

Promising Materials for Unconventional Superconductivity

Master thesis Herman Muzychko

Supervisor: Prof. Dr. Rudolf Gross Advisor: Dr. Stephan Geprägs

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Chapter 1 Introduction

Superconductivity, a remarkable quantum phenomenon, has captivated the imagination of scientists for more than a century. Over the years, extensive research has been dedicated to understanding the underlying mechanisms and discovering new superconducting materials. Among the materials investigated, unconventional superconductors have emerged as a particularly intriguing class, offering the potential for applications in advanced technologies. This master thesis explores unconventional superconducting materials, specifically focusing on two material systems: the iridate compound Sr_2IrO_4 , which has similarities to the high-temperature cuprate superconductors, and the infinite-layer Sr-doped NdNiO₂ nickelate. While the latter shows superconductivity below 15 K [1], a superconducting phase has not been found in Sr_2IrO_4 up to now. In the framework of this thesis, we have fabricated and investigated the iridate compounds Sr_2IrO_4 and $Sr_3Ir_2O_7$, which are the first two members of the Ruddlesden Popper series $Sr_{n+1}Ir_nO_{3n+1}$, as well as the Nd_{0.8}Sr_{0.2}NiO₃ perovskite material system to provide deeper insights into their magnetic properties and structural characteristics.

The first part of this thesis delves into the fabrication of thin films of Sr_2IrO_4 and $Nd_{0.8}Sr_{0.2}NiO_3$ using pulsed laser deposition (PLD). Sr_2IrO_4 , a strongly correlated electron system, shares structural similarities with high-temperature cuprate superconductors, making it an attractive candidate for studying unconventional superconductivity. The study aims to optimize the growth parameters, such as substrate temperature, oxygen pressure, and the laser fluence of the excimer laser using a new PLD system, to improve the quality of the thin films. Although the primary focus of this part is not the exploration of superconductivity, it is a crucial step towards enabling future investigations into the superconducting properties of Sr_2IrO_4 and with a particular interest in the infinite-layer nickelate phase, $Nd_{0.8}Sr_{0.2}NiO_2$, due to its recent discovery of superconductivity.

In the second, more critical part of the thesis, we investigate the influence of epitaxial strain on the magnetic properties of Sr_2IrO_4 and $Sr_3Ir_2O_7$ thin films grown on different substrates. The application of epitaxial strain is a powerful tool in tailoring the physical properties of thin films, and it has been shown to impact the magnetic properties of complex oxide materials significantly. We employ resonant inelastic X-ray scattering (RIXS) to probe the spin wave dispersion relation of the strontium iridate thin films. By comparing the obtained spin wave dispersion relations to bulk values obtained from the literature, we aim to gain a deeper understanding of the impact of epitaxial strain on the magnetic properties of these materials. To insight into the exchange constants as well as anisotropy parameters of the iridate thin films, we have employed linear spin wave theory (LSWT) using the SpinW package to simulate the spin wave dispersion relation, helping to elucidate the role of epitaxial strain in modifying the magnetic exchange in these materials.

This two-part master thesis represents a comprehensive exploration of unconventional superconducting materials, encompassing both their growth optimization and the intricate influence of epitaxial strain on their magnetic properties. Through these endeavors, we aim to contribute to the evolving field of superconductivity and complex oxide materials, shedding light on the potential for high-temperature superconductivity in materials like Sr_2IrO_4 and $Nd_{0.8}Sr_{0.2}NiO_2$ while advancing our understanding of the fundamental interactions between structure and magnetism in condensed matter physics.

Chapter 2 Theory

The observation of unconventional superconductivity in $(La, Ba)_2CuO_4$ [2] has inspired the investigation of materials possessing analogous crystal and electronic structures. The primary objectives are to identify new superconductors and gain insights into the fundamental principles governing superconductivity in copper oxide compounds. This chapter is devoted to two perovskite families, strontium iridate oxides and neodymium nickelate oxides, which show similarities to the cuprate high-temperature superconductors.

The Ruddlesden-Popper series $Sr_{n+1}Ir_nO_{3n+1}$ are of particular scientific interest because they possess similar crystal structures to high-temperature cuprate superconductors. Examples with a shared crystal structure encompass the bulk superconductor Sr_2RuO_4 and surface-electrondoped Sr_2IrO_4 . The latter displays spectroscopic features indicative of a superconducting energy gap, although the presence of a zero-resistance state has not been confirmed up to now [1]. Here, we will introduce the first two material compounds, namely Sr_2IrO_4 (SIO-214) and $Sr_3Ir_2O_7$ (SIO-327), which we have investigated in the framework of this thesis.

Additionally, the Sr-doped Ruddlesden-Popper series $Nd_{n+1}Ni_nO_{3n+1}$ have recently become popular, due to its $Nd_{0.8}Sr_{0.2}NiO_3$ ($n \rightarrow \infty$) perovskite phase, which shows superconductivity in the topotactically reduced infinite-layer phase $Nd_{0.8}Sr_{0.2}NiO_2$. There is a possibility of the potential existence of a family of nickelate superconductors similar to copper oxides and pnictides [1].

2.1 Strontium iridates $Sr_{n+1}Ir_nO_{3n+1}$

In this section, we will discuss the physical properties of strontium iridates $Sr_{n+1}Ir_nO_{3n+1}$ with n = 1 and 2.

2.1.1 Crystal structures of strontium iridates

In the first n = 1 member of the Ruddlesden-Popper series $Sr_{n+1}Ir_nO_{3n+1}$, Sr_2IrO_4 (SIO-214), a material that has been studied extensively due to its interesting physical properties. The large spin-orbit coupling in this 5d transition-metal compound combined with a moderate Coulomb repulsion results in a Mott insulating $J_{eff} = 1/2$ ground state, which is similar to the S = 1/2ground state of high-temperature superconducting cuprates. The compound crystallizes in the tetragonal space group I41/acd, with lattice parameters $a = b \approx 5.48$ Å and $c \approx 25.8$ Å [3]. This space group is derived from the K₂NiF₄-type structure (space group I4/*mmm*) through a correlated staggered rotation of the IrO₆ octahedra by 11.8° about the *c* axis, resulting in a larger unit cell $\sqrt{2}a \times \sqrt{2}b \times 2c$ than the unit cell in the space group I4/*mmm*. The crystal structure of Sr₂IrO₄ can be visualized schematically in Fig. 2.1.1(a). The atomic coordinates of each element are shown in Table 2.1.1 The IrO₆ layers contain Ir ions at the center of corner-sharing oxygen octahedra, separated by Sr ions [3].

Site	Element	X	У	Z	Spin	Oxidation	Occupation
Sr	Sr	0	1/4	0.05072	0	+2	1
Ir	Ir	0	1/4	3/8	1/2	+4	1
O 1	0	0.19372	0.44372	1/8	0	-2	1
O 2	Ο	0	1/4	0.29045	0	-2	1

Table 2.1.1: Atomic coordinates and isotropic displacement of SIO-214 in the I41/*acd* space group. Lattice constants are a = b = 5.493 Å and c = 25.777 Å. O1 and O2 are different oxygen sites. Data taken from Ref. [4].

One significant feature of Sr_2IrO_4 's crystal structure is that the IrO_6 octahedra are slightly elongated by 4% along the *c* axis. This makes it unclear whether the pure $J_{eff} = 1/2$ state is realized in a system that deviates from perfect cubic symmetry. Although neutron studies recently questioned the exact tetragonal space group [5, 6], the difference from the commonly used I41/*acd* is small and not significant in terms of the magnetic structure [3].

The second (n = 2) member of the Ruddlesden-Popper series $Sr_{n+1}Ir_nO_{3n+1}$ is $Sr_3Ir_2O_7$ (SIO-327). The exact crystal structure of SIO-327 has been the subject of debate, with initial reports suggesting that it crystallizes in the tetragonal I4/*mmm* space group and recent reports suggesting an orthorhombic *Bbcb* space group [7–9]. The crystal structure of $Sr_3Ir_2O_7$ contains strongly coupled double Ir–O layers, separated by layers of Sr–O and offset along the *c* axis, which results in a double-layered framework of Ir ions centered inside oxygen octahedra. The rotation of these octahedra leads to subtle differences in the crystal structure that have been reported thus far. Therefore the exact crystal structure remains debated. However, in this thesis, we will use the tetragonal I4/*mmm* structure model.



Figure 2.1.1: Tetragonal crystal structures of (a) Sr_2IrO_4 (SIO-214) and (b) $Sr_3Ir_2O_7$ (SIO-327). The Sr^{2+} , the Ir^{4+} , and the O^{2-} ions are represented as green, red, and blue spheres. The oxygen octahedra are highlighted. Scales are not considered.

The tetragonal crystal structure of $Sr_3Ir_2O_7$ is shown in Fig. 2.1.1(b) and the atomic positions and site symmetries are given in Table 2.1.2. The crystal structure of $Sr_3Ir_2O_7$ contains three oxygen sites: O1, O2, and O3 with 50% occupancy. The partial occupation of the O3 sites generates the octahedral rotation around *c* axis in analogy with SIO-214, which was supported by electron diffraction experiments that revealed the presence of two sets of reflections with different intensities and spacing [7, 9].

The presence of octahedral rotations in the crystal structure of $Sr_3Ir_2O_7$ has a significant impact on its electronic and magnetic properties. In this compound, the oxygen octahedra surrounding the Ir^{4+} ions undergo rotational distortions. These distortions cause changes in the Ir-O-Ir bond angles, leading to a reduction in the hopping matrix element between neighboring Ir ions. As a result, the material exhibits suppressed metallic behavior and instead displays insulating properties [10].

Site	Element	X	У	Z	Spin	Oxidation	Occupation
Sr1	Sr	0	0	1/2	0	+2	1
Sr2	Sr	0	0	0.3128	0	+2	1
Ir	Ir	0	0	0.09743	1/2	+4	1
01	0	0	0	0	0	-2	1
O2	0	0	0	0.1939	0	-2	1
O 3	0	0	0.3957	0.404	0	-2	0.5

Table 2.1.2: Atomic coordinates and isotropic displacement of SIO-327 in the I4/*mmm* space group. Lattice constants are a = b = 3.896 Å and c = 20.879 Å. Sr1 and Sr2 are different strontium sites. O1, O2, and O3 are different oxygen sites. Data taken from Ref. [11].

