. Kim, V. Hinkov, and B. Keimer, "Orbital reflectometry of oxide heterostructures," *Nature Materials*, vol. 10, pp. 189–193, Mar 2011.
- [92] M. Wu, E. Benckiser, M. W. Haverkort, A. Frano, Y. Lu, U. Nwankwo, S. Brück, P. Audehm, E. Goering, S. Macke, V. Hinkov, P. Wochner, G. Christiani, S. Heinze, G. Logvenov, H.-U. Habermeier, and B. Keimer, "Strain and composition dependence of orbital polarization in nickel oxide superlattices," *Phys. Rev. B*, vol. 88, p. 125124, Sep 2013.
- [93] H. Chen, D. P. Kumah, A. S. Disa, F. J. Walker, C. H. Ahn, and S. Ismail-Beigi, "Modifying the Electronic Orbitals of Nickelate Heterostructures via Structural Distortions," *Phys. Rev. Lett.*, vol. 110, p. 186402, May 2013.
- [94] A. S. Disa, D. P. Kumah, A. Malashevich, H. Chen, D. A. Arena, E. D. Specht, S. Ismail-Beigi, F. J. Walker, and C. H. Ahn, "Orbital Engineering in Symmetry-Breaking Polar Heterostructures," *Phys. Rev. Lett.*, vol. 114, p. 026801, Jan 2015.
- [95] M. Gibert, P. Zubko, R. Scherwitzl, J. Íñiguez, and J.-M. Triscone, "Exchange bias in LaNiO₃/LaMnO₃ superlattices," *Nature Materials*, vol. 11, pp. 195–198, Mar 2012.
- [96] M. Gibert, M. Viret, P. Zubko, N. Jaouen, J.-M. Tonnerre, A. Torres-Pardo, S. Catalano, A. Gloter, O. Stéphan, and J.-M. Triscone, "Interlayer coupling through a dimensionality-induced magnetic state," *Nature Communications*, vol. 7, p. 11227, Apr 2016.

- [97] J. C. Rojas Sánchez, B. Nelson-Cheeseman, M. Granada, E. Arenholz, and L. B. Steren, "Exchange-bias effect at La_{1-x}Sr_xMnO₃/LaNiO₃ interfaces," *Phys. Rev. B*, vol. 85, p. 094427, Mar 2012.
- [98] J. Hoffman, I. C. Tung, B. B. Nelson-Cheeseman, M. Liu, J. W. Freeland, and A. Bhattacharya, "Charge transfer and interfacial magnetism in (LaNiO₃)_n/(LaMnO₃)₂ superlattices," *Phys. Rev. B*, vol. 88, p. 144411, Oct 2013.
- [99] J. D. Hoffman, B. J. Kirby, J. Kwon, G. Fabbris, D. Meyers, J. W. Freeland, I. Martin, O. G. Heinonen, P. Steadman, H. Zhou, C. M. Schlepütz, M. P. M. Dean, S. G. E. te Velthuis, J.-M. Zuo, and A. Bhattacharya, "Oscillatory Noncollinear Magnetism Induced by Interfacial Charge Transfer in Superlattices Composed of Metallic Oxides," *Phys. Rev. X*, vol. 6, p. 041038, Nov 2016.
- [100] A. J. Grutter, H. Yang, B. J. Kirby, M. R. Fitzsimmons, J. A. Aguiar, N. D. Browning, C. A. Jenkins, E. Arenholz, V. V. Mehta, U. S. Alaan, and Y. Suzuki, "Interfacial Ferromagnetism in LaNiO₃/CaMnO₃ Superlattices," *Phys. Rev. Lett.*, vol. 111, p. 087202, Aug 2013.
- [101] C. Piamonteze, M. Gibert, J. Heidler, J. Dreiser, S. Rusponi, H. Brune, J.-M. Triscone, F. Nolting, and U. Staub, "Interfacial properties of LaMnO₃/LaNiO₃ superlattices grown along (001) and (111) orientations," *Phys. Rev. B*, vol. 92, p. 014426, Jul 2015.
- [102] P. Di Pietro, J. Hoffman, A. Bhattacharya, S. Lupi, and A. Perucchi, "Spectral Weight Redistribution in (LaNiO₃)_n/(LaMnO₃)₂ Superlattices from Optical Spectroscopy," *Phys. Rev. Lett.*, vol. 114, p. 156801, Apr 2015.
- [103] M. N. Grisolia, J. Varignon, G. Sanchez-Santolino, A. Arora, S. Valencia, M. Varela, R. Abrudan, E. Weschke, E. Schierle, J. E. Rault, J.-P. Rueff, A. Barthélémy, J. Santamaria, and M. Bibes, "Hybridization-controlled charge transfer and induced magnetism at correlated oxide interfaces," *Nature Physics*, vol. 12, pp. 484–492, May 2016.
- [104] M. Hepting, M. Minola, A. Frano, G. Cristiani, G. Logvenov, E. Schierle, M. Wu, M. Bluschke, E. Weschke, H.-U. Habermeier, E. Benckiser, M. Le Tacon, and B. Keimer, "Tunable Charge and Spin Order in PrNiO₃ Thin Films and Superlattices," *Phys. Rev. Lett.*, vol. 113, p. 227206, Nov 2014.
- [105] G. Catalan, "Progress in perovskite nickelate research," *Phase Transitions*, vol. 81, no. 7-8, pp. 729–749, 2008.
- [106] P. Monthoux, A. V. Balatsky, and D. Pines, "Weak-coupling theory of hightemperature superconductivity in the antiferromagnetically correlated copper oxides," *Phys. Rev. B*, vol. 46, pp. 14803–14817, Dec 1992.
- [107] S. Chakravarty, A. Sudbo, P. W. Anderson, and S. Strong, "Interlayer Tunneling and Gap Anisotropy in High-Temperature Superconductors," *Science*, vol. 261, no. 5119, pp. 337–340, 1993.
- [108] Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, "Iron-Based Layered Superconductor: LaOFeP," *Journal of the Ameri*can Chemical Society, vol. 128, no. 31, pp. 10012–10013, 2006. PMID: 16881620.

- [109] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, "Iron-Based Layered Superconductor La[O_{1-x}F_x]FeAs (x = 0.05 0.12) with T_c = 26 K," Journal of the American Chemical Society, vol. 130, no. 11, pp. 3296–3297, 2008. PMID: 18293989.
- [110] D. Li, K. Lee, B. Y. Wang, M. Osada, S. Crossley, H. R. Lee, Y. Cui, Y. Hikita, and H. Y. Hwang, "Superconductivity in an infinite-layer nickelate," *Nature*, vol. 572, pp. 624–627, Aug 2019.
- [111] V. I. Anisimov, D. Bukhvalov, and T. M. Rice, "Electronic structure of possible nickelate analogs to the cuprates," *Phys. Rev. B*, vol. 59, pp. 7901–7906, Mar 1999.
- [112] V. V. Poltavets, M. Greenblatt, G. H. Fecher, and C. Felser, "Electronic Properties, Band Structure, and Fermi Surface Instabilities of Ni¹⁺/Ni²⁺ Nickelate La₃Ni₂O₆, Isoelectronic with Superconducting Cuprates," *Phys. Rev. Lett.*, vol. 102, p. 046405, Jan 2009.
- [113] V. V. Poltavets, K. A. Lokshin, A. H. Nevidomskyy, M. Croft, T. A. Tyson, J. Hadermann, G. Van Tendeloo, T. Egami, G. Kotliar, N. ApRoberts-Warren, A. P. Dioguardi, N. J. Curro, and M. Greenblatt, "Bulk Magnetic Order in a Two-Dimensional Ni¹⁺/Ni²⁺ (d⁹/d⁸) Nickelate, Isoelectronic with Superconducting Cuprates," *Phys. Rev. Lett.*, vol. 104, p. 206403, May 2010.
- [114] J. Zhang, A. S. Botana, J. W. Freeland, D. Phelan, H. Zheng, V. Pardo, M. R. Norman, and J. F. Mitchell, "Large orbital polarization in a metallic square-planar nickelate," *Nature Physics*, vol. 13, pp. 864–869, Sep 2017.
- [115] G. A. Pan, D. Ferenc Segedin, H. LaBollita, Q. Song, E. M. Nica, B. H. Goodge, A. T. Pierce, S. Doyle, S. Novakov, D. Córdova Carrizales, A. T. N'Diaye, P. Shafer, H. Paik, J. T. Heron, J. A. Mason, A. Yacoby, L. F. Kourkoutis, O. Erten, C. M. Brooks, A. S. Botana, and J. A. Mundy, "Superconductivity in a quintuple-layer square-planar nickelate," *Nature Materials*, vol. 21, pp. 160–164, Feb 2022.
- [116] F. Wrobel, A. F. Mark, G. Christiani, W. Sigle, H.-U. Habermeier, P. A. van Aken, G. Logvenov, B. Keimer, and E. Benckiser, "Comparative study of LaNiO₃/LaAlO₃ heterostructures grown by pulsed laser deposition and oxide molecular beam epitaxy," *Applied Physics Letters*, vol. 110, no. 4, p. 041606, 2017.
- [117] K.-W. Lee and W. E. Pickett, "Infinite-layer LaNiO₂: Ni¹⁺ is not Cu²⁺," *Phys. Rev.* B, vol. 70, p. 165109, Oct 2004.
- [118] M. Crespin, P. Levitz, and L. Gatineau, "Reduced forms of LaNiO₃ perovskite. Part 1.- Evidence for new phases: La₂Ni₂O₅ and LaNiO₂," J. Chem. Soc., Faraday Trans. 2, vol. 79, pp. 1181–1194, 1983.
- [119] M. A. Hayward, M. A. Green, M. J. Rosseinsky, and J. Sloan, "Sodium Hydride as a Powerful Reducing Agent for Topotactic Oxide Deintercalation Synthesis and Characterization of the Nickel(I) Oxide LaNiO₂," *Journal of the American Chemical Society*, vol. 121, no. 38, pp. 8843–8854, 1999.
- [120] M. Crespin, O. Isnard, F. Dubois, J. Choisnet, and P. Odier, "LaNiO₂: Synthesis and structural characterization," *Journal of Solid State Chemistry*, vol. 178, no. 4, pp. 1326 – 1334, 2005.