The suppression of metallicity in SIO-327 is further enhanced by the strong spin-orbit coupling of the Ir^{4+} ions. In $Sr_3Ir_2O_7$, the spin-orbit coupling of the Ir^{4+} ions plays a significant role in shaping the electronic properties of the material. It leads to the formation of an energy gap in the electronic band structure, which contributes to the insulating behavior observed in SIO-327. This energy gap has important implications for various aspects of the material, including its conductivity and magnetic properties [10].

Beyond its electronic properties, the octahedral rotations in SIO-327 also give rise to intriguing magnetic characteristics. The Ir^{4+} ions within the double-layered structure of the material are arranged in a triangular lattice. This triangular arrangement, combined with the competing exchange interactions between the Ir spins, leads to frustrated magnetism. Frustrated magnetism arises when the arrangement of magnetic moments cannot simultaneously satisfy all pairwise interactions, leading to complex and unconventional magnetic behaviors [12].

Additionally, the spin-orbit coupling of the Ir^{4+} ions in SIO-327 generates a strong magnetic anisotropy, which results in highly anisotropic magnetic behavior, where the magnetic response of the material strongly depends on the orientation of the external magnetic field [13].

The interplay between frustrated magnetism and magnetic anisotropy in $Sr_3Ir_2O_7$ gives rise to a rich magnetic phase diagram. The material exhibits various magnetic phases depending on external factors such as temperature and magnetic field. These phases include antiferromagnetic, ferromagnetic, and spin liquid phases, each characterized by different arrangements and orientations of the magnetic moments in the material [14].

2.1.2 Electronic states of strontium iridates

Strontium iridates, including Sr_2IrO_4 , have attracted significant attention due to their intriguing electronic properties. The fundamental concept in understanding these materials is the presence of Ir⁴⁺ ions in a 5d⁵ electron configuration situated within octahedral IrO₆ coordination (see Fig. 2.1.2). The 5d orbitals, initially 5-fold degenerate, undergo splitting under the influence of a strong cubic crystal field (O_h symmetry). This splitting results in a lower orbital triplet, known as the t_{2g} states, and an upper orbital doublet, the e_g states. Due to this considerable crystal field effect, the 5*d*-electrons primarily reside in the t_{2g} manifold, leaving the Ir ion in a low spin configuration. Notably, the contribution of the e_g orbitals can be largely neglected. This simplification allows the system to be effectively described as having a single hole in the t_{2g} subspace [10].



Figure 2.1.2: Schematic energy diagram of IrO₆ octahedra with Ir⁴⁺ ions in the 5d (t_{2g}^5) configuration. The energy levels of the Ir⁴⁺ ion undergo two significant splittings: first, due to the influence of a robust octahedral crystal field, and second, as a result of the strong spin-orbit coupling effect. The spin-orbit coupling causes the formation of a fully occupied $J_{\text{eff}} = 3/2$ quartet and a $J_{\text{eff}} = 1/2$ doublet with half occupancy. Consequently, the system's ground state features a hole residing in the $J_{\text{eff}} = 1/2$ state. This illustration is further complemented by a spatial representation of the wave functions for the $J_{\text{eff}} = 3/2$ state (comprising $|1, \pm \rangle$ and $|2, \pm \rangle$ doublets) and the $J_{\text{eff}} = 1/2$ state (comprising the $|0, \pm \rangle$ doublet). Figure taken from Ref. [10].

However, the presence of a strong spin-orbit coupling (SOC) of the Ir⁴⁺ 5*d*-ions makes strontium iridates especially interesting. This SOC results in a remarkably narrow $J_{\text{eff}} = 1/2$ band. While the electronic correlations are relatively modest in comparison to 3*d*-transition metals, they act on an effective bandwidth that has been significantly reduced by the influence of the SOC. Consequently, the system is situated close to the Mott insulating regime, where U/W is approximately 1 (see Fig. 2.1.3). The cooperative interplay between U and SOC leads to the establishment of an insulating state. In this insulating state, the $J_{\text{eff}} = 1/2$ band is further split into lower (LHB) and upper Hubbard (UHB) bands, and these bands are separated by a small energy gap of approximately 0.5 eV. This phenomenon has been observed in various iridates, but particularly including layered perovskites like Sr₂IrO₄ and Sr₃Ir₂O₇ [10].



Figure 2.1.3: Schematic representation of the density of states of electrons in a material as a function of the ratio between the local Coulomb interaction U and the bandwidth of non-interacting electrons W within the Hubbard model. In the figure, we see how spectral features evolve in the dynamic mean-field solution of the Hubbard model under different conditions. (a) When electrons are entirely independent, the density of states is assumed to resemble a half ellipse, characteristic of a metal. The Fermi level (E_F) is situated in the middle of the band. (b) In weakly correlated materials (small U), electrons behave as quasiparticles, and their density of states remains akin to that of free electrons. The Fermi liquid model explains the slight peak narrowing. (c) Highly correlated metals exhibit a distinct three-peak structure in the spectrum: the Hubbard bands, arising from local "atomic" excitations and electron scattering at the atomic level, alongside the quasiparticle peak near the Fermi level. (d) The Mott-metal-insulator transition occurs when electron interactions are strong enough to eliminate the quasiparticle peak, redistributing its spectral weight to higher frequency components, including Hubbard bands. Figure taken from Ref. [15].

The crucial point of interest is that these unique electronic properties position strontium iridates as potential candidates for superconductivity. This stems from their closeness to a Mott insulating state and the presence of the $J_{\text{eff}} = 1/2$ band. However, the high degree of SOC and electronic correlations adds complexity to the situation. 5d transition metals, with their large SOC, exhibit intricate ground states. The potential for a complex interplay between spin-singlet and spin-triplet superconducting order parameters emerges, making it a challenging problem to determine the ground states in multi-orbital systems like iridates. These intricacies are a source of ongoing theoretical and experimental research [16].



Figure 2.1.4: Schematic phase diagram of Sr_2IrO_4 as a function of the band filling *n* and Hund's coupling J_H . A variety of possible phases appear such as an antiferromagnetic insulator (AF-I) and metal (AF-M), a paramagnetic metal (PM-M), a ferromagnetic metal (FM-M) as well as possibly two distinct superconducting (SC) phases. Figure taken from Ref. [16].

In the search for superconductivity in iridates, especially Sr_2IrO_4 , various experimental studies have been conducted to investigate the effects of doping with electrons or holes (see Fig. 2.1.4). These studies include methods such as oxygen depletion, La substitution, surface doping, and Rh substitution for Ir. While superconductivity has not been observed in these materials, the impact of even modest doping on their magnetic and transport properties is notable. For instance in bilayer $Sr_3Ir_2O_7$, the introduction of 5 % La leads to the emergence of a robust metallic state, with a significant drop in resistivity occurring below 20 K. This contrasts with La-doped Sr_2IrO_4 , where the magnetic order is entirely suppressed in the metallic state. Additionally, angle-resolved photoemission spectroscopy (ARPES) has provided valuable insights into the electronic behavior of doped iridates, revealing features reminiscent of doped cuprates. These observations motivate the continued exploration of superconductivity in doped iridates, with a focus on Sr_2IrO_4 , both theoretically and experimentally [16].

2.1.3 Strain effects in strontium iridates

The properties of strontium iridates (SIO) are strongly influenced by its unique structural and magnetic characteristics. As discussed in Sec. 2.1.1, the SIO unit cell consists of four IrO₂ layers separated by Sr^{2+} ions along the *c*-axis. In the *ab* plane, the Ir⁴⁺ ions are positioned within elongated oxygen octahedra. These octahedra exhibit an alternate rotation by about $\rho = 11.8^{\circ}$ degrees about the *c*-axis concerning the ideal tetragonal crystal structure I4/mmm [17].

SIO-214 undergoes an antiferromagnetic transition below the Néel temperature of around 240 K where Ir^{4+} spins and coupled orbital moments follow the rotation of the oxygen octahedra, forming a canted antiferromagnetic structure with a next-nearest-neighbor exchange constant J_1 of approximately 60 meV and a canting angle of the Ir^{4+} moments of around $\phi = 12.2 - 13.0^{\circ}$. This magnetoelastic locking of Ir⁴⁺ moments with the oxygen octahedra rotation was initially predicted by Jackeli and Khaliullin [18] and makes SIO-214 sensitive to strain effects.

The magnetic structure of SIO is similar to that of the superconducting parent compound La_2CuO_4 . However, there are differences. In La_2CuO_4 , the spin canting is out of the plane with a much smaller tilting angle, while in SIO, it's within the *ab* plane. This results in a smaller net magnetic moment in La_2CuO_4 [17].

Understanding the physical effects that promote or suppress superconductivity in oxide materials, especially by manipulating them to mimic each other more closely using external perturbations, such as doping, pressure, or elastic strain (see Fig. 2.1.5), is of great interest. Elastic strain can be particularly promising due to the strong magnetoelastic locking of the canting of Ir moments to the rotation of the oxygen octahedra [17].



Figure 2.1.5: (Left) Schematic of the Sr_2IrO_4 unit cell. Blue spheres represent O^{2-} , green spheres Ir^{4+} , and red spheres Sr^{2+} ions. The oxygen octahedra are highlighted. (Middle) Schematic representation of each IrO_2 plane in the unit cell of Sr_2IrO_4 with different net magnetic moments m_{net} of Ir^{4+} ions below the Néel temperature of 240 K. (**Right**) Schematic representation of the expected structural changes of the IrO_2 planes under compressive strain compared to the unstrained bulk, and tensile strain cases. The green arrows display the magnetic moments of the Ir^{4+} ions. The finite tilting of the moments results in a net magnetic moment m_{net} .

When epitaxial thin films are grown on substrates with significant lattice mismatch, they may undergo strain-induced modifications in bond lengths and angles [17].

Tensile strain tends to increase the rotation angle ρ of the IrO₆ octahedra and the Ir-O bond length, which can enhance the Coulomb correlation and the spin-orbit interaction. The compressive strain has the opposite effect. It's worth noting that larger changes in bond lengths and ρ can lead to a transition from the canted-antiferromagnetic ground state to a collinearantiferromagnetic ordering or a reorientation of Ir moments from the *a*-*b* plane to the out-ofplane direction along the *c*-axis [17].

The impact of epitaxial strain on the Néel temperature is subject to ongoing research. Some studies suggest an increase in Néel temperature for tensile-strained SIO, while others indicate a decrease. Raman spectroscopy has also revealed that compressive strain results in higher coupling strength J and hopping integral t in SIO thin films [17].

These findings underscore the complex and multifaceted nature of the interaction between structural strain and magnetic properties in SIO and similar materials. Understanding these effects is crucial for tailoring their properties for specific applications [17].

2.2 Neodymium nickelates

In the following section, we will discuss the physical properties of neodymium nickelates, which yield superconductivity in the infinite-layer nickelate compound.

2.2.1 Crystal structures of strontium-doped nickelates

 $Nd_{0.8}Sr_{0.2}NiO_3$ is a member of the perovskite family, which is characterized by the general formula ABO_3 . In this structure, A-sites are occupied by rare earth elements, such as neodymium (Nd) and strontium (Sr), while the B-sites are populated by transition metals, including nickel (Ni) (see Table 2.2.1).

Site	Element	X	У	Z	Spin	Oxidation	Occupation
0.8Nd + 0.2 Sr	0.8Nd + 0.2 Sr	0.43745	1/4	0.01537	3/2	+3	1
Ni	Ni	0	0	0	0	+3	1
O 1	0	0.1988	0.0528	0.3044	0	-2	1
O 2	0	0.5323	1/4	0.5996	0	-2	1

Table 2.2.1: Atomic coordinates and isotropic displacement of $Nd_{0.8}Sr_{0.2}NiO_3$ in the Pnma space group. Lattice constants are a = 5.365 Å, b = 7.613 Å and c = 5.396 Å. O1 and O2 are different oxygen sites. Data taken from Ref. [19].

The orthorhombic Pnma crystal structure of $Nd_{0.8}Sr_{0.2}NiO_3$ results from deviations from the ideal cubic perovskite arrangement. These deviations occur due to factors such as differences in the ionic radii of the A and B cations and the presence of oxygen octahedra that exhibit

tilting and rotation. These distortions from the cubic symmetry are often quantified using Goldschmidt's tolerance factor or Glazer angles.

The angle formed by the B-O-B bonds offers a quantifiable gauge of distortion within perovskite compounds, and it exhibits a proportional relationship with the Goldschmidt tolerance factor. For oxide materials, especially perovskites, it is common practice to employ pseudocubic notation, which simplifies the process of comparing lattice parameters. This notation proves highly beneficial when assessing lattice mismatches within the plane connecting a substrate to an oxide thin film, a critical aspect to ensure the high-quality growth of these materials [20].

In contrast, $Nd_{0.8}Sr_{0.2}NiO_2$ (see Table 2.2.2) exhibits a tetragonal P4/*mmm* crystal structure with infinite layers. This compound belongs to the emerging family of infinite-layered nickelates, which have gained substantial attention due to their potential for high-temperature superconductivity.

Site	Element	Х	У	Z	Spin	Oxidation	Occupation
0.8Nd + 0.2 Sr	0.8Nd + 0.2 Sr	1/2	1/2	1/2	3/2	+3	1
Ni	Ni	0	0	0	0	+1	1
Ο	0	0	1/2	0	0	-2	1

Table 2.2.2: Atomic coordinates and isotropic displacement of $Nd_{0.8}Sr_{0.2}NiO_2$ in the P4/*mmm* space group. Lattice constants are a = b = 3.921 Å and c = 3.281 Å. Data taken from Ref. [21].

The transition from the perovskite structure in $Nd_{0.8}Sr_{0.2}NiO_3$ to the tetragonal infinite-layer structure in $Nd_{0.8}Sr_{0.2}NiO_2$ is achieved through a topotactic reduction process. This process involves the removal of oxygen species from the host structure, leading to significant structural modification (see Fig. 2.2.1).



Figure 2.2.1: Crystal structures of orthorombic perovskite $Nd_{0.8}Sr_{0.2}NiO_3$ and tetragonal infinitelayer $Nd_{0.8}Sr_{0.2}NiO_2$. The figure illustrates the transition from one phase to another utilizing the CaH_2 reduction method. Scales are not considered.

One effective method to achieve the transition from the perovskite phase of $Nd_{0.8}Sr_{0.2}NiO_3$ to the infinite-layer phase of $Nd_{0.8}Sr_{0.2}NiO_2$ is through the use of calcium hydride (CaH₂) as a reducing agent. During this topotactic reduction process, CaH₂ reacts with the perovskite

compound, causing the removal of oxygen species, and leading to the formation of the tetragonal infinite-layer phase. The reaction involving CaH_2 as a reducing agent is a soft chemical process in which atoms undergo small displacements, requiring minimal energy. The reaction's efficiency is related to the strong reducing power of hydrides, making them suitable for inducing structural transitions in solid-state materials [20].

2.2.2 Discovery of superconductivity in infinite-layered nickelates

The discovery of superconductivity in infinite-layer Nd_{0.8}Sr_{0.2}NiO₂ suggests that it exhibits type-II superconducting behavior. Resistivity measurements with varying magnetic field perpendicular to the *a*-*b* plane observe a critical temperature at $T_C \approx 10.8$ K [1] (see Fig. 2.2.2). This finding was notably influenced by the analogy to copper oxides, which has opened up exciting possibilities for exploration in this new superconducting compound. However, it's important to acknowledge several key differences between these two systems.



Figure 2.2.2: Resistivity as a function of temperature of Nd_{0.8}Sr_{0.2}NiO₂ measured using different magnetic field strengths perpendicular to the a-b plane. Superconductivity has been observed at zero-field at $T_{\rm C} \approx 10.8$ K. Adapted from Ref. [1].

One prominent distinction lies in the energy level alignments of their orbital electronic structures. In copper oxides, the presence of holes is often described in terms of Zhang–Rice singlets, characterized by strong oxygen character. This arises from the close spatial overlap and nearenergetic degeneracy of the Cu $d_{x^2-y^2}$ orbitals and the O 2p orbitals. This feature naturally leads to large in-plane antiferromagnetic coupling, a factor many consider crucial for the superconducting pairing mechanism [1].

2.2 Neodymium nickelates

Conversely, in the infinite-layer nickelates, the chemical potential is positioned several electronvolts higher compared to copper oxides, mainly due to Ni¹⁺ being one column to the left of Cu^{2+} on the periodic table and one oxidation state lower. Consequently, when introducing holes into nickelates, one can anticipate far less hybridization with the O 2p band. Furthermore, studies utilizing powder neutron diffraction for LaNiO₂ and NdNiO₂ have not shown any indication of magnetic order down to temperatures of 5 K and 1.7 K, respectively [1].

Therefore, it becomes apparent that two essential features that play a central role in copper oxides – namely, the Zhang–Rice singlet and large planar spin fluctuations may either be absent or significantly reduced in the nickelate superconductors. These distinctions emphasize the unique electronic and magnetic properties of this newly discovered superconducting compound [1].

Part I

Unconventional superconductors

Chapter 3 New pulsed laser deposition system

This particular chapter provides a brief overview of the new pulsed laser deposition (PLD) system by DCA Instruments. PLD plays a pivotal role in creating complex thin film materials with unique properties such as strontium iridates and neodymium nickelates thin films. The details, advantages, challenges as well as our own experience working with a new system will be also provided in this chapter.

3.1 Ultra-high vacuum thin film cluster system

The pulsed laser deposition (PLD) system is part of an advanced state-of-the-art thin film deposition system dedicated to cutting-edge materials research provided by DCA Instruments. What distinguishes DCA Instruments thin film deposition systems (Fig. 3.1.1 and Fig. 3.2.3) is their seamless integration into a unified ecosystem. A buffer line connects the loadlock, sputtering, molecular beam epitaxy (MBE), and pulsed laser deposition (PLD) systems in ultra-high vacuum (UHV) environment, allowing for efficient sample transfer between processes without exposing samples to atmospheric conditions. Moreover, the entire system is controlled by computers, ensuring precise and reproducible deposition processes. All these systems form a coherent and versatile platform for the synthesis and characterization of thin films with unprecedented precision. The different parts of the UHV cluster are:



Figure 3.1.1: Top view of the new UHV cluster deposition system provided by DCA Instruments employing sputtering, MBE, and PLD systems connected to one buffer line enabling sample transfer without contaminating samples to ambient conditions.

Loadlock: The journey through the cluster deposition system begins with the loadlock, a critical component designed to maintain the integrity of the UHV environment. The loadlock serves as a gateway for introducing samples, substrates, and PLD targets into the system without compromising the vacuum conditions of the other chambers. The base pressure of 5×10^{-9} mbar minimizes contamination and ensures the purity of the subsequent deposition processes.

Sputtering: Within the integrated system, the sputtering chamber is dedicated to fabricated Nb- and Al-based superconducting thin films. Employing a plasma discharge, sputtering enables precise control over the deposition rate and composition, making it ideal for creating superconducting thin films with tailored properties.

Molecular beam epitaxy (MBE): MBE represents the epitome of precision in thin film deposition. This technique enables the growth of epitaxial layers with atomic-scale precision, making it invaluable for fabricating quantum materials, topological insulators, and metallic thin films with low microwave damping. In the MBE chamber, elemental or compound sources are thermally evaporated within different effusion cells, allowing the precise control of film compo-

sition, thickness, and crystalline structure at the atomic level. The MBE chamber is equipped with a turbo molecular pump, an ion getter pump as well as a cryo-shield to reach a base pressure of 2×10^{-10} mbar. In addition, to the thermal evaporation of materials a six-pocket electronbeam evaporation system allows the fabrication of thin films with materials with high melting temperatures such as Pt.

Pulsed laser deposition (PLD): PLD is another pivotal component of this integrated system, offering unique capabilities for the fabrication of complex oxide thin films. Using a pulsed highenergy excimer UV-laser, PLD ablates a target material, generating a plasma plume of vaporized atoms or molecules that condense onto the substrate. This technique is particularly suitable for creating oxide materials, superconductors, and multilayer structures with exceptional quality and stoichiometry.

Buffer line: The connection between these core components is made by a UHV buffer line with a base pressure of 2×10^{-10} mbar that facilitates the smooth transfer of samples between modules while maintaining the UHV environment. This ensures that researchers can seamlessly switch between deposition techniques, enabling the fabrication of high-quality thin film heterostructures with well-defined interfaces.