- [121] M. A. Hayward and M. J. Rosseinsky, "Synthesis of the infinite layer Ni(I) phase NdNiO_{2+x} by low temperature reduction of NdNiO₃ with sodium hydride," *Solid State Sciences*, vol. 5, no. 6, pp. 839 – 850, 2003. International Conference on Inorganic Materials 2002.
- [122] M. Kawai, S. Inoue, M. Mizumaki, N. Kawamura, N. Ichikawa, and Y. Shimakawa, "Reversible changes of epitaxial thin films from perovskite LaNiO₃ to infinite-layer structure LaNiO₂," *Applied Physics Letters*, vol. 94, no. 8, p. 082102, 2009.
- [123] M. Kawai, K. Matsumoto, N. Ichikawa, M. Mizumaki, O. Sakata, N. Kawamura, S. Kimura, and Y. Shimakawa, "Orientation Change of an Infinite-Layer Structure LaNiO₂ Epitaxial Thin Film by Annealing with CaH₂," *Crystal Growth & Design*, vol. 10, pp. 2044–2046, May 2010.
- [124] D. Kaneko, K. Yamagishi, A. Tsukada, T. Manabe, and M. Naito, "Synthesis of infinite-layer LaNiO₂ films by metal organic decomposition," *Physica C: Superconductivity*, vol. 469, no. 15, pp. 936–939, 2009. Proceedings of the 21st International Symposium on Superconductivity (ISS 2008).
- [125] A. Ikeda, T. Manabe, and M. Naito, "Improved conductivity of infinite-layer LaNiO₂ thin films by metal organic decomposition," *Physica C: Superconductivity*, vol. 495, pp. 134–140, 2013.
- [126] D. Li, B. Y. Wang, K. Lee, S. P. Harvey, M. Osada, B. H. Goodge, L. F. Kourkoutis, and H. Y. Hwang, "Superconducting Dome in Nd_{1-x}Sr_xNiO₂ Infinite Layer Films," *Phys. Rev. Lett.*, vol. 125, p. 027001, Jul 2020.
- [127] S. Zeng, C. S. Tang, X. Yin, C. Li, M. Li, Z. Huang, J. Hu, W. Liu, G. J. Omar, H. Jani, Z. S. Lim, K. Han, D. Wan, P. Yang, S. J. Pennycook, A. T. S. Wee, and A. Ariando, "Phase Diagram and Superconducting Dome of Infinite-Layer Nd_{1-x}Sr_xNiO₂ Thin Films," *Phys. Rev. Lett.*, vol. 125, p. 147003, Oct 2020.
- [128] M. Hepting, D. Li, C. J. Jia, H. Lu, E. Paris, Y. Tseng, X. Feng, M. Osada, E. Been, Y. Hikita, Y.-D. Chuang, Z. Hussain, K. J. Zhou, A. Nag, M. Garcia-Fernandez, M. Rossi, H. Y. Huang, D. J. Huang, Z. X. Shen, T. Schmitt, H. Y. Hwang, B. Moritz, J. Zaanen, T. P. Devereaux, and W. S. Lee, "Electronic structure of the parent compound of superconducting infinite-layer nickelates," *Nature Materials*, vol. 19, pp. 381–385, Apr 2020.
- [129] Q. Gu, Y. Li, S. Wan, H. Li, W. Guo, H. Yang, Q. Li, X. Zhu, X. Pan, Y. Nie, and H.-H. Wen, "Single particle tunneling spectrum of superconducting Nd_{1-x}Sr_xNiO₂ thin films," *Nature Communications*, vol. 11, p. 6027, Nov 2020.
- [130] Q. Gao, Y. Zhao, X.-J. Zhou, and Z. Zhu, "Preparation of Superconducting Thin Films of Infinite-Layer Nickelate Nd_{0.8}Sr_{0.2}NiO₂," *Chinese Physics Letters*, vol. 38, p. 077401, jul 2021.
- [131] X.-R. Zhou, Z.-X. Feng, P.-X. Qin, H. Yan, X.-N. Wang, P. Nie, H.-J. Wu, X. Zhang, H.-Y. Chen, Z.-A. Meng, Z.-W. Zhu, and Z.-Q. Liu, "Negligible oxygen vacancies, low critical current density, electric-field modulation, in-plane anisotropic and highfield transport of a superconducting Nd_{0.8}Sr_{0.2}NiO₂/SrTiO₃ heterostructure," *Rare Metals*, vol. 40, pp. 2847–2854, Oct 2021.

- [132] Q. Li, C. He, J. Si, X. Zhu, Y. Zhang, and H.-H. Wen, "Absence of superconductivity in bulk Nd_{1-x}Sr_xNiO₂," *Communications Materials*, vol. 1, p. 16, Apr 2020.
- [133] B.-X. Wang, H. Zheng, E. Krivyakina, O. Chmaissem, P. P. Lopes, J. W. Lynn, L. C. Gallington, Y. Ren, S. Rosenkranz, J. F. Mitchell, and D. Phelan, "Synthesis and characterization of bulk Nd_{1-x}Sr_xNiO₂ and Nd_{1-x}Sr_xNiO₃," *Phys. Rev. Materials*, vol. 4, p. 084409, Aug 2020.
- [134] P. Puphal, Y.-M. Wu, K. Fürsich, H. Lee, M. Pakdaman, J. A. N. Bruin, J. Nuss, Y. E. Suyolcu, P. A. van Aken, B. Keimer, M. Isobe, and M. Hepting, "Topotactic transformation of single crystals: From perovskite to infinite-layer nickelates," *Science Advances*, vol. 7, no. 49, p. eabl8091, 2021.
- [135] M. Osada, B. Y. Wang, K. Lee, D. Li, and H. Y. Hwang, "Phase diagram of infinite layer praseodymium nickelate Pr_{1-x}Sr_xNiO₂ thin films," *Phys. Rev. Materials*, vol. 4, p. 121801, Dec 2020.
- [136] S. Zeng, C. Li, L. E. Chow, Y. Cao, Z. Zhang, C. S. Tang, X. Yin, Z. S. Lim, J. Hu, P. Yang, and A. Ariando, "Superconductivity in infinite-layer nickelate La_{1-x}Ca_xNiO₂ thin films," *Science Advances*, vol. 8, no. 7, p. eabl9927, 2022.
- [137] M. Rossi, H. Lu, A. Nag, D. Li, M. Osada, K. Lee, B. Y. Wang, S. Agrestini, M. Garcia-Fernandez, J. J. Kas, Y.-D. Chuang, Z. X. Shen, H. Y. Hwang, B. Moritz, K.-J. Zhou, T. P. Devereaux, and W. S. Lee, "Orbital and spin character of doped carriers in infinite-layer nickelates," *Phys. Rev. B*, vol. 104, p. L220505, Dec 2021.
- [138] Y. Cui, C. Li, Q. Li, X. Zhu, Z. Hu, Y. feng Yang, J. Zhang, R. Yu, H.-H. Wen, and W. Yu, "NMR Evidence of Antiferromagnetic Spin Fluctuations in Nd_{0.85}Sr_{0.15}NiO₂," *Chinese Physics Letters*, vol. 38, p. 067401, jun 2021.
- [139] H. Lu, M. Rossi, A. Nag, M. Osada, D. F. Li, K. Lee, B. Y. Wang, M. Garcia-Fernandez, S. Agrestini, Z. X. Shen, E. M. Been, B. Moritz, T. P. Devereaux, J. Zaanen, H. Y. Hwang, K.-J. Zhou, and W. S. Lee, "Magnetic excitations in infinite-layer nickelates," *Science*, vol. 373, no. 6551, pp. 213–216, 2021.
- [140] A. S. Botana and M. R. Norman, "Similarities and Differences between LaNiO₂ and CaCuO₂ and Implications for Superconductivity," *Phys. Rev. X*, vol. 10, p. 011024, Feb 2020.
- [141] H. Sakakibara, H. Usui, K. Suzuki, T. Kotani, H. Aoki, and K. Kuroki, "Model Construction and a Possibility of Cupratelike Pairing in a New d⁹ Nickelate Superconductor (Nd, Sr)NiO₂," *Phys. Rev. Lett.*, vol. 125, p. 077003, Aug 2020.
- [142] X. Wu, D. Di Sante, T. Schwemmer, W. Hanke, H. Y. Hwang, S. Raghu, and R. Thomale, "Robust $d_{x^2-y^2}$ -wave superconductivity of infinite-layer nickelates," *Phys. Rev. B*, vol. 101, p. 060504, Feb 2020.
- [143] P. Jiang, L. Si, Z. Liao, and Z. Zhong, "Electronic structure of rare-earth infinitelayer RNiO₂ (R = La, Nd)," *Phys. Rev. B*, vol. 100, p. 201106, Nov 2019.
- [144] J. Gao, S. Peng, Z. Wang, C. Fang, and H. Weng, "Electronic structures and topological properties in nickelates Ln_{n+1}Ni_nO_{2n+2}," *National Science Review*, vol. 8, 09 2020. nwaa218.

- [145] E. Been, W.-S. Lee, H. Y. Hwang, Y. Cui, J. Zaanen, T. Devereaux, B. Moritz, and C. Jia, "Electronic Structure Trends Across the Rare-Earth Series in Superconducting Infinite-Layer Nickelates," *Phys. Rev. X*, vol. 11, p. 011050, Mar 2021.
- [146] F. Bernardini, V. Olevano, and A. Cano, "Magnetic penetration depth and T_c in superconducting nickelates," *Phys. Rev. Research*, vol. 2, p. 013219, Feb 2020.
- [147] J. Kapeghian and A. S. Botana, "Electronic structure and magnetism in infinitelayer nickelates RNiO₂ (R = La – Lu)," *Phys. Rev. B*, vol. 102, p. 205130, Nov 2020.
- [148] J. Krishna, H. LaBollita, A. O. Fumega, V. Pardo, and A. S. Botana, "Effects of Sr doping on the electronic and spin-state properties of infinite-layer nickelates: Nature of holes," *Phys. Rev. B*, vol. 102, p. 224506, Dec 2020.
- [149] F. Petocchi, V. Christiansson, F. Nilsson, F. Aryasetiawan, and P. Werner, "Normal State of Nd_{1-x}Sr_xNiO₂ from Self-Consistent GW + EDMFT," *Phys. Rev. X*, vol. 10, p. 041047, Dec 2020.
- [150] M. Jiang, M. Berciu, and G. A. Sawatzky, "Critical Nature of the Ni Spin State in Doped NdNiO₂," *Phys. Rev. Lett.*, vol. 124, p. 207004, May 2020.
- [151] V. Olevano, F. Bernardini, X. Blase, and A. Cano, "Ab initio many-body GW correlations in the electronic structure of LaNiO₂," Phys. Rev. B, vol. 101, p. 161102, Apr 2020.
- [152] J. Karp, A. Hampel, M. Zingl, A. S. Botana, H. Park, M. R. Norman, and A. J. Millis, "Comparative many-body study of Pr₄Ni₃O₈ and NdNiO₂," *Phys. Rev. B*, vol. 102, p. 245130, Dec 2020.
- [153] Y. Wang, C.-J. Kang, H. Miao, and G. Kotliar, "Hund's metal physics: From SrNiO₂ to LaNiO₂," *Phys. Rev. B*, vol. 102, p. 161118, Oct 2020.
- [154] F. Lechermann, "Late transition metal oxides with infinite-layer structure: Nickelates versus cuprates," *Phys. Rev. B*, vol. 101, p. 081110, Feb 2020.
- [155] X. Wan, V. Ivanov, G. Resta, I. Leonov, and S. Y. Savrasov, "Exchange interactions and sensitivity of the Ni two-hole spin state to Hund's coupling in doped NdNiO₂," *Phys. Rev. B*, vol. 103, p. 075123, Feb 2021.
- [156] H. Zhang, L. Jin, S. Wang, B. Xi, X. Shi, F. Ye, and J.-W. Mei, "Effective Hamiltonian for nickelate oxides Nd_{1-x}Sr_xNiO₂," *Phys. Rev. Research*, vol. 2, p. 013214, Feb 2020.
- [157] Y. Gu, S. Zhu, X. Wang, J. Hu, and H. Chen, "A substantial hybridization between correlated Ni-d orbital and itinerant electrons in infinite-layer nickelates," *Communications Physics*, vol. 3, p. 84, May 2020.
- [158] Z. Liu, Z. Ren, W. Zhu, Z. Wang, and J. Yang, "Electronic and magnetic structure of infinite-layer NdNiO₂: trace of antiferromagnetic metal," *npj Quantum Materials*, vol. 5, p. 31, May 2020.

- [159] M.-Y. Choi, W. E. Pickett, and K.-W. Lee, "Fluctuation-frustrated flat band instabilities in NdNiO₂," *Phys. Rev. Research*, vol. 2, p. 033445, Sep 2020.
- [160] G.-M. Zhang, Y.-f. Yang, and F.-C. Zhang, "Self-doped Mott insulator for parent compounds of nickelate superconductors," *Phys. Rev. B*, vol. 101, p. 020501, Jan 2020.
- [161] Y. Nomura, M. Hirayama, T. Tadano, Y. Yoshimoto, K. Nakamura, and R. Arita, "Formation of a two-dimensional single - component correlated electron system and band engineering in the nickelate superconductor NdNiO₂," *Phys. Rev. B*, vol. 100, p. 205138, Nov 2019.
- [162] T. Zhou, Y. Gao, and Z. Wang, "Spin excitations in nickelate superconductors," Science China Physics, Mechanics & Astronomy, vol. 63, p. 287412, Jun 2020.
- [163] P. Adhikary, S. Bandyopadhyay, T. Das, I. Dasgupta, and T. Saha-Dasgupta, "Orbital-selective superconductivity in a two-band model of infinite-layer nickelates," *Phys. Rev. B*, vol. 102, p. 100501, Sep 2020.
- [164] M. Kitatani, L. Si, O. Janson, R. Arita, Z. Zhong, and K. Held, "Nickelate superconductors - a renaissance of the one-band Hubbard model," *npj Quantum Materials*, vol. 5, p. 59, Aug 2020.
- [165] P. Werner and S. Hoshino, "Nickelate superconductors: Multiorbital nature and spin freezing," *Phys. Rev. B*, vol. 101, p. 041104, Jan 2020.
- [166] F. Bernardini and A. Cano, "Stability and electronic properties of LaNiO₂/SrTiO₃ heterostructures," *Journal of Physics: Materials*, vol. 3, p. 03LT01, jul 2020.
- [167] B. Geisler and R. Pentcheva, "Fundamental difference in the electronic reconstruction of infinite-layer versus perovskite neodymium nickelate films on SrTiO₃ (001)," *Phys. Rev. B*, vol. 102, p. 020502, Jul 2020.
- [168] Y. Zhang, L.-F. Lin, W. Hu, A. Moreo, S. Dong, and E. Dagotto, "Similarities and differences between nickelate and cuprate films grown on a SrTiO₃ substrate," *Phys. Rev. B*, vol. 102, p. 195117, Nov 2020.
- [169] A. S. Botana, F. Bernardini, and A. Cano, "Nickelate Superconductors: An Ongoing Dialog between Theory and Experiments," *Journal of Experimental and Theoretical Physics*, vol. 132, pp. 618–627, Apr 2021.
- [170] Y. Ji, J. Liu, L. Li, and Z. Liao, "Superconductivity in infinite layer nickelates," *Journal of Applied Physics*, vol. 130, no. 6, p. 060901, 2021.
- [171] Qiangqiang Gu and Hai-Hu Wen, "Superconductivity in nickel-based 112 systems," *The Innovation*, vol. 3, no. 1, p. 100202, 2022.
- [172] M. A. Hayward and M. J. Rosseinsky, "Cool conditions for mobile ions," Nature, vol. 450, pp. 960–961, Dec 2007.
- [173] H. J. Kitchen, I. Saratovsky, and M. A. Hayward, "Topotactic reduction as a synthetic route for the preparation of low-dimensional Mn(II) oxide phases: The structure and magnetism of LaAMnO_{4-x} (A = Sr, Ba)," *Dalton Trans.*, vol. 39, pp. 6098– 6105, 2010.

- [174] C. Tassel and H. Kageyama, "Square planar coordinate iron oxides," Chem. Soc. Rev., vol. 41, pp. 2025–2035, 2012.
- [175] T. Yamamoto and H. Kageyama, "Hydride Reductions of Transition Metal Oxides," *Chemistry Letters*, vol. 42, no. 9, pp. 946–953, 2013.
- [176] D. P. Norton, Pulsed Laser Deposition of Complex Materials: Progress Toward Applications, ch. 1, pp. 1–31. John Wiley & Sons, Ltd, 2006.
- [177] J. A. Grant-Jacob, S. J. Beecher, H. Riris, A. W. Yu, D. P. Shepherd, R. W. Eason, and J. I. Mackenzie, "Dynamic control of refractive index during pulsed-laser-deposited waveguide growth," *Opt. Mater. Express*, vol. 7, pp. 4073–4081, Nov 2017.
- [178] J. A. Grant-Jacob, S. J. Beecher, J. J. Prentice, D. P. Shepherd, J. I. Mackenzie, and R. W. Eason, "Pulsed laser deposition of crystalline garnet waveguides at a growth rate of 20μm per hour," *Surface and Coatings Technology*, vol. 343, pp. 7–10, 2018. Selected papers of the "E-MRS 2017 - Symposium Q".
- [179] D. Preziosi, A. Sander, A. Barthélémy, and M. Bibes, "Reproducibility and offstoichiometry issues in nickelate thin films grown by pulsed laser deposition," *AIP Advances*, vol. 7, no. 1, p. 015210, 2017.
- [180] J. Lee, K. S. Choi, T. K. Lee, I.-S. Jeong, S. Kim, J. Song, C. W. Bark, J.-H. Lee, J. H. Jung, J. Lee, T. H. Kim, and S. Lee, "Non-stoichiometry-induced metal-toinsulator transition in nickelate thin films grown by pulsed laser deposition," *Current Applied Physics*, vol. 18, no. 12, pp. 1577–1582, 2018.
- [181] J. S. Choi, M. Sheeraz, J.-S. Bae, J. H. Lee, J. Lee, J. Lee, S. Lee, H. Jeen, Y. S. Oh, C. W. Ahn, and T. H. Kim, "Effect of Ceramic-Target Crystallinity on Metal-to-Insulator Transition of Epitaxial Rare-Earth Nickelate Films Grown by Pulsed Laser Deposition," ACS Applied Electronic Materials, vol. 1, pp. 1952–1958, Sep 2019.
- [182] J. Gopalakrishnan, "Low-temperature synthesis of novel metal oxides by topochemical reactions," Proc. Indian natn. Sci. Acad., vol. 52, no. 1, pp. 48–66, 1986.
- [183] V. Boldyrev, "Topochemistry and topochemical reactions," *Reactivity of Solids*, vol. 8, no. 3, pp. 231–246, 1990.
- [184] Y. Tsujimoto, C. Tassel, N. Hayashi, T. Watanabe, H. Kageyama, K. Yoshimura, M. Takano, M. Ceretti, C. Ritter, and W. Paulus, "Infinite-layer iron oxide with a square-planar coordination," *Nature*, vol. 450, pp. 1062–1065, Dec 2007.
- [185] T. Takamatsu, M. Kato, T. Noji, and Y. Koike, "Low-Temperature Synthesis of the Infinite-Layer Compound LaNiO₂ by Soft-Chemical Techniques," *Japanese Journal* of Applied Physics, vol. 49, p. 093101, sep 2010.
- [186] T. Takamatsu, M. Kato, T. Noji, and Y. Koike, "Low-temperature synthesis of the infinite-layer compound LaNiO₂ using CaH₂ as reductant," *Physica C: Superconductivity and its Applications*, vol. 470, pp. S764–S765, 2010. Proceedings of the 9th International Conference on Materials and Mechanisms of Superconductivity.