Within this thesis, we have fabricated oxide thin films using PLD, which will be described in more detail in the next section.

3.2 Pulsed laser deposition

PLD is a complex and advanced technique for controllable thin film growth. Since the detailed physics behind the complex pulsed laser deposition process is not the main topic of this thesis, this section will provide a brief overview of the PLD process. For an in-depth discussion of the PLD process, the reader is referred to the review by Haider *et al.* [22] and references therein.

3.2.1 Concepts of pulsed laser deposition

Pulsed laser deposition (PLD) stands as a widely adopted thin-film deposition method with applications spanning academia and industry [23]. Its distinct advantages over alternative deposition techniques make it a preferred choice. PLD offers exceptional adaptability, enabling precise control over growth rates, stoichiometric transfer, and a virtually limitless range of ablation geometries [22].

One of the most notable features of PLD is its superior control over deposition stoichiometry, which is based on a stoichiometric transfer of material from a target to a substrate through the intermediate plasma plume. Therefore, this technique is particularly suitable for complex deposition compositions. While PLD may appear deceptively straightforward, it involves a series of intricate processes. These encompass laser absorption, plasma plume formation, and thin film growth. The complexity of the PLD approach is further magnified, especially at elevated

pressures, underscoring the need for a nuanced understanding of its underlying principles and intricacies [22].

During ablation, a high-energy nanosecond UV laser pulse is focused onto a target surface using a lens system and interacts with its material. This interaction is influenced by several factors, including the absorption coefficient, target material's reflectivity, laser pulse frequency, laser wavelength, and laser fluence [22]. The interaction causes rapid conversion of photons into electronic excitations affecting a depth of only a few tens to hundreds of nanometers of the target material [22]. These excitations swiftly transit into lattice, chemical, and mechanical energy, which results in abrupt ablation of the target material, driven by high laser fluences and power densities. The temperature at any point in the material during the laser pulse is determined by the heat flow equation. While the equation accounts for various parameters, including density, thermal heat capacity, thermal conductivity, and laser intensity, it remains complex due to these parameters' temperature-dependent nature. Thermal ablation can occur in vaporization and explosive boiling modes. However, only vaporization and explosive boiling are compatible with the nanosecond laser pulse timescale. The rate of material vaporization can be calculated using the Hertz-Knudsen equation, taking into account the material's latent heat of vaporization, pressure, and temperature [22].

After the laser ablation, a dense vapor layer forms in front of the target surface. The absorbed energy elevates the pressure and temperature of this vapor, eventually leading to partial ionization. The intense pressure propels this layer, termed the "plasma plume", away from the target surface. During this adiabatic expansion with high velocities [22], internal heat and ionization energies are transformed into kinetic energy, reaching several hundred electron volts. These energetic particles then scatter as they encounter a low-pressure background gas and condense on a substrate surface [22, 24]. Importantly, this ablation process occurs before thermal equilibrium in the target material is reached, ensuring a stoichiometric transfer of the target material into the plasma plume and ultimately onto the substrate surface (see Fig. 3.2.1).



(a) Plasma plume from top-side view

(b) Plasma plume from side view



On the substrate surface, there is a transition from the plasma plume to a crystalline solid phase. This crystalline thin film nucleation depends on different factors, namely the laser energy, pulse repetition rate, density and degree of ionization of the ablated material, substrate temperature, physicochemical properties of the substrate, as well as the background gas [25]. However, the substrate temperature and the so-called supersaturation taking place between the plasma and solid phase transition are the main thermodynamic parameters. A high supersaturation rate may be needed to initiate crystalline nucleation at the substrate surface, while a low supersaturation rate is required to facilitate a single crystal film growth with low roughness. In general, three growth modes can be distinguished [26]: In the island or Volmer-Weber growth mode, small clusters nucleate directly on the substrate surface and into three-dimensional islands. In this case, the atoms or molecules of the deposited material are more strongly bound to each other than to the substrate surface. This is the opposite in the Frank-van der Merwe growth mode. Since the deposited material is more strongly bound to the substrate than to each other, a two-dimensional layer-by-layer growth mode with low surface roughness can be achieved. The third growth mode, the Stranski-Krastanov growth mode, describes a transition from a twodimensional layer-by-layer into a three-dimensional island growth mode after a few monolayers. In the case of substrates with finite miscut angles, a second two-dimensional growth mode can be realized by two-dimensional nucleation on substrate terraces, the so-called step-flow growth mode. Which mode occurs depends on the atomistic processes in the early stages of thin film growth described by competing kinetic and thermodynamic effects of the deposited atoms. The reader is referred to Refs. [26, 27] for a detailed overview of atomistic properties of thin film growth.

3.2.2 Advantages and challenges of pulsed laser deposition

The PLD technology has demonstrated exceptional effectiveness in developing epitaxial films, facilitating the creation of multilayers, heterostructures, and superlattices on lattice-matched substrates [28]. PLD offers the unique advantage of enabling film growth in highly reactive gas environments across a range of pressures. It achieves suitable kinetic energy (10 - 100 eV) and photochemical excitation during film growth, which can enhance the quality of the deposited films compared to other deposition techniques. However, PLD's practical limitations include its relatively low duty cycle and the potential incorporation of particles into deposited films [29, 30].

The simplicity of PLD has made it a staple in research laboratories for thin film development, ablation, and deposition. Its potential extends to various commercial applications, including coated conductors, microwave filters, solar cells, sensors, and satellite communication. PLD employs a high-power density laser with a narrow, wide bandwidth to vaporize the target material effectively. In summary, PLD offers ease of generating multicomponent films with precise stoichiometric ratios, rapid deposition rates, short processing times, and low substrate temperatures. Its adaptability, development potential, compatibility, and ability to control growth make it a promising choice for materials research and commercial applications. Furthermore, PLD's ability to generate plasma using a UV pulsed laser with high photon capacity and energy density makes it an environmentally friendly and manageable technology [22].

3.2.3 The pulsed laser system PLD500 from DCA instruments

Within this thesis, we have fabricated thin films using the PLD500 system from DCA Instruments (see Figs. 3.2.2 and 3.2.3). One distinguishing feature of the PLD system is its base pressure of 8×10^{-10} mbar after bakeout the chamber for at least 24h. This ultra-high vacuum environment is based on turbomolecular pumps together with a well-designed differential pumping module, which ensures minimal contamination during the deposition process.



(a) Pulsed laser deposition (PLD) system

(b) Sample holder

Figure 3.2.2: Side view of the PLD system and bottom view of a laser-heated substrate in the substrate holder.

For the laser ablation process, we use a Coherent KrF-excimer UV-laser with a wavelength of 248 nm and pulse duration of approximately 10 ns. In principle, PLD employs short-wavelength nanosecond UV-pulses. Longer wavelengths and pulses are prone to thermal effects associated with droplet formation [22]. To focus the laser pulse on the target surface, we use a three-lenszoom system with a magnification of 0.09 creating a sharp laser spot with an area of 0.084 cm^2 on the target surface. Together with a software-controlled attenuator module within the beam path of the UV laser, the energy density at the target surface can be continuously tuned from 1 J/cm^2 to 4 J/cm^2 . The laser fluence at the target is an essential parameter in PLD. It must exceed the binding energy of the target material elements for laser pulse ablation and determine the ablation rate. Furthermore, higher fluence can impact the target's surface characteristics, including morphology, optical, and electrical properties [22]. To realize precise control of the laser fluence, the power and energy of the UV laser pulses can be automatically measured within the PLD chamber using a laser power meter.

The target is placed on one of the six one-inch target holders of the target manipulator. Each of the targets can be removed and installed separately via the buffer line. To optimize target efficiency and homogeneity as well as operational uptime, the PLD500 system incorporates an oscillating target movement. During ablation, this component orchestrates a continuous rotation and a simultaneous rocking motion of the target material. This dynamic movement pattern

ensures uniform target erosion, thereby minimizing target costs and increasing ablation homogeneity. Additionally, a water-cooled cover safeguards the front of the target manipulator during high-temperature substrate annealing, preserving target integrity. An electro-pneumatic rotary shutter further protects the selected target area. Additionally, specially designed aperture plates can be installed enabling plasma-plume shaping mainly to decrease the formation of droplets at the substrate surface.

The substrate with a maximum size of $10 \text{ mm} \times 10 \text{ mm}$ is installed in a sample manipulator, which is equipped with a magnetic rotary drive for motorized rotation (< 60 RPM) to increase deposition homogeneity. Using a motorized z-drive, the target to substrate distance can be varied from 55 to 65 cm. At this distance, growth monitoring by reflection high-energy electron diffraction (RHEED) is still possible. By using a high-power IR laser together with a laser head equipped with a fiber-coupled pyrometer and camera the substrate is heated from the backside (see Fig. 3.2.2(b)). This laser heating module occupies a prominent role in the PLD system and allows for precise control of the substrate temperature up to $1300 \,^{\circ}\text{C}$.



Figure 3.2.3: Technical drawing of the PLD500 provided by DCA Instruments.

The choice of the background gas type as well as an accurate control of the background gas pressure within the chamber during deposition is a further crucial aspect of PLD operation. The PLD500 system offers four different gas types (Ar, O_2 , N_2 , and H_2) and a mixture of them.

The pressure control is carried out by up-stream (flow control) and down-stream (throttle-valve control) approaches. The former adjusts the flow rate using precise mass-flow controllers at a fixed throttle-valve position, while the latter represents the opposite control scheme.

Although the PLD500 system offers detailed and precise control of PLD parameters mainly influencing the thin films growth. It is important to acknowledge that the PLD system is not without its challenges. Its operational life is inherently limited, necessitating periodic maintenance that can be intricate and demanding. Moreover, PLD demands the use of extensive and high-purity gases, with continuous replenishment, which can be resource-intensive. Additionally, the system's footprint can be considerable due to its various components and requirements.

3.2 Pulsed laser deposition

Chapter 4

Fabrication of strontium iridate thin films

With the previously described PLD500 system, we have fabricated strontium iridate strontium iridium oxide thin film, strontium iridate thin film (SIO) thin films on $SrTiO_3$ (STO) and $(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.7}$ (LSAT) substrates. To optimize the crystalline structure of the thin films, we have varied the substrate temperature, gas pressure, and laser fluence. This chapter emphasizes the great variability of PLD fabrication process for SIO thin films.