- [187] Y. Shimakawa, S. Inoue, M. Kawai, N. Ichikawa, M. Mizumaki, and N. Kawamura, "Single-Crystal Thin Films of SrFeO₂ and LaNiO₂ with Infinite-Layer Structures," *MRS Online Proceedings Library*, vol. 1148, p. 708, May 2009.
- [188] Y. Kobayashi, Z. Li, K. Hirai, C. Tassel, F. Loyer, N. Ichikawa, N. Abe, T. Yamamoto, Y. Shimakawa, K. Yoshimura, M. Takano, O. J. Hernandez, and H. Kageyama, "Gas phase contributions to topochemical hydride reduction reactions," *Journal of Solid State Chemistry*, vol. 207, pp. 190–193, 2013.
- [189] R. A. Ortiz, P. Puphal, M. Klett, F. Hotz, R. K. Kremer, H. Trepka, M. Hemmida, H.-A. K. von Nidda, M. Isobe, R. Khasanov, H. Luetkens, P. Hansmann, B. Keimer, T. Schäfer, and M. Hepting, "Magnetic correlations in infinite-layer nickelates: An experimental and theoretical multimethod study," *Phys. Rev. Research*, vol. 4, p. 023093, May 2022.
- [190] E. Dixon and M. A. Hayward, "The Topotactic Reduction of Sr₃Fe₂O₅Cl₂ Square Planar Fe(II) in an Extended Oxyhalide," *Inorganic Chemistry*, vol. 49, pp. 9649– 9654, Oct 2010.
- [191] M. Birkholz, Principles of X-ray Diffraction, ch. 1, pp. 1–40. John Wiley & Sons, Ltd, 2005.
- [192] D. M. J. Als-Nielsen, X-rays and their interaction with matter, ch. 1, pp. 1–28. John Wiley & Sons, Ltd, 2011.
- [193] P. P. Ewald, "Die Berechnung optischer und elektrostatischer Gitterpotentiale," Annalen der Physik, vol. 369, no. 3, pp. 253–287, 1921.
- [194] C. Cohen-Tannoudji, B. Claude Cohen-Tannoudji, P. Davies, B. Dui, D. Betts, B. Diu, F. Laloe, S. Hemley, N. Ostrowsky, D. Ostrowsky, et al., , year=1977Quantum Mechanics. A Wiley-interscience publication, Wiley, 1977.
- [195] A. M. Frano Pereira, Ordering phenomena in transition-metal-oxide heterostructures. Doctoral thesis, Technische Universität Berlin, Fakultät II - Mathematik und Naturwissenschaften, Berlin, 2014.
- [196] J. J. Sakurai and J. Napolitano, Modern Quantum Mechanics. Cambridge University Press, 2 ed., 2017.
- [197] M. Wu, E. Benckiser, P. Audehm, E. Goering, P. Wochner, G. Christiani, G. Logvenov, H.-U. Habermeier, and B. Keimer, "Orbital reflectometry of PrNiO₃/PrAlO₃ superlattices," *Phys. Rev. B*, vol. 91, p. 195130, May 2015.
- [198] M. Haverkort, Spin and orbital degrees of freedom in transition metal oxides and oxide thin films studied by soft x-ray absorption spectroscopy. PhD thesis, University of Cologne, 2005.
- [199] B. T. Thole and G. van der Laan, "Sum rules for magnetic dichroism in rare earth 4f photoemission," Phys. Rev. Lett., vol. 70, pp. 2499–2502, Apr 1993.
- [200] G. van der Laan, "Sum Rules and Fundamental Spectra of Magnetic X-Ray Dichroism in Crystal Field Symmetry," *Journal of the Physical Society of Japan*, vol. 63, no. 6, pp. 2393–2400, 1994.

- [201] M. J. Han, C. A. Marianetti, and A. J. Millis, "Chemical control of orbital polarization in artificially structured transition-metal oxides: La_2NiXO_6 (X = B, Al, Ga, In) from first principles," *Phys. Rev. B*, vol. 82, p. 134408, Oct 2010.
- [202] M. J. Han, X. Wang, C. A. Marianetti, and A. J. Millis, "Dynamical Mean-Field Theory of Nickelate Superlattices," *Phys. Rev. Lett.*, vol. 107, p. 206804, Nov 2011.
- [203] J. Kirz, D. Attwood, B. Henke, M. Howells, K. Kennedy, K.-J. Kim, J. Kortright, R. Perera, P. Pianetta, J. Riordan, J. Scofield, G. Stradling, A. Thompson, J. Underwood, D. Vaughan, G. Williams, and H. Winick, *X-ray Data Booklet*. Lawrence Berkeley National Laboratory, University of California, 2001.
- [204] M. Born, E. Wolf, A. B. Bhatia, P. C. Clemmow, D. Gabor, A. R. Stokes, A. M. Taylor, P. A. Wayman, and W. L. Wilcock, *Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light.* Cambridge University Press, 7 ed., 1999.
- [205] D. Zhao, H. Höchst, and D. L. Huber, "Dielectric tensor formulation of magnetic dichroism sum rules," *Journal of Applied Physics*, vol. 84, no. 5, pp. 2858–2860, 1998.
- [206] A. Nelson, "Co-refinement of multiple-contrast neutron/X-ray reflectivity data using MOTOFIT," Journal of Applied Crystallography, vol. 39, pp. 273–276, Apr 2006.
- [207] M. Björck and G. Andersson, "GenX: an extensible X-ray reflectivity refinement program utilizing differential evolution," Journal of Applied Crystallography, vol. 40, pp. 1174–1178, Dec 2007.
- [208] S. Macke, A. Radi, J. E. Hamann-Borrero, A. Verna, M. Bluschke, S. Brück, E. Goering, R. Sutarto, F. He, G. Cristiani, M. Wu, E. Benckiser, H.-U. Habermeier, G. Logvenov, N. Gauquelin, G. A. Botton, A. P. Kajdos, S. Stemmer, G. A. Sawatzky, M. W. Haverkort, B. Keimer, and V. Hinkov, "Element Specific Monolayer Depth Profiling," *Advanced Materials*, vol. 26, no. 38, pp. 6554–6559, 2014.
- [209] G. Vignaud and A. Gibaud, "*REFLEX*: a program for the analysis of specular X-ray and neutron reflectivity data," *Journal of Applied Crystallography*, vol. 52, pp. 201– 213, Feb 2019.
- [210] S. Macke and E. Goering, "Magnetic reflectometry of heterostructures," Journal of Physics: Condensed Matter, vol. 26, no. 36, p. 363201, 2014.
- [211] L. G. Parratt, "Surface Studies of Solids by Total Reflection of X-Rays," Phys. Rev., vol. 95, pp. 359–369, Jul 1954.
- [212] L. G. Parratt and C. F. Hempstead, "Anomalous Dispersion and Scattering of X-Rays," Phys. Rev., vol. 94, pp. 1593–1600, Jun 1954.
- [213] L. N. et P. Croce, "Caractérisation des surfaces par réflexion rasante de rayons X. Application à l'étude du polissage de quelques verres silicates," *Rev. Phys. Appl.*, vol. 15, pp. 761–779, 1980.
- [214] J. Zak, E. Moog, C. Liu, and S. Bader, "Universal approach to magneto-optics," *Journal of Magnetism and Magnetic Materials*, vol. 89, no. 1, pp. 107–123, 1990.

- [215] J. Zak, E. R. Moog, C. Liu, and S. D. Bader, "Magneto-optics of multilayers with arbitrary magnetization directions," *Phys. Rev. B*, vol. 43, pp. 6423–6429, Mar 1991.
- [216] B. Henke, E. Gullikson, and J. Davis, "X-Ray Interactions: Photoabsorption, Scattering, Transmission, and Reflection at E = 50-30,000 eV, Z = 1-92," Atomic Data and Nuclear Data Tables, vol. 54, no. 2, pp. 181–342, 1993.
- [217] C. T. Chantler, "Theoretical Form Factor, Attenuation, and Scattering Tabulation for Z=1-92 from E=1-10 eV to E=0.4-1.0 MeV," Journal of Physical and Chemical Reference Data, vol. 24, no. 1, pp. 71-643, 1995.
- [218] C. T. Chantler, "Detailed Tabulation of Atomic Form Factors, Photoelectric Absorption and Scattering Cross Section, and Mass Attenuation Coefficients in the Vicinity of Absorption Edges in the Soft X-Ray (Z=30–36, Z=60–89, E=0.1 keV–10 keV), Addressing Convergence Issues of Earlier Work," Journal of Physical and Chemical Reference Data, vol. 29, no. 4, pp. 597–1056, 2000.
- [219] P. Radhakrishnan, B. Geisler, K. Fürsich, D. Putzky, Y. Wang, S. E. Ilse, G. Christiani, G. Logvenov, P. Wochner, P. A. van Aken, E. Goering, R. Pentcheva, and E. Benckiser, "Orbital engineering in YVO₃ – LaAlO₃ superlattices," *Phys. Rev. B*, vol. 104, p. L121102, Sep 2021.
- [220] P. Willmott, Synchrotron Physics, ch. 3, pp. 51–106. John Wiley & Sons, Ltd, 2019.
- [221] BESSY, "Operation modes of an APPLE II type undulator." Accessed: 2022-04-30.
- [222] L. J. van der Pauw, "A method of measuring specific resistivity and Hall effect of discs of arbitrary shape," *Philips Research Reports*, vol. 13, pp. 1–9, February 1958.
- [223] L. J. van der Pauw, "A method of measuring the resistivity and Hall coefficient on lamellae of arbitrary shape," *Philips Technical Review*, vol. 20, pp. 220–224, February 1958.
- [224] G. Herranz, F. Sánchez, B. Martínez, J. Fontcuberta, M. V. García-Cuenca, C. Ferrater, M. Varela, and P. Levy, "Weak localization effects in some metallic perovskites," *The European Physical Journal B - Condensed Matter and Complex Systems*, vol. 40, pp. 439–444, Aug 2004.
- [225] W. Noun, B. Berini, Y. Dumont, P. R. Dahoo, and N. Keller, "Correlation between electrical and ellipsometric properties on high-quality epitaxial thin films of the conductive oxide LaNiO₃ on STO (001)," *Journal of Applied Physics*, vol. 102, no. 6, p. 063709, 2007.
- [226] D. Pontes, F. Pontes, M. A. P. da Silva, O. Berengue, A. Chiquito, and E. Longo, "Structural and electrical properties of LaNiO₃ thin films grown on (100) and (001) oriented SrLaAlO₄ substrates by chemical solution deposition method," *Ceramics International*, vol. 39, no. 7, pp. 8025–8034, 2013.
- [227] Y. Kumar, H. Bhatt, C. L. Prajapat, H. K. Poswal, S. Basu, and S. Singh, "Effect of structural disorder on transport properties of LaNiO₃ thin films," *Journal of Applied Physics*, vol. 124, no. 6, p. 065302, 2018.