4.1 Substrates

For the fabrication of SIO-214 thin films, we have chosen two different but structurally similar single-crystalline substrates – $SrTiO_3$ (STO) and $(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.7}$ (LSAT). Both crystallize in a cubic crystal structure. The lattice parameters are close to that of the SIO-214 phase with a epitaxial relation of $[100]_{STO}$ || $[110]_{SIO}$ and $[001]_{STO}$ || $[001]_{SIO}$. Another important reason is that they are chemically compatible with SIO-214 thin films during the growth process, ensuring that the desired material properties are maintained, and lastly, they can withstand high temperatures.

4.2 Growth optimization

Our goal was to fabricate high crystalline SIO-214 thin films with the new PLD500 system. There are different PLD parameters that influence the growth process of the thin films. Therefore, we have conducted three sets of optimization series – firstly varying substrate temperature, then changing partial oxygen pressure, and lastly the varying fluence at the target surface. These steps will eventually lead to single-crystalline thin films of the desired SIO-214 phase.

4.2.1 Substrate temperature series

The substrate temperature has the biggest influence on the quality of the SIO thin films. To investigate this influence on the crystalline structure, we have fabricated SIO thin films in the range $550 \,^{\circ}\text{C} - 900 \,^{\circ}\text{C}$ with $50 \,^{\circ}\text{C}$ step. We have been guided by the paper by Nishio *et al.* [31] to expect at a SIO-214 phase at $850 \,^{\circ}\text{C}$. To investigate the structural properties, we have performed high-resolution X-ray diffractometry (HRXRD) measurements around the expected SIO-214 (0 0 12) as well as the STO (0 0 2) substrate reflection. Figure 4.2.1 displays the results of the $2\theta - \omega$ scans of the SIO thin films fabricated by different substrate temperatures

using an oxygen pressure of $10 \,\mu$ bar and $25 \,\mu$ bar, respectively. The 2θ -angle of the SIO-214 $(0 \ 0 \ 12)$ reflection is indicated by the vertical dashed line. We clearly see that the SIO-214 $(0 \ 0 \ 12)$ reflection is clearly visible at substrate temperatures $T_S > 750 \,^{\circ}$ C, slowly fading out by increasing even further. We have found that SIO thin films fabricated at a substrate temperature of $850 \,^{\circ}$ C and an oxygen pressure of $25 \,\mu$ bar exhibit a single SIO-214 phase with the highest crystallinity. The SIO-214 (0012) reflection is shifted to higher 2θ angles mainly due to epitaxial strain.



Figure 4.2.1: HRXRD measurements of SIO thin films fabricated with different substrate temperatures on STO substrates using an oxygen pressure of 10 μ bar and 25 μ bar with the same 72 % transmission of the UV laser which equates to a 2.1 J/cm² fluence at the target surface (T-series). The vertical dashed line corresponds to the theoretical bulk 2θ -value of the SIO-214 (0 0 12) reflection.

4.2.2 Pressure series

After finding the best crystallinity of SIO-214 thin films at a substrate temperature of $850 \,^{\circ}\text{C}$ we have varied the oxygen pressure in the PLD chamber. Guided by Ref. [31] we have fabricated SIO in the range of $5 \,\mu\text{bar} - 55 \,\mu\text{bar}$ on LSAT using a fixed substrate temperature of $850 \,^{\circ}\text{C}$ as well as an UV laser pulse transmission of 90 %, which corresponds to an energy density of around $3.5 \,\text{J/cm}^2$ at the target surface. The HRXRD measurements on these SIO thin film samples reveal different SIO phases for oxygen pressures lower than $25 \,\mu\text{bar}$ as well as larger than $40 \,\mu\text{bar}$ (see Fig. 4.2.2). It is clear that $25 \,\mu\text{bar}$ and $40 \,\mu\text{bar}$ show the best results.



Figure 4.2.2: HRXRD measurements of SIO thin films grown on LSAT substrates at different oxygen pressures and fixed substrate temperature of $850 \,^{\circ}$ C with the same $90 \,\%$ transmission of UV-laser which equates to $3.5 \,\text{J/cm}^2$ energy fluence at the target surface (p-series). The vertical dashed line corresponds to the theoretical bulk 2θ -value of the SIO-214 (0 0 12) reflection.

4.2.3 Fluence series

Lastly, we have determined which laser fluence is the most compatible with the SIO-214 phase. Figure 4.2.3 displays the results of the HRXRD measurements of different SIO thin films fabricated with different laser fluences on the target using the determined optimal substrate temperature of 850 °C and oxygen pressures of 25 μ bar as well as 10 μ bar on the two different substrates STO and LSAT. Interestingly, by varying the transmittance of the UV excimer laser pulses from 50% to 90%, we can produce two different phases of the strontium iridate Ruddlesden-Popper series. For a transmission of 50% of the UV laser pulse, HRXRD measurements reveal a possible SrIrO₃ phase with Laue oscillations demonstrating a coherent thin film growth with high crystallinity and low roughness (see black curve in Fig. 4.2.3 top left panel). At higher fluence, we have produced higher crystallinity of the SIO-214 phase. We therefore have chosen the sample fabricated at 850 °C, 25 μ bar and 90% transmittance which equates to 3.5 J/cm² fluence for further measurements.



Figure 4.2.3: HRXRD measurements of SIO thin films fabricated on STO and LSAT substrates at $10 \,\mu$ bar and $25 \,\mu$ bar with a substrate temperature of $850 \,^{\circ}$ C using different transmission of the UV-laser pulses (TR-series). Different phases of SIO can be observed in different SIO thin films fabricated using different transmissions of the UV laser pulses. The vertical dashed line corresponds to the theoretical 2θ -value of the SIO-214 (0 0 12) reflection.

4.3 Summary

After growth optimization, fabricating a variety of SIO thin films with different substrate temperatures, different oxygen pressures, and different energy fluence of the excimer UV laser at the SIO target, we have found that the best crystalline quality of strontium iridate thin films with Sr₂IrO₄ phase have been found for SIO thin films fabricated with a substrate temperature of 850 °C, an oxygen pressure of 25 μ bar and a 90 % transmittance of the UV laser pulses, which corresponds to an energy fluence at the target of 3.5 J/cm². However, as obvious from Fig. 4.2.3, these SIO thin films exhibit a good, but not perfect crystalline quality. In particular, they do not show any finite thickness fringes (Laue oscillation) demonstrating a more disordered growth. Furthermore, the rocking curves around the SIO-214 (0 0 12) reflection reveal a high
mosaicity demonstrated by a large full width at half maximum of around 0.5° . Since we have scanned through nearly the full thin film growth phase diagram, other restraints might be present explaining the poor crystallinity of the SIO thin films.

In PLD deposition, the state of the target material is also a crucial parameter. We therefore fabricated a new SIO target and produced SIO thin films using the above-determined optimum growth parameters. We further found that an increase of the target to substrate distance by 5 mm to 65 mm reveals SIO thin films with good crystalline qualities as shown in Fig. 4.3.1.

The 2θ -scan reveals two prominent reflections of the thin film and the substrate indicating high crystallinity of our film and no presence of other $Sr_{n+1}Ir_nO_{3n+1}$ phases. It is also worth mentioning the finite thickness fringes (Laue oscillations) around the thin film reflection due to the finite size of the thin film. They indicate a coherent growth over the whole thickness, which points to a high crystalline quality. To investigate the crystalline quality of the SIO-214 thin film even further we have performed a rocking curve around the SIO-214 (0 0 12) reflection (Fig. 4.3.1). We have fitted the rocking curve with a Two-Gaussian model. The thin peak with high intensity exhibits a full width at half maximum (FWHM) of 0.02° demonstrating an excellent crystalline quality of the thin film. The second more broad component with a FWHM of 0.0873° points to structural imperfections, and/or a strain relaxation of SIO-214 grown on STO substrate.



Figure 4.3.1: HRXRD data of a SIO thin film produced using a newly fabricated polycrystalline SIO target. The thin film is deposited using a substrate temperature of $850 \,^{\circ}$ C, an oxygen pressure of $25 \,\mu$ bar, and a 90 % transmittance of the UV-laser pulses. Furthermore, the substrate-target distance has been increased by 5 mm to 65 mm. The good crystalline quality is revealed by finite thickness fringes around the SIO-214 (0 0 12) reflection (top left panel) as well as the narrow rocking curve with a full width at half maximum (FWHM) of 0.02° (top right panel). The simulation of the X-ray reflectometry data reveals a low roughness as well as a thickness of 112 nm (bottom panel).

We have also performed an X-ray reflectometry scan (see Fig. 4.3.1 bottom panel). The simulation of the data reveals a root mean square roughness of approximately 1.5 nm as well as a thickness of the SIO-214 thin films of 112 nm.

To investigate the magnetic properties of this SIO thin film, we have performed SQUID magnetometry measurements at different temperatures and external magnetic fields. Figure 4.3.2 shows the magnetization as a function of temperature with an external magnetic field of 0.2 T applied in the film plane. The change in slope of the M(T)-curve indicates a magnetic ordering temperature of around 225 K, which is close to the bulk value of SIO-214 ($T_N = 250$ K [3]). Figures 4.3.1 and 4.3.2 therefore represent the starting point for further optimization of SIO-214 thin films using the new PLD500 system from DCA instruments.



Figure 4.3.2: SQUID magnetometry measurements of a SIO thin film grown on a STO substrate using a new polycrystalline SIO target. The magnetization is normalized to 100 K. The change in slope at $T_{\rm N} \approx 225$ K indicates the magnetic ordering temperature of the SIO-214 phase, which is close to the bulk temperature value of 250 K [3].

Chapter 5

Growth optimization of neodymium nickelate thin films

The parent material to investigate superconductivity in infinite-layer neodymium nickelate thin films is the perovskite-based material system $Nd_{0.8}Sr_{0.2}NiO_3$. This chapter therefore discusses the growth optimization of $Nd_{0.8}Sr_{0.2}NiO_3$ thin films on $(LaAIO_3)_{0.3}(Sr_2TaAIO_6)_{0.7}$ (LSAT) substrates using the new PLD500 system from DCA instruments. To this end, we have varied the substrate temperature, gas pressure, and laser fluence to find the best parameters to fabricate $Nd_{0.8}Sr_{0.2}NiO_3$ thin films.