- [228] C. Wang, C.-H. Chang, A. Huang, P.-C. Wang, P.-C. Wu, L. Yang, C. Xu, P. Pandey, M. Zeng, R. Böttger, H.-T. Jeng, Y.-J. Zeng, M. Helm, Y.-H. Chu, R. Ganesh, and S. Zhou, "Tunable disorder and localization in the rare-earth nickelates," *Phys. Rev. Materials*, vol. 3, p. 053801, May 2019.
- [229] V. Hien-Hoang, N.-K. Chung, and H.-J. Kim, "Electrical transport properties and Kondo effect in La_{1-x}Pr_xNiO_{3-δ} thin films," *Scientific Reports*, vol. 11, p. 5391, Mar 2021.
- [230] E. J. Moon, B. A. Gray, M. Kareev, J. Liu, S. G. Altendorf, F. Strigari, L. H. Tjeng, J. W. Freeland, and J. Chakhalian, "Strain-dependent transport properties of the ultra-thin correlated metal, LaNiO₃," *New Journal of Physics*, vol. 13, p. 073037, jul 2011.
- [231] Y. Li, W. Sun, J. Yang, X. Cai, W. Guo, Z. Gu, Y. Zhu, and Y. Nie, "Impact of Cation Stoichiometry on the Crystalline Structure and Superconductivity in Nickelates," *Frontiers in Physics*, vol. 9, 2021.
- [232] C. C. Tam, J. Choi, X. Ding, S. Agrestini, A. Nag, B. Huang, H. Luo, M. García-Fernández, L. Qiao, and K.-J. Zhou, "Charge density waves in infinite-layer NdNiO₂ nickelates," 2021.
- [233] W. Sun, Y. Li, R. Liu, J. Yang, J. Li, S. Yan, H. Sun, W. Guo, Z. Gu, Y. Deng, X. Wang, and Y. Nie, "Evidence for quasi-two-dimensional superconductivity in infinite-layer nickelates," 2022.
- [234] K. Lee, B. H. Goodge, D. Li, M. Osada, B. Y. Wang, Y. Cui, L. F. Kourkoutis, and H. Y. Hwang, "Aspects of the synthesis of thin film superconducting infinite-layer nickelates," *APL Materials*, vol. 8, no. 4, p. 041107, 2020.
- [235] M. Osada, B. Y. Wang, B. H. Goodge, S. P. Harvey, K. Lee, D. Li, L. F. Kourkoutis, and H. Y. Hwang, "Nickelate Superconductivity without Rare-Earth Magnetism: (La, Sr)NiO₂," *Advanced Materials*, vol. 33, no. 45, p. 2104083, 2021.
- [236] P. Levitz, M. Crespin, and L. Gatineau, "Reduced forms of LaNiO₃ perovskite. Part 2.—X-ray structure of LaNiO₂ and extended X-ray absorption fine structure study: local environment of monovalent nickel," J. Chem. Soc., Faraday Trans. 2, vol. 79, pp. 1195–1203, 1983.
- [237] T. Moriga, O. Usaka, I. Nakabayashi, T. Kinouchi, S. Kikkawa, and F. Kanamaru, "Characterization of oxygen-deficient phases appearing in reduction of the perovskite-type LaNiO₃ to LaNiO_{2.5}," *Solid State Ionics*, vol. 79, pp. 252–255, 1995. Proceedings of the 20th Commemorative Symposium on Solid State Ionics in Japan.
- [238] V. M. Katukuri, N. A. Bogdanov, O. Weser, J. van den Brink, and A. Alavi, "Electronic correlations and magnetic interactions in infinite-layer NdNiO₂," *Phys. Rev. B*, vol. 102, p. 241112, Dec 2020.
- [239] R. Zhang, C. Lane, B. Singh, J. Nokelainen, B. Barbiellini, R. S. Markiewicz, A. Bansil, and J. Sun, "Magnetic and *f*-electron effects in LaNiO₂ and NdNiO₂ nickelates with cuprate-like 3d_{x²-y²} band," Communications Physics, vol. 4, p. 118, Jun 2021.

- [240] Y. Nomura, T. Nomoto, M. Hirayama, and R. Arita, "Magnetic exchange coupling in cuprate-analog d⁹ nickelates," *Phys. Rev. Research*, vol. 2, p. 043144, Oct 2020.
- [241] B. Geisler and R. Pentcheva, "Correlated interface electron gas in infinite-layer nickelate versus cuprate films on SrTiO₃ (001)," *Phys. Rev. Research*, vol. 3, p. 013261, Mar 2021.
- [242] C. Lane and J.-X. Zhu, "Landscape of coexisting excitonic states in the insulating single-layer cuprates and nickelates," *Phys. Rev. B*, vol. 101, p. 155135, Apr 2020.
- [243] M. Jiang, "Relevance of 3d multiplet structure in nickelate and cuprate superconductors," *Chinese Physics B*, vol. 30, p. 107103, oct 2021.
- [244] J. Q. Lin, P. Villar Arribi, G. Fabbris, A. S. Botana, D. Meyers, H. Miao, Y. Shen, D. G. Mazzone, J. Feng, S. G. Chiuzbăian, A. Nag, A. C. Walters, M. García-Fernández, K.-J. Zhou, J. Pelliciari, I. Jarrige, J. W. Freeland, J. Zhang, J. F. Mitchell, V. Bisogni, X. Liu, M. R. Norman, and M. P. M. Dean, "Strong Superexchange in a d^{9-δ} Nickelate Revealed by Resonant Inelastic X-Ray Scattering," Phys. Rev. Lett., vol. 126, p. 087001, Feb 2021.
- [245] G. A. Sawatzky, "Superconductivity seen in a non-magnetic nickel oxide," Nature, vol. 572, p. 241112, Aug 2019.
- [246] J. Alonso, M. Martínez-Lope, J. García-Muñoz, and M. Fernández, "Crystal structure and magnetism in the defect perovskite LaNiO_{2.5}," *Physica B: Condensed Matter*, vol. 234-236, pp. 18–19, 1997. Proceedings of the First European Conference on Neutron Scattering.
- [247] X. Liao, V. Singh, and H. Park, "Oxygen vacancy induced site-selective Mott transition in LaNiO₃," *Phys. Rev. B*, vol. 103, p. 085110, Feb 2021.
- [248] K. Matsumoto, M. Haruta, M. Kawai, A. Sakaiguchi, N. Ichikawa, H. Kurata, and Y. Shimakawa, "Selective reduction of layers at low temperature in artificial superlattice thin films," *Scientific Reports*, vol. 1, p. 27, Jun 2011.
- [249] G. Balestrino, S. Martellucci, P. G. Medaglia, A. Paoletti, G. Petrocelli, and A. A. Varlamov, "Dependence of the critical temperature on n in (BaCuO₂)₂/(CaCuO₂)_n superlattices," *Phys. Rev. B*, vol. 58, pp. R8925–R8928, Oct 1998.
- [250] D. Di Castro, M. Salvato, A. Tebano, D. Innocenti, C. Aruta, W. Prellier, O. I. Lebedev, I. Ottaviani, N. B. Brookes, M. Minola, M. Moretti Sala, C. Mazzoli, P. G. Medaglia, G. Ghiringhelli, L. Braicovich, M. Cirillo, and G. Balestrino, "Occurrence of a high-temperature superconducting phase in (CaCuO₂)_n/(SrTiO₃)_m superlattices," *Phys. Rev. B*, vol. 86, p. 134524, Oct 2012.
- [251] A. Ikeda, Y. Krockenberger, Y. Taniyasu, and H. Yamamoto, "Designing Superlattices of Cuprates and Ferrites for Superconductivity," ACS Applied Electronic Materials, Jun 2022.
- [252] M. Bluschke, A. Frano, E. Schierle, M. Minola, M. Hepting, G. Christiani, G. Logvenov, E. Weschke, E. Benckiser, and B. Keimer, "Transfer of Magnetic Order and Anisotropy through Epitaxial Integration of 3d and 4f Spin Systems," *Phys. Rev. Lett.*, vol. 118, p. 207203, May 2017.