5.1 Growth optimization

In this thesis, we have focused on the material system $Nd_{0.8}Sr_{0.2}NiO_3$, which can then be reduced to the superconducting infinite-layer nickelate compound $Nd_{0.8}Sr_{0.2}NiO_2$ as discussed in Ch. 2. Therefore, it is important to first realize $Nd_{0.8}Sr_{0.2}NiO_3$ thin films with high crystalline quality. To this end, we have conducted three sets of optimization series – firstly varying the substrate temperature, then changing the partial oxygen pressure via gas flow, and lastly varying the energy fluence at the target surface similar to the optimization of the thin film growth of strontium iridate thin films discussed in the previous chapter.

5.1.1 Substrate temperature series

The variation of the substrate temperature for the fabrication of neodymium nickel oxide (NNO) thin films has delivered a great variety of different crystalline phases as revealed by high-resolution X-ray diffractometry (HRXRD) measurements (see Fig. 5.1.1). Some phases were hard to identify since epitaxial strain as well as oxygen deficiencies might play a dominant role. However, we interpret the different reflections visible in the HRXRD data as different phases of the Sr-doped Ruddlesden-Popper series Nd_{n+1}Ni_nO_{3n+1}. In Fig. 5.1.1 the 2 θ -position of the bulk (0 0 6) reflection of the Nd₂NiO₄-phase (n = 2), the (0 0 14) reflection of the Nd₄Ni₃O₁₀-phase (n = 3) as well as of the (002) reflection of the desired Sr-doped NdNiO₃-phase ($n \to \infty$) are indicated with vertical dashed lines. Furthermore, the 2 θ position of a possible NiO parasitic phase is also indicated. As obvious from Fig. 5.1.1 none of the NNO thin films show the NdNiO₃ phase. However, as the NNO thin film fabricated with a substrate temperature of 600 °C seems to deliver the best crystalline quality, we have chosen this substrate temperature for further optimizations.



Figure 5.1.1: HRXRD data of NNO-thin films fabricated with different substrate temperatures on LSAT substrates at an oxygen pressure of 100 μ bar and with a 72 % transmission of the UV laser pulses which equates to 2.3 J/cm² energy fluence at the target surface (T-series). Different phases of the Sr-doped Ruddlesden-Popper series Nd_{n+1}Ni_nO_{3n+1} have been observed. The dashed vertical lines correspond to theoretical 2θ values of the bulk reflections of the Nd₂NiO₄-phase (NNO-214) with n = 2, the Nd₄Ni₃O₁₀-phase (NNO-4310) with n = 3 as well as the NdNiO₃-phase (NNO-113) with $n \to \infty$. Furthermore, the 2θ reflection of a possible NiO parasitic phase is also indicated. The reflection at $2\theta \approx 42.1^{\circ}$ corresponds to the LSAT substrate reflection with Cu K- β wavelength.

5.1.2 Pressure series

Changing the oxygen gas pressure has also created a great variety of different NNO phases. We clearly can see Laue oscillations in Fig. 5.1.2, indicating a good crystalline growth of NNO-214 and NNO-4310 phases with some possible epitaxial strain. But most importantly this time we have spotted Nd_{0.8}Sr_{0.2}NiO₃ "shoulders" right to the LSAT (0 0 4) substrate reflection using an oxygen pressure of 150 μ bar.



Figure 5.1.2: HRXRD measurements of NNO thin films fabricated using different oxygen pressures (*p* series) on LSAT at 600 °C with the 80 % transmission of UV laser which equates to an energy fluence of 2.9 J/cm² at the target surface (p-series). Different Sr-doped Nd_{*n*+1}Ni_{*n*}O_{3*n*+1} phases can be observed. The vertical dashed lines represent the 2 θ position of reflections from these phases with n = 1, n = 2, and $n \to \infty$ (see Fig. 5.1.1).

5.1.3 Fluence series

The results of the HRXRD measurements of NNO thin films fabricated at a substrate temperature of 600 °C as well as an oxygen pressure of 100 μ bar with different excimer laser transmission are not much different to the HRXRD data of the temperature series. Low fluences with transmission < 72 % produce NNO phases with no or little crystallinity. On the other hand, at high fluences with a transmission of 90 % the crystallinity is also reduced. Furthermore, X-ray reflectometry as well as atomic force microscopy measurements reveal an increase in surface roughness. We will stick to a transmission of 72 % of the UV laser pulses because it produces NNO thin films with the highest X-ray intensity and visible Laue oscillations.



Figure 5.1.3: HRXRD measurement data of NNO thin films fabricated at different UV-laser transmission on LSAT substrates using a substrate temperature of 600 °C and an oxygen pressure of 100 μ bar (TR series). The 2 θ position of different NNO-phases of the Sr-doped Ruddlesden-Popper series Nd_{n+1}Ni_nO_{3n+1} are marked as vertical dashed lines similar to Figs. 5.1.1 and 5.1.2.

5.2 Summary

As the Sr-doped perovskite compound NdNiO₃ (NNO) is the starting point for the investigation of superconductivity in infinite-layer nickelates (see Chapter 2), we have fabricated a variety of Sr-doped NNO thin films under different growth conditions to find the optimum growth parameters. By analyzing the structural properties of these thin films by high-resolution X-ray diffraction, we have found a set of parameters, which yield the best crystalline quality of the NNO thin films so far. However, NNO thin films fabricated under these conditions, namely a substrate temperature of 600 °C, an oxygen pressure of 150 µbar as well as an energy fluence at the target surface of 2.4 J/cm^2 show additional phases of the Sr-doped Ruddlesden-Popper series Nd_{n+1}Ni_nO_{3n+1} (as indicated by vertical dashed lines in Fig. 5.2.1) demonstrating the complex nature of neodymium nickelate thin films. In this HRXRD data the desired Sr-doped NNO-113 phase is visible as a broad reflection at around 24° as well as a shoulder at slightly larger 2θ -angles than the LSAT (0 0 4) substrate reflection.



Figure 5.2.1: HRXRD measurements of a neodymium nickelate thin film fabricated at a substrate temperature of 600 °C, an oxygen pressure of 150 µbar and a 72 % transmission of the UV laser which equates to an energy fluence of 2.4 J/cm^2 at the target surface. The vertical dashed lines mark the different phases of the Sr-doped Ruddlesden-Popper series $Nd_{n+1}Ni_nO_{3n+1}$.

As demonstrated by the optimization of SIO thin films discussed in the previous chapter, the distance between target and substrate could also play a significant role in the fabrication of single-phase $Nd_{0.8}Sr_{0.2}NiO_3$ thin films and needs to take into account in further optimization processes. Furthermore, the oxygen gas pressure should be delicately adjusted to get rid of other phases.

Part II

Resonant inelastic X-ray scattering of strontium iridate thin films

Chapter 6

Theory and experimental set-up

Strontium iridate thin films (SIO) are an interesting class of materials that exhibit a range of intriguing electronic properties, including topological insulating behavior and the possibility for high-temperature superconductivity. The perovskite-based Ruddlesden-Popper series $Sr_{n+1}Ir_nO_{3n+1}$ attracted considerable scientific attention due to the possibility of generating new physics properties within a strong spin-orbit coupling regime (see Ch. 2). However, understanding the nature of these properties requires a detailed understanding of the electronic ground state of these materials, which can be challenging to obtain using conventional spectroscopic techniques.

This is where resonant inelastic X-ray scattering (RIXS) comes in – by providing a way to directly probe the electronic and magnetic excitations in strontium iridate thin films. RIXS can provide valuable analysis into the underlying physics of these materials. By measuring the energy and momentum of the emitted X-rays, RIXS can reveal information on the electronic structure, magnetic interactions, and excitations of these materials, providing a powerful tool for studying their properties and potential applications.

6.1 Resonant inelastic X-ray scattering

This subsection is completely referred to the paper provided by Ament *et al.*, titled "Resonant inelastic X-ray scattering studies of elementary excitations" [32]. The paper discusses the use of resonant inelastic X-ray scattering (RIXS) as a tool for studying elementary excitations in various materials. We only took basic knowledge without deepening in details.

RIXS is a powerful experimental photon-in photon-out spectroscopic technique that can analyze the electronic structure and excitations of materials. RIXS is particularly useful for studying transition metal compounds and their complex electronic interactions. This technique uses synchrotron radiation to excite an atom or molecule and measure the energy of the emitted X-rays.

Compared to other scattering techniques, RIXS has several unique features. It covers a large scattering phase space, is polarization and penetration depth dependent, element and orbital specific, and requires only small sample volumes. The scattering phase space available to X-rays is larger than that of electrons or neutrons, enabling RIXS to probe the full dispersion of low-energy excitations in solids. RIXS is element and orbital-specific, with chemical sensitivity



Figure 6.1.1: Direct RIXS is a two-step process: An electron in the core level is excited into the valence band by an incoming photon (initial step). The hole is then filled by an electron from another valence state emitting an outgoing photon. In the indirect RIXS process, there is an intermediate state: the valence electrons scatter off the hole in the core level through the Coulomb interaction $U_{\rm C}$. This leads to excitations of the valence electrons (intermediate step). In the final stage the photoelectron decays leaving the resulting excitation in the valence band with a momentum $\hbar \mathbf{k}' - \hbar \mathbf{k}$ and an energy $\hbar \omega_{\mathbf{k}} - \hbar \omega_{\mathbf{k}'}$. \mathbf{k}' and \mathbf{k} are the outgoing and incoming wave vectors as well as $\hbar \omega_{\mathbf{k}'}$ and $\hbar \omega_{\mathbf{k}}$ are photon energies after and before excitation, respectively. Figure from Ref. [32].

arising from tuning the incident photon energy to specific atomic transitions of different types of atoms in a material. It is also bulk sensitive, with a penetration depth of a few microns for hard X-rays and around $0.1 \,\mu\text{m}$ for soft X-rays, making it possible to study small volume samples, thin films, surfaces, and nano-objects. It can utilize the polarization of the photon to disentangle the nature of the excitations created in the material and to characterize their symmetry and nature, allowing for the probing of a broad class of intrinsic excitations of the system under study, as long as these excitations are overall charge neutral.