- [253] C. Ji, G. Wu, S. Yang, G. Wu, and X. Yang, "Completely polarized e_g orbitals realized in $d^7 \text{Ni}^{3+}$ based heterointerface," *Phys. Rev. Materials*, vol. 4, p. 124804, Dec 2020.
- [254] R. A. Ortiz, "Selective layer reduction of nickel oxide superlattices," Master's thesis, University of Stuttgart, november 2017.
- [255] P. Ganguly and N. Vasanthacharya, "Infrared and Mössbauer spectroscopic study of the metal-insulator transition in some oxides of perovskite structure," *Journal of Solid State Chemistry*, vol. 61, no. 2, pp. 164–170, 1986.
- [256] J. Clark, P. Richter, and L. Toit, "High-pressure synthesis of YScO₃, HoScO₃, ErScO₃ and TmScO₃ and a reevaluation of the lattice constants of the rare earth scandates," *Journal of Solid State Chemistry*, vol. 23, no. 1, pp. 129–134, 1978.
- [257] R. P. Liferovich and R. H. Mitchell, "A structural study of ternary lanthanide orthoscandate perovskites," *Journal of Solid State Chemistry*, vol. 177, no. 6, pp. 2188–2197, 2004.
- [258] B. Veličkov, V. Kahlenberg, R. Bertram, and M. Bernhagen, "Crystal chemistry of GdScO₃, DyScO₃, SmScO₃ and NdScO₃," *Zeitschrift für Kristallographie*, vol. 222, no. 9, pp. 466–473, 2007.
- [259] A. Biswas, C.-H. Yang, R. Ramesh, and Y. H. Jeong, "Atomically flat single terminated oxide substrate surfaces," *Progress in Surface Science*, vol. 92, no. 2, pp. 117– 141, 2017.
- [260] E. E. Fullerton, I. K. Schuller, H. Vanderstraeten, and Y. Bruynseraede, "Structural refinement of superlattices from x-ray diffraction," *Phys. Rev. B*, vol. 45, pp. 9292– 9310, Apr 1992.
- [261] Y. Kumar, R. J. Choudhary, A. P. Singh, G. Anjum, and R. Kumar, "Evidence of quantum correction to conductivity in strained epitaxial LaNiO₃ films," *Journal of Applied Physics*, vol. 108, no. 8, p. 083706, 2010.
- [262] Y.-f. Yang and G.-M. Zhang, "Self-Doping and the Mott-Kondo Scenario for Infinite-Layer Nickelate Superconductors," *Frontiers in Physics*, vol. 9, 2022.
- [263] G. Herranz, F. Sánchez, J. Fontcuberta, V. Laukhin, J. Galibert, M. V. García-Cuenca, C. Ferrater, and M. Varela, "Magnetic field effect on quantum corrections to the low-temperature conductivity in metallic perovskite oxides," *Phys. Rev. B*, vol. 72, p. 014457, Jul 2005.
- [264] N. F. Mott, "Conduction in non-crystalline materials," The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics, vol. 19, no. 160, pp. 835–852, 1969.
- [265] T. Onozuka, A. Chikamatsu, T. Katayama, T. Fukumura, and T. Hasegawa, "Formation of defect-fluorite structured NdNiO_xH_y epitaxial thin films via a soft chemical route from NdNiO₃ precursors," *Dalton Trans.*, vol. 45, pp. 12114–12118, 2016.

- [266] T. Moriga, O. Usaka, I. Nakabayashi, Y. Hirashima, T. Kohno, S. Kikkawa, and F. Kanamaru, "Reduction of the perovskite-type LnNiO₃ (Ln = Pr, Nd) to Ln₃Ni₃O₇ with monovalent nickel ions," *Solid State Ionics*, vol. 74, no. 3, pp. 211– 217, 1994.
- [267] J. Li, R. J. Green, Z. Zhang, R. Sutarto, J. T. Sadowski, Z. Zhu, G. Zhang, D. Zhou, Y. Sun, F. He, S. Ramanathan, and R. Comin, "Sudden Collapse of Magnetic Order in Oxygen-Deficient Nickelate Films," *Phys. Rev. Lett.*, vol. 126, p. 187602, May 2021.
- [268] M. Hepting, R. J. Green, Z. Zhong, M. Bluschke, Y. E. Suyolcu, S. Macke, A. Frano, S. Catalano, M. Gibert, R. Sutarto, F. He, G. Cristiani, G. Logvenov, Y. Wang, P. A. van Aken, P. Hansmann, M. Le Tacon, J.-M. Triscone, G. A. Sawatzky, B. Keimer, and E. Benckiser, "Complex magnetic order in nickelate slabs," *Nature Physics*, vol. 14, pp. 1097–1102, Nov 2018.
- [269] J. Fowlie, M. Hadjimichael, M. M. Martins, I. Li, M. Osada, B. Y. Wang, K. Lee, Y. Lee, Z. Salman, T. Prokscha, J.-M. Triscone, H. Y. Hwang, and A. Suter, "Intrinsic magnetism in superconducting infinite-layer nickelates," 2022.
- [270] T. Moriga, M. Hayashi, T. Sakamoto, M. Orihara, and I. Nakabayashi, "Reduction processes of rare-earth nickelate perovskites LnNiO₃ (Ln = La, Pr, Nd)," *Solid State Ionics*, vol. 154-155, pp. 251–255, 2002.
- [271] R. D. Sánchez, M. T. Causa, A. Caneiro, A. Butera, M. Vallet-Regí, M. J. Sayagués, J. González-Calbet, F. García-Sanz, and J. Rivas, "Metal-insulator transition in oxygen-deficient LaNiO_{3-x} perovskites," *Phys. Rev. B*, vol. 54, pp. 16574–16578, Dec 1996.
- [272] S. Macke, J. E. Hamann-Borrero, R. J. Green, B. Keimer, G. A. Sawatzky, and M. W. Haverkort, "Dynamical Effects in Resonant X-Ray Diffraction," *Phys. Rev. Lett.*, vol. 117, p. 115501, Sep 2016.
- [273] R. A. Ortiz, H. Menke, F. Misják, D. T. Mantadakis, K. Fürsich, E. Schierle, G. Logvenov, U. Kaiser, B. Keimer, P. Hansmann, and E. Benckiser, "Superlattice approach to doping infinite-layer nickelates," *Phys. Rev. B*, vol. 104, p. 165137, Oct 2021.
- [274] L. Tröger, D. Arvanitis, K. Baberschke, H. Michaelis, U. Grimm, and E. Zschech, "Full correction of the self-absorption in soft-fluorescence extended x-ray-absorption fine structure," *Phys. Rev. B*, vol. 46, pp. 3283–3289, Aug 1992.
- [275] J. Stöhr and H. C. Siegmann, Magnetism: From Fundamentals to Nanoscale Dynamics. Springer, Berlin, Heidelberg, 1 ed., 2006.
- [276] C. T. Chen, L. H. Tjeng, J. Kwo, H. L. Kao, P. Rudolf, F. Sette, and R. M. Fleming, "Out-of-plane orbital characters of intrinsic and doped holes in La_{2-x}Sr_xCuO₄," *Phys. Rev. Lett.*, vol. 68, pp. 2543–2546, Apr 1992.
- [277] F. Y. Bruno, J. Garcia-Barriocanal, M. Varela, N. M. Nemes, P. Thakur, J. C. Cezar, N. B. Brookes, A. Rivera-Calzada, M. Garcia-Hernandez, C. Leon, S. Okamoto, S. J. Pennycook, and J. Santamaria, "Electronic and Magnetic Reconstructions in

La_{0.7}Sr_{0.3}MnO₃/SrTiO₃ Heterostructures: A Case of Enhanced Interlayer Coupling Controlled by the Interface," *Phys. Rev. Lett.*, vol. 106, p. 147205, Apr 2011.

- [278] R. F. Need, P. B. Marshall, E. Weschke, A. J. Grutter, D. A. Gilbert, E. Arenholz, P. Shafer, S. Stemmer, and S. D. Wilson, "Resolving interfacial charge transfer in titanate superlattices using resonant x-ray reflectometry," *Phys. Rev. Materials*, vol. 2, p. 093801, Sep 2018.
- [279] J. Son, J. M. LeBeau, S. J. Allen, and S. Stemmer, "Conductivity enhancement of ultrathin LaNiO₃ films in superlattices," *Applied Physics Letters*, vol. 97, no. 20, p. 202109, 2010.
- [280] A. M. Kaiser, A. X. Gray, G. Conti, J. Son, A. Greer, A. Perona, A. Rattanachata, A. Y. Saw, A. Bostwick, S. Yang, S.-H. Yang, E. M. Gullikson, J. B. Kortright, S. Stemmer, and C. S. Fadley, "Suppression of Near-Fermi Level Electronic States at the Interface in a LaNiO₃/SrTiO₃ Superlattice," *Phys. Rev. Lett.*, vol. 107, p. 116402, Sep 2011.
- [281] J. Hwang, J. Son, J. Y. Zhang, A. Janotti, C. G. Van de Walle, and S. Stemmer, "Structural origins of the properties of rare earth nickelate superlattices," *Phys. Rev.* B, vol. 87, p. 060101, Feb 2013.
- [282] Z. Zhang, S. Soltan, H. Schmid, H.-U. Habermeier, B. Keimer, and U. Kaiser, "Revealing the atomic and electronic structure of a SrTiO₃/LaNiO₃/SrTiO₃ heterostructure interface," *Journal of Applied Physics*, vol. 115, no. 10, p. 103519, 2014.
- [283] M. J. Han and M. van Veenendaal, "Fermi level density of states modulation without charge transfer in nickelate superlattices," *Journal of Physics: Condensed Matter*, vol. 26, p. 145501, mar 2014.
- [284] H.-S. Kim and M. J. Han, "Effect of charge doping on the electronic structure, orbital polarization, and structural distortion in nickelate superlattice," *Phys. Rev. B*, vol. 91, p. 235102, Jun 2015.
- [285] D. Eiteneer, G. Pálsson, S. Nemšák, A. Gray, A. Kaiser, J. Son, J. LeBeau, G. Conti, A. Greer, A. Keqi, A. Rattanachata, A. Saw, A. Bostwick, E. Rotenberg, E. Gullikson, S. Ueda, K. Kobayashi, A. Janotti, C. Van de Walle, A. Blanca-Romero, R. Pentcheva, C. Schneider, S. Stemmer, and C. Fadley, "Depth-Resolved Composition and Electronic Structure of Buried Layers and Interfaces in a LaNiO₃/SrTiO₃ Superlattice from Soft- and Hard- X-ray Standing-Wave Angle-Resolved Photoemission," Journal of Electron Spectroscopy and Related Phenomena, vol. 211, pp. 70–81, 2016.
- [286] B. Geisler, A. Blanca-Romero, and R. Pentcheva, "Design of n- and p-type oxide thermoelectrics in LaNiO₃/SrTiO₃(100) superlattices exploiting interface polarity," *Phys. Rev. B*, vol. 95, p. 125301, Mar 2017.
- [287] B. Chen, N. Gauquelin, R. J. Green, J. H. Lee, C. Piamonteze, M. Spreitzer, D. Jannis, J. Verbeeck, M. Bibes, M. Huijben, G. Rijnders, and G. Koster, "Spatially Controlled Octahedral Rotations and Metal–Insulator Transitions in Nickelate Superlattices," *Nano Letters*, vol. 21, pp. 1295–1302, Feb 2021.