When an incident X-ray photon is absorbed by a material, an electron in the material is excited to an unoccupied state at higher energy. In the RIXS process, the energy and momentum of the emitted photon can change from the incident one due to two different scattering mechanisms known as direct and indirect RIXS.

In direct RIXS, a core electron is excited by an incoming photon into the valence band (see

the initial state in Fig. 6.1.1). The empty state in the core level is then filled by an electron from another valence state emitting an outgoing photon (see the final state in Fig. 6.1.1). In this case, the energy and momentum of the emitted photon are directly related to the energy and momentum of the incident photon.

In indirect RIXS, there is an intermediate step (see Fig. 6.1.1). The electron is excited from a core level into the valence shell. Excitations are created through the Coulomb interaction $U_{\rm C}$ between the core hole (and in some cases the excited electron) and the valence electrons. The photoelectron subsequently decays, leaving behind an excitation in the valence band as shown in Fig. 6.1.1 with momentum $\hbar \mathbf{k}' - \hbar \mathbf{k}$, where \mathbf{k}' and \mathbf{k} are outgoing and incoming wave vectors respectively. This process involves a more complicated scattering mechanism, and the energy and momentum of the emitted photon can change due to the interactions between the excited electron and other electrons in the material.

The classification of a RIXS process as being either direct or indirect is useful because the cross sections for each are quite different. For the direct RIXS process, both photoelectron transitions (the initial transition from the core level to the valence band and the final one from the valence to the core level) must be allowed. In transition metal ions, for example, this could be a dipole transition $2p \rightarrow 3d$ followed by a $3d \rightarrow 2p$ transition. When direct scattering is allowed, as the energy levels and electronic transitions in the material satisfy the selection rules for both the initial and final transitions, it is the dominant inelastic scattering channel, with indirect processes contributing only in higher order. In contrast, for the large class of experiments for which direct scattering is forbidden, RIXS relies exclusively on indirect scattering channels. In the following, we imply only the indirect process as the direct process is not applicable for a complex Ruddlesden-Popper series $Sr_{n+1}Ir_nO_{3n+1}$. These complex materials, like many others with intricate energy levels, orbital symmetries, and spatial electron distributions, do not readily satisfy the selection rules for direct RIXS, making indirect RIXS the primary scattering channel in RIXS experiments on such materials.

Resonant scattering in the context of RIXS refers to the phenomenon where the incident Xrays have an energy close to the resonant energy level of the sample's core electrons. When the incident X-rays are tuned to this resonant energy, they can excite core-level electrons to higher energy states through a process called resonant absorption. The resonant energy is specific to each element and corresponds to the energy difference between the core-level electron's ground state and an excited state. This energy is typically in the range of X-ray energies. When the incident X-rays are resonant with this energy, the probability of exciting the core electrons is greatly enhanced compared to off-resonant energies. In our RIXS measurements on strontium iridate thin films we have tuned the energy of the incoming X-rays to the L_3 -edge of Ir (the excitation of a metal 2p electron to unfilled 5d orbitals).

By using the RIXS intensity formula, we can predict and interpret the experimental RIXS spectra. It allows us to extract valuable information about the electronic and magnetic properties of the material, such as the energy and dispersion of excitations, the spin and orbital states, and the coupling between different degrees of freedom. Comparing the calculated intensity with the

experimental data helps in understanding the underlying physical processes and properties of the material. The RIXS intensity can in general be written in terms of a scattering amplitude as

$$I\left(\omega, \mathbf{k}, \mathbf{k}', \boldsymbol{\epsilon}, \boldsymbol{\epsilon}'\right) = \sum_{f} \left| \mathcal{F}_{fg}\left(\mathbf{k}, \mathbf{k}', \boldsymbol{\epsilon}, \boldsymbol{\epsilon}', \omega_{\mathbf{k}}\right) \right|^{2} \delta\left(E_{f} + \hbar\omega_{\mathbf{k}'} - E_{g} - \hbar\omega_{\mathbf{k}}\right)$$
(6.1)

where the sum goes over-excited states f. E_g and E_f are ground state and final state energies, respectively. The delta function preserves energy conservation and the amplitude $\mathcal{F}_{fg}(\mathbf{k}, \mathbf{k}', \boldsymbol{\epsilon}, \boldsymbol{\epsilon}', \omega_{\mathbf{k}})$ decides which excitations (plasmons, phonons, charge-transfer, crystal-field, orbital, or magnetic excitations) are probed and how the spectral weights of final state excitations depend on the polarization vectors $\boldsymbol{\epsilon}$ and $\boldsymbol{\epsilon}'$ of the incoming and outgoing X-rays respectively. RIXS spectroscopy takes advantage of photon polarization to unravel the properties of excitations generated in a material. By analyzing the polarization of the incident and scattered photons, one can characterize the symmetry and nature of these excitations using selection rules. That is why polarization vectors should not be abandoned. Moreover, the polarization effects such as dipole and quadrupole transitions are crucial in the interpretation of the RIXS at the L- and M-edges in transition-metal compounds, where our interest in investigating Ir atoms lies.

To derive the specific scattering amplitude, particularly for strontium iridates, one would need to consider the relevant theoretical models, the crystal structure and properties of strontium iridates, and the experimental setup. This derivation typically involves applying quantum mechanical and computational techniques to describe the scattering process and incorporate the specific properties of the material under investigation. It is worth noting that the derivation of the scattering amplitude for a particular material involves sophisticated calculations and often requires advanced theoretical and experimental techniques.

The fundamental scattering amplitudes can be obtained numerically, and several approximation schemes have been developed to provide more insight into the scattering amplitude. These approximation schemes involve the propagation of the system in the time between absorption and emission processes. Generally, these schemes allow the separation of the fundamental scattering amplitudes into a resonance function $P(\omega_{\mathbf{k}}, \omega_{\mathbf{k}'})$ and an effective transition between ground and final states $\langle f | W^x | g \rangle$. The resonance function gives the strength of the fundamental scattering amplitude, which is a combination of radial matrix elements of transition operators and energy denominators that describe the resonant effect as a function of $\omega_{\mathbf{k}}$. The effective transition operators create excitations in the valence shell similar to an optical excitation and can be related to correlation functions such as the dynamic structure factor.

The indirect RIXS process is more complex than simple absorption or emission because it involves both the creation and annihilation of a photon and an intermediate state, which makes it a higher-order process that cannot be simply described by Fermi's golden rule, just like in Eq. (6.1). Instead, the Kramers-Heisenberg formula is used to describe RIXS. In this formula, the RIXS intensity is proportional to the square of the scattering amplitude, which is a function of the energy and momentum transfer between the incident and outgoing photons, as well as the

polarization of the photons and the sample. X-rays are described by an electromagnetic field with vector potential $\mathbf{A}(\mathbf{r},t)$ and their interaction with electrons is governed by the theory of quantum electrodynamics. The electrons are assumed to move slowly compared to the speed of light ($v \sim \hbar Z/ma_0 \approx 0.21c$, where Z the atomic number of the probed element and a_0 the Bohr radius), and the potentials related to both electrons and photons are assumed to be small compared to twice the mass of the electron $e\phi/2m_ec^2$, $e|\mathbf{A}|/2m_ec \ll 1$. These assumptions are valid for existing X-ray sources but may not hold for future X-ray free-electron lasers. For simplification, relativistic effects are neglected, and formalism is developed for non-relativistic electrons in small potentials. In these limits, one obtains for a system with N electrons the total Hamiltonian:

$$H = \sum_{i=1}^{N} \left(\frac{[\mathbf{p}_{i} + e\mathbf{A}(\mathbf{r}_{i})]^{2}}{2m} + \frac{e\hbar}{2m} \boldsymbol{\sigma}_{i} \cdot \mathbf{B}(\mathbf{r}_{i}) + \frac{e\hbar}{2(2mc)^{2}} \boldsymbol{\sigma}_{i} \cdot \{\mathbf{E}(\mathbf{r}_{i}) \times [\mathbf{p}_{i} + e\mathbf{A}(\mathbf{r}_{i})] - [\mathbf{p}_{i} + e\mathbf{A}(\mathbf{r}_{i})] \times \mathbf{E}(\mathbf{r}_{i})\} \right) + \frac{e\hbar^{2}\rho(\mathbf{r}_{i})}{8(m_{e}c)^{2}\epsilon_{0}} + H_{\text{Coulomb}} + \sum_{\mathbf{k},\boldsymbol{\varepsilon}} \hbar\omega_{\mathbf{k}} \left(a_{\mathbf{k}\boldsymbol{\varepsilon}}^{\dagger}a_{\mathbf{k}\boldsymbol{\varepsilon}} + \frac{1}{2}\right)$$
(6.2)

where $\mathbf{p}_i, \mathbf{r}_i$, and $\boldsymbol{\sigma}_i$ are, respectively, the momentum and position operators and the Pauli matrices acting on electron *i*. $\mathbf{A}(\mathbf{r})$ is the vector potential, $\mathbf{E}(\mathbf{r}) = -\nabla\phi - \partial \mathbf{A}/\partial t$ the electric field, and $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}$ the magnetic field. $a_{\mathbf{k}\varepsilon}^{\dagger}$ annihilates (creates) a photon in the mode with wave vector \mathbf{k} and polarization vector ε . The second term yields the Zeeman splitting, and the third includes spin-orbit coupling. The interaction of electrons with an external electric potential and with other electrons and nuclei in the sample (including the Darwin term) are all described by H_{Coulomb} . The vector potential can be expanded in plane waves as

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{k},\varepsilon} \sqrt{\frac{\hbar}{2\mathcal{V}\epsilon_0 \omega_{\mathbf{k}}}} \left(\varepsilon a_{\mathbf{k}\varepsilon} e^{i\mathbf{k}\cdot\mathbf{r}} + \varepsilon^* a_{\mathbf{k}\varepsilon}^{\dagger} e^{-i\mathbf{k}\cdot\mathbf{r}} \right)$$
(6.3)

where \mathcal{V} is the volume of the system.

The process of deriving the photon scattering cross section involves splitting the Hamiltonian H into two parts: the electron-photon interaction part H', in which all terms are dependent on \mathbf{A} , and the remaining terms H_0 , which describe the electron and photon dynamics in the absence of electron-photon interactions. The perturbation theory is then used to calculate the RIXS cross section by assuming the presence of a single photon in the initial state with momentum $\hbar \mathbf{k}$, energy $\hbar \omega_{\mathbf{k}}$, and polarization ε that is scattered to $(\hbar \mathbf{k}', \hbar \omega_{\mathbf{k}'}, \varepsilon')$ in the final state.