- [288] Y.-C. Liang, T.-B. Wu, H.-Y. Lee, and Y.-W. Hsieh, "Structural characteristics of epitaxial BaTiO₃/LaNiO₃ superlattice," *Journal of Applied Physics*, vol. 96, no. 1, pp. 584–589, 2004.
- [289] S. Brück, Magnetic resonant reflectometry on exchange bias systems. PhD thesis, University of Stuttgart, 2009.
- [290] P. Radhakrishnan, *Electronic properties of rare earth vanadate heterostructures*. PhD thesis, University of Stuttgart, 2022.
- [291] M. W. Haverkort, M. Zwierzycki, and O. K. Andersen, "Multiplet ligand-field theory using Wannier orbitals," *Phys. Rev. B*, vol. 85, p. 165113, Apr 2012.
- [292] M. W. Haverkort, G. Sangiovanni, P. Hansmann, A. Toschi, Y. Lu, and S. Macke, "Bands, resonances, edge singularities and excitons in core level spectroscopy investigated within the dynamical mean-field theory," *EPL (Europhysics Letters)*, vol. 108, p. 57004, Dec 2014.
- [293] C. Yang, R. A. Ortiz, Y. Wang, W. Sigle, H. Wang, G. Logvenov, E. Benckiser, B. Keimer, and P. A. van Aken, "STEM study of infinite-layer nickelate superlattices." in preparation.
- [294] S. W. Zeng, X. M. Yin, C. J. Li, L. E. Chow, C. S. Tang, K. Han, Z. Huang, Y. Cao, D. Y. Wan, Z. T. Zhang, Z. S. Lim, C. Z. Diao, P. Yang, A. T. S. Wee, S. J. Pennycook, and A. Ariando, "Observation of perfect diamagnetism and interfacial effect on the electronic structures in infinite layer Nd_{0.8}Sr_{0.2}NiO₂ superconductors," *Nature Communications*, vol. 13, p. 743, Feb 2022.
- [295] M. Abbate, G. Zampieri, F. Prado, A. Caneiro, J. M. Gonzalez-Calbet, and M. Vallet-Regi, "Electronic structure and metal-insulator transition in LaNiO_{3-δ}," *Phys. Rev. B*, vol. 65, p. 155101, Mar 2002.
- [296] J. Elp, The electronic structure of doped late transition metal monoxides. PhD thesis, University of Groningen, 1991.
- [297] A. Ikeda, Y. Krockenberger, H. Irie, M. Naito, and H. Yamamoto, "Direct observation of infinite NiO₂ planes in LaNiO₂ films," *Applied Physics Express*, vol. 9, p. 061101, may 2016.
- [298] D. J. Scalapino, "A common thread: The pairing interaction for unconventional superconductors," *Rev. Mod. Phys.*, vol. 84, pp. 1383–1417, Oct 2012.
- [299] B. Keimer, S. A. Kivelson, M. R. Norman, S. Uchida, and J. Zaanen, "From quantum matter to high-temperature superconductivity in copper oxides," *Nature*, vol. 518, pp. 179–186, Feb 2015.
- [300] Q. Si, R. Yu, and E. Abrahams, "High-temperature superconductivity in iron pnictides and chalcogenides," *Nature Reviews Materials*, vol. 1, p. 16017, Mar 2016.
- [301] P. A. Lee, N. Nagaosa, and X.-G. Wen, "Doping a Mott insulator: Physics of hightemperature superconductivity," *Rev. Mod. Phys.*, vol. 78, pp. 17–85, Jan 2006.

- [302] J. Rodríguez-Carvajal, "Recent advances in magnetic structure determination by neutron powder diffraction," *Physica B: Condensed Matter*, vol. 192, no. 1, pp. 55– 69, 1993.
- [303] A. Amato, H. Luetkens, K. Sedlak, A. Stoykov, R. Scheuermann, M. Elender, A. Raselli, and D. Graf, "The new versatile general purpose surface-muon instrument (GPS) based on silicon photomultipliers for μSR measurements on a continuouswave beam," *Review of Scientific Instruments*, vol. 88, no. 9, p. 093301, 2017.
- [304] A. Suter and B. Wojek, "MuSRfit: A Free Platform-Independent Framework for μSR Data Analysis," *Physics Procedia*, vol. 30, pp. 69–73, 2012. 12th International Conference on Muon Spin Rotation, Relaxation and Resonance (μSR2011).
- [305] O. O. Bernal, D. E. MacLaughlin, G. D. Morris, P.-C. Ho, L. Shu, C. Tan, J. Zhang, Z. Ding, K. Huang, and V. V. Poltavets, "Charge-stripe order, antiferromagnetism, and spin dynamics in the cuprate-analog nickelate La₄Ni₃O₈," *Phys. Rev. B*, vol. 100, p. 125142, Sep 2019.
- [306] Y. J. Uemura, T. Yamazaki, D. R. Harshman, M. Senba, and E. J. Ansaldo, "Muonspin relaxation in AuFe and CuMn spin glasses," *Phys. Rev. B*, vol. 31, pp. 546–563, Jan 1985.
- [307] H. Lin, D. J. Gawryluk, Y. M. Klein, S. Huangfu, E. Pomjakushina, F. von Rohr, and A. Schilling, "Universal spin-glass behaviour in bulk LaNiO₂, PrNiO₂ and NdNiO₂," *New Journal of Physics*, vol. 24, p. 013022, jan 2022.
- [308] S. Huangfu, Z. Guguchia, D. Cheptiakov, X. Zhang, H. Luetkens, D. J. Gawryluk, T. Shang, F. O. von Rohr, and A. Schilling, "Short-range magnetic interactions and spin-glass behavior in the quasi-two-dimensional nickelate Pr₄Ni₃O₈," *Phys. Rev. B*, vol. 102, p. 054423, Aug 2020.
- [309] R. Sanchez, M. Causa, M. Tovar, J. Alonso, and M. Martinez-Lope, "High temperature magnetic properties of RNiO₃," *Journal of Magnetism and Magnetic Materials*, vol. 272-276, pp. 390–391, 2004. Proceedings of the International Conference on Magnetism (ICM 2003).
- [310] X. Q. Xu, J. L. Peng, Z. Y. Li, H. L. Ju, and R. L. Greene, "Resisitivity, thermopower, and susceptibility of RNiO₃ (R = La, Pr)," *Phys. Rev. B*, vol. 48, pp. 1112–1118, Jul 1993.
- [311] D. Zhao, Y. B. Zhou, Y. Fu, L. Wang, X. F. Zhou, H. Cheng, J. Li, D. W. Song, S. J. Li, B. L. Kang, L. X. Zheng, L. P. Nie, Z. M. Wu, M. Shan, F. H. Yu, J. J. Ying, S. M. Wang, J. W. Mei, T. Wu, and X. H. Chen, "Intrinsic Spin Susceptibility and Pseudogaplike Behavior in Infinite-Layer LaNiO₂," *Phys. Rev. Lett.*, vol. 126, p. 197001, May 2021.
- [312] T. Nakano, M. Oda, C. Manabe, N. Momono, Y. Miura, and M. Ido, "Magnetic properties and electronic conduction of superconducting La_{2-x}Sr_xCuO₄," *Phys. Rev. B*, vol. 49, pp. 16000–16008, Jun 1994.

- [313] D. R. Harshman, G. Aeppli, G. P. Espinosa, A. S. Cooper, J. P. Remeika, E. J. Ansaldo, T. M. Riseman, D. L. Williams, D. R. Noakes, B. Ellman, and T. F. Rosenbaum, "Freezing of spin and charge in La_{2-x}Sr_xCuO₄," *Phys. Rev. B*, vol. 38, pp. 852–855, Jul 1988.
- [314] F. C. Chou, N. R. Belk, M. A. Kastner, R. J. Birgeneau, and A. Aharony, "Spin-Glass Behavior in La_{1.96}Sr_{0.04}CuO₄," *Phys. Rev. Lett.*, vol. 75, pp. 2204–2207, Sep 1995.
- [315] M.-H. Julien, F. Borsa, P. Carretta, M. Horvatić, C. Berthier, and C. T. Lin, "Charge Segregation, Cluster Spin Glass, and Superconductivity in La_{1.94}Sr_{0.06}CuO₄," *Phys. Rev. Lett.*, vol. 83, pp. 604–607, Jul 1999.
- [316] X. Liu, M. Kotiuga, H.-S. Kim, A. T. N'Diaye, Y. Choi, Q. Zhang, Y. Cao, M. Kareev, F. Wen, B. Pal, J. W. Freeland, L. Gu, D. Haskel, P. Shafer, E. Arenholz, K. Haule, D. Vanderbilt, K. M. Rabe, and J. Chakhalian, "Interfacial charge-transfer Mott state in iridate-nickelate superlattices," *Proceedings of the National Academy* of Sciences, vol. 116, no. 40, pp. 19863–19868, 2019.
- [317] J. Hoffman, I. C. Tung, B. B. Nelson-Cheeseman, M. Liu, J. W. Freeland, and A. Bhattacharya, "Charge transfer and interfacial magnetism in (LaNiO₃)_n/(LaMnO₃)₂ superlattices," *Phys. Rev. B*, vol. 88, p. 144411, Oct 2013.
- [318] A. T. Lee and M. J. Han, "Charge transfer, confinement, and ferromagnetism in LaMnO₃/LaNiO₃ (001) superlattices," *Phys. Rev. B*, vol. 88, p. 035126, Jul 2013.
- [319] R. N. Singh, L. Bahadur, J. P. Pandey, S. P. Singh, P. Chartier, and G. Poillerat, "Preparation and characterization of thin films of LaNiO₃ for anode application in alkaline water electrolysis," *Journal of Applied Electrochemistry*, vol. 24, pp. 149– 156, Feb 1994.
- [320] L. Xuchen, X. Tingxian, and D. Xianghong, "Preparation and characterization of LaNiO₃ A/F ratio-sensitive thin film by sol–gel process based on amorphous citrate precursors," Sensors and Actuators B: Chemical, vol. 67, no. 1, pp. 24–28, 2000.
- [321] T.-R. Ling, Z.-B. Chen, and M.-D. Lee, "Studies on catalytic and conductive properties of LaNiO₃ for oxidation of C₂H₅OH₃CHO, and CHO₄," *Catalysis Today*, vol. 26, no. 1, pp. 79–86, 1995. Catalysis in Environmental Applications Selected Papers from the International Symposium on Catalysis and Zeolites.
- [322] J. Shi, Y. Zhou, and S. Ramanathan, "Colossal resistance switching and band gap modulation in a perovskite nickelate by electron doping," *Nature Communications*, vol. 5, p. 4860, Sep 2014.
- [323] Y. Zhou, X. Guan, H. Zhou, K. Ramadoss, S. Adam, H. Liu, S. Lee, J. Shi, M. Tsuchiya, D. D. Fong, and S. Ramanathan, "Strongly correlated perovskite fuel cells," *Nature*, vol. 534, pp. 231–234, Jun 2016.
Acknowledgements

The completion of this Ph.D. thesis and the work presented in it would not have been possible without many people's help, which I would like to thank in the following paragraphs.

First, I would like to express my gratitude to Prof. Bernhard Keimer for allowing me to be part of such a prestigious research group at the Max Planck Institute. I learned a lot while I was working, learning, and doing research in the solid-state spectroscopy department.

I sincerely thank my day-to-day supervisor, Dr. Eva Benckiser, for presenting me with a very promising project in which I worked during my Master's and Ph.D. time. I also thank Eva for her supervision, guidance, and patience during all these years we have worked together. I am also grateful to Dr. Matthias Hepting, whom I consider my second day-to-day supervisor, for including me in a new research project, which led to the publication of my second paper. I am especially grateful to Friederike Wrobel, who was my mentor during the first years at the institute and who taught me how to perform the reduction process and to use the laboratory equipment.

I would like to thank Prof. Maria Daghofer, whom I remember from my days as a master's student, and Prof. Harald Gießen, who has shown interest in my publications from day one. Thank you for accepting and being on my thesis committee. In addition, I would like to also thank my external advisor Jürgen Nuss for providing yearly feedback about the status of my research.

I appreciate the help of the members of the department who gave me support with the equipment, measurements, and administrative matters. Thank you Benjamin Bruha, Michael Schulz, Peter Wochner and Sonja Balkema. I also would like to thank other members of the Max Planck Institute for their support. Many thanks to Birgit King for helping me with visa and administrative-related topics. Special thanks to the entire department of Quantum Materials of Prof. Hidenori Takagi for allowing me to use their equipment and for the valuable discussions.

I especially like to thank the thin-film technology group members for providing technical support and samples for the measurements. Thanks to Gennady Logvenov for allowing me to work alongside with members of his group. Thanks to Georg Cristiani for teaching me how to use the PLD and to grow samples and for providing me with samples in the early stage of my Ph.D. Thanks to Benjamin Stuhlhofer for providing support with such delicate equipment and for preparing the ovens in which I worked. I also would like to thank the persons who assisted me with the preparation of samples for the subsequent measurements, Marion Hagel, Birgit Lemke, and Stephan Schmid helped me with the contacts and bondings of the samples required for transport measurements.

I am grateful to Martin Bluschke, Enrico Schierle, Eugen Weschke, Daniel Putsky for helping me with measurements at the large scale facilities in Berlin and in Karlsruhe. I like to thank the people with whom I had very enlightening discussions. Thank you, Juan Porras, Christopher Dietl, Matteo Minola, Gideok Kim, and Toshinao Loew. I also want to say thank you to my colleagues in the department Hun-ho Kim, Suguru Nakata, Lichen Wang, Zichen Yang, Rebecca Pons, Ksenia Rabinovic, Valentin Zimmermann, Laura Guasco, Huimei Liu, Alexander Boris, Robert Dawson. Also, I thank to my officemates and closest colaborators Katrin Fürsich, Padma Radhakrishnan and Jorge Sauceda for the countless everyday discussions.

Finally, I would like to express my deep gratitude towards my family in Honduras, my brother Wilber Ortiz, my mother Maria Ortiz, my grandmother Petronila Ortiz, my second parents, Miriam and Marco Zelaya, and all my cousins for the unconditional support I receive from them despite the distances. I also thank my girlfriend, Stefanie Volke, for supporting and motivating me while I wrote this thesis.

List of Publications

- R. A. Ortiz, H. Menke, K. Fürsich, R. Pons, E. Schierle, G. Logvenov, P. Hansmann, B. Keimer, and E. Benckiser, "Oxygen stoichiometry and hybridization in infinitelayer nickelate superlattices," 2022. (In Preparation).
- [2] C. Yang, R. A. Ortiz, Y. Wang, W. Sigle, H. Wang, G. Logvenov, E. Benckiser, B. Keimer, and P. A. van Aken, "Stem study of infinite-layer nickelate superlattices," 2022. (In Preparation).
- [3] F. Misjak, R. A. Ortiz, E. Benckiser, and U. Kaiser, "Atomic-scale investigation of nickelate-based perovskite superlattice interfaces," 2022. (In Preparation).
- [4] R. A. Ortiz, C. Chan, H. Menke, K. Fürsich, R. Pons, E. Schierle, G. Logvenov, P. Hansmann, B. Keimer, P. A. van Aken, and E. Benckiser, "Orbital and valencestate reflectometry of infinite-layer nickelate superlattices," 2022. (In Preparation).
- [5] R. A. Ortiz^{*}, P. Puphal^{*}, M. Klett, F. Hotz, R. K. Kremer, H. Trepka, M. Hemmida, H.-A. K. von Nidda, M. Isobe, R. Khasanov, H. Luetkens, P. Hansmann, B. Keimer, T. Schäfer, and M. Hepting, "Magnetic correlations in infinite-layer nickelates: An experimental and theoretical multimethod study," *Phys. Rev. Research*, vol. 4, p. 023093, May 2022.
- [6] C. Yang, Y. Wang, D. Putzky, W. Sigle, H. Wang, R. A. Ortiz, G. Logvenov, E. Benckiser, B. Keimer, and P. A. van Aken, "Ruddlesden-Popper Faults in NdNiO₃ Thin Films," *Symmetry*, vol. 14, no. 3, 2022.
- [7] P. Puphal, V. Pomjakushin, R. A. Ortiz, S. Hammoud, M. Isobe, B. Keimer, and M. Hepting, "Investigation of Hydrogen Incorporations in Bulk Infinite-Layer Nickelates," *Frontiers in Physics*, vol. 10, 2022.
- [8] K. Fürsich, R. Pons, M. Bluschke, R. A. Ortiz, S. Wintz, E. Schierle, M. Weigand, G. Logvenov, G. Schütz, B. Keimer, and E. Benckiser, "Oxygen Hole Character and Lateral Homogeneity in PrNiO_{2+δ} Thin Films," *Frontiers in Physics*, vol. 9, 2022.
- [9] R. A. Ortiz, H. Menke, F. Misják, D. T. Mantadakis, K. Fürsich, E. Schierle, G. Logvenov, U. Kaiser, B. Keimer, P. Hansmann, and E. Benckiser, "Superlattice approach to doping infinite-layer nickelates," *Phys. Rev. B*, vol. 104, p. 165137, Oct 2021.
- [10] C. Yang, R. A. Ortiz, Y. Wang, D. Putzky, E. Benckiser, B. Keimer, and P. A. van Aken, "Generation of Ruddlesden-Popper faults in Sr doped NdNiO₂," *Microscopy* and Microanalysis, vol. 27, pp. 1198–1200, Jul 2021.

- [11] K. Fürsich, Y. Lu, D. Betto, M. Bluschke, J. Porras, E. Schierle, R. A. Ortiz, H. Suzuki, G. Cristiani, G. Logvenov, N. B. Brookes, M. W. Haverkort, M. Le Tacon, E. Benckiser, M. Minola, and B. Keimer, "Resonant inelastic x-ray scattering study of bond order and spin excitations in nickelate thin-film structures," *Phys. Rev. B*, vol. 99, p. 165124, Apr 2019.
- [12] M. Bluschke, A. Frano, E. Schierle, D. Putzky, F. Ghorbani, R. A. Ortiz, H. Suzuki, G. Christiani, G. Logvenov, E. Weschke, R. J. Birgeneau, E. H. da Silva Neto, M. Minola, S. Blanco-Canosa, and B. Keimer, "Stabilization of three-dimensional charge order in YBa₂Cu₃O_{6+x} via epitaxial growth," *Nature Communications*, vol. 9, p. 2978, Jul 2018.

*: Authors contributed equally.