To derive H', the terms of Eq. (6.2) are classified by their powers of **A**. The terms of H that are quadratic in **A** are the only ones to contribute to the first-order amplitude, as they contain terms proportional to $a^{\dagger}_{\mathbf{k}'\varepsilon'}a_{\mathbf{k}'\varepsilon}$ and $a_{\mathbf{k}\varepsilon}a^{\dagger}_{\mathbf{k}'\varepsilon'}$. The quadratic contribution from the first term of H gives rise to non-resonant scattering, while the third term of H yields magnetic non-resonant scattering. Although both these terms appear in the first-order scattering amplitude, they in principle also contribute to the second order, but they are neglected because they are of order $\alpha^{3/2}$.

Therefore, the relevant electron-photon interaction part H' is

$$H' = \sum_{i=1}^{N} \left[\frac{e}{m} \mathbf{A}(\mathbf{r}_{i}) \cdot \mathbf{p}_{i} + \frac{e^{2}}{2m} \mathbf{A}^{2}(\mathbf{r}_{i}) + \frac{e\hbar}{2m} \boldsymbol{\sigma}_{i} \cdot \nabla \times \mathbf{A}(\mathbf{r}_{i}) - \frac{e^{2}\hbar}{(2mc)^{2}} \boldsymbol{\sigma}_{i} \cdot \frac{\partial \mathbf{A}(\mathbf{r}_{i})}{\partial t} \times \mathbf{A}(\mathbf{r}_{i}) \right]$$
(6.4)

The interaction of photons with the material leads to a change in the system from the ground state $|g\rangle$ to the final state $|f\rangle$ with energies E_g and E_f , respectively. During this process, the photon loses momentum $\hbar \mathbf{q} = \hbar \mathbf{k} - \hbar \mathbf{k}'$ and energy $\hbar \omega = \hbar \omega_{\mathbf{k}} - \hbar \omega_{\mathbf{k}'}$ to the sample. To calculate the transition rate for this process, Fermi's golden rule to second order is used:

$$w = \frac{2\pi}{\hbar} \sum_{f} \left| \langle f|H'|g \rangle + \sum_{n} \frac{\langle f|H'|n \rangle \langle n|H'|g \rangle}{E_g - E_n} \right|^2 \delta\left(E_f - E_g\right)$$
(6.5)

The transition rate for the process is given by the sum of two terms: the first-order amplitude, which yields non-resonant scattering, and the second-order amplitude causing resonant scattering. Although the first-order amplitude usually dominates the second-order, when the incoming X-rays are in resonance with a specific transition in the material $(E_g \approx E_n)$, the second-order terms become large.

Skipping rigorous calculations for the sake of simplification one arrives at the final form of the scattering intensity, where the double-differential cross section is now obtained referring to Kramers-Heisenberg equations:

$$I\left(\omega,\mathbf{k},\mathbf{k}',\boldsymbol{\varepsilon},\boldsymbol{\varepsilon}'\right) = r_e^2 m^2 \omega_{\mathbf{k}'}^3 \omega_{\mathbf{k}} \sum_{f} \left| \mathcal{F}_{fg}\left(\mathbf{k},\mathbf{k}',\boldsymbol{\varepsilon},\boldsymbol{\varepsilon}',\omega_{\mathbf{k}},\omega_{\mathbf{k}'}\right) \right|^2 \delta\left(E_g - E_f + \hbar\omega\right)$$
(6.6)

where $r_e = (1/4\pi\varepsilon_0)e^2/mc^2$ is the classical electron radius and the scattering amplitude at zero temperature is given by

$$\mathcal{F}_{fg}\left(\mathbf{k},\mathbf{k}',\boldsymbol{\varepsilon},\boldsymbol{\varepsilon}',\omega_{\mathbf{k}},\omega_{\mathbf{k}'}\right) = \sum_{n} \frac{\left\langle f\left|\mathcal{D}'^{\dagger}\right|n\right\rangle \left\langle n|\mathcal{D}|g\right\rangle}{E_{g} + \hbar\omega_{\mathbf{k}} - E_{n} + i\Gamma_{n}}$$
(6.7)

where transition operator for the RIXS cross-section \mathcal{D} and \mathcal{D}' refer to transitions related to the incoming and outgoing X-rays, respectively:

$$\mathcal{D} = \frac{1}{im\omega_{\mathbf{k}}} \sum_{i=1}^{N} e^{i\mathbf{k}\cdot\mathbf{r}_{i}} \boldsymbol{\varepsilon} \cdot \mathbf{p}_{i}$$
(6.8)

Equations (6.6) and (6.7) represent the Kramers-Heisenberg expression for RIXS. To yield better understandable transition operators, separation into a part containing the geometry of the experiment as well as to fundamental scattering amplitudes, relating the physical properties of the probed system (see Ref. [32] for more details).

6.2 Experimental set-up

The RIXS experiment presented in the framework of this thesis has been carried out at the ID20 beamline at the European Synchrotron Radiation Facility (ESRF), which is specialized in the investigation of electronic and magnetic excitations in matter using RIXS, non-resonant inelastic X-ray scattering (NIXS) as well as emission spectroscopy in the hard X-ray regime. The main scientific activities of ID20 are focused on the investigation of strongly correlated electron systems, functional materials, and the study of matter at extreme conditions such as using diamond anvil cells for high-pressure experiments, or other complex sample environments, e.g. for in-situ and operando studies of batteries, fuel cells, and chemical reactors [33].



Figure 6.2.1: Schematic view of the beamline ID20 (top panel) and the spectrometer used for RIXS. The beamline ID20 is equipped with a collimating mirror (CM), a double-crystal Si (1 1 1) and a channel-cut Si (8 4 4) monochromator. The monochromatic beam is focused using a toroidal focusing mirror (FM) and a Kirkpatrick-Baez mirror (KB) on the sample at the center of the resonant inelastic X-ray scattering (RIXS) spectrometer. Experimental energy resolution at the Ir atom L_3 edge (~ 12.8 keV) determined from energy scans on polymer results to $\Delta E \approx 26 \text{ meV}$. Figure taken from Ref. [10].

6.2 Experimental set-up

The ID20 beamline employs Maxipix 2D detectors, a 5-element Avalanche Photodiode array, and a Pilatus 300K-W detector (from the loan pool) to detect the X-rays scattered by the samples. These detectors enable high-resolution measurements and high signal-to-noise ratios. The beamline is equipped with two spectrometers: one for NIXS studies and the other is a RIXS spectrometer equipped with five spherical crystal analyzers, operating in the horizontal or vertical scattering plane. The overall energy resolution of this spectrometer depends on the chosen monochromatization scheme and the crystal analyzer reflection and ranges from 25 meV to 2 meV [34].



Figure 6.2.2: Crystal analyzers and detector assembly. Where θ_i and χ_i are analyzer rotations, θ_D is detector rotation, x_i , y_i , and z_i are analyzer translations, and x_D , y_D , and z_D are detector translations. The sample position is shown as a red sphere. Figure taken from Ref. [35].

ID20 also offers a range of sample environments to researchers, such as a Dynaflow He exchange gas cryostat (3 - 300 K), Miniflow He cryostat (3 - 300 K), Cryostream (80 - 300 K), Heat blower (300 - 800 K), and high-pressure cells (up 1 Mbar and beyond). These sample environments enable researchers to study the properties of materials at a wide range of temperatures and pressures [34].

In summary, the ID20 beamline provides a unique opportunity for researchers to study the electronic and magnetic properties of materials, using a variety of techniques and sample environments. The experimental observables that can be studied include magnons, *d-d* and charge transfer excitations, plasmons, core- and valence emission lines, and mono-, dipolar- and multipolar transitions from core levels. The ID20 beamline is an important facility for advancing our understanding of fundamental materials science, as well as for the development of new materials for various applications, such as energy storage and conversion.

Chapter 7 Experimental data

In this chapter, we will investigate the structural and magnetic properties of two first members of the Ruddlesden-Popper series $Sr_{n+1}Ir_nO_{3n+1}$, namely Sr_2IrO_4 (SIO-214) and $Sr_3Ir_2O_7$ (SIO-327) thin films, along with their resonant inelastic X-ray scattering (RIXS) data. We will first discuss the structural and magnetic properties of the thin films used for RIXS experiments and then present the results of the RIXS measurements at different momentum and temperatures.

7.1 Resonant inelastic X-ray scattering on Sr₂IrO₄ thin films

In the following section the structural and magnetic properties, as well as resonant inelastic Xray scattering (RIXS) data of a Sr_2IrO_4 (SIO-214) thin films are discussed. The SIO-214 thin film is fabricated by pulsed laser deposition (PLD) on a (0 0 1)-oriented SrTiO₃ (STO) substrate using the former PLD500 system from the DCA Instruments (see Part I, Ch. 3). The deposition is carried out at a substrate temperature of 650 °C in an oxygen atmosphere with a pressure of 25 µbar using a laser fluence at the polycrystalline target of 2 J/m² and a repetitive rate of the excimer laser of 2 Hz. These deposition parameters are quite different from the optimal parameters found for the fabrication of SIO-214 thin films using the new PLD500 system (see Part I, Ch. 3).

7.1.1 Structural and magnetic properties of the Sr₂IrO₄ thin films used for the RIXS experiment



Figure 7.1.1: SQUID magnetometry measurement of the SIO-214 thin film. The magnetization is normalized to 100 K temperature. The magnetic ordering temperature $T_{\rm N} \approx 228$ K is marked by a vertical arrow.

Magnetic properties According to Cao *et al.* [36], the magnetic susceptibility $\chi(T) = M(T)/H$ of Sr₂IrO₄ shows evidence for weak ferromagnetism below $T_N = 240$ K above a critical magnetic field of $\mu_0 H = 0.2$ T. The magnitude of the weak ferromagnetic moment was estimated to be $\mu_{\text{FM}} \approx 0.07 \ \mu_{\text{B}}/\text{Ir}$ [37], but this value cannot be attributed to $J_{\text{eff}} = 1/2$ magnetic moments that are perfectly aligned ferromagnetically. As was shown by Boseggia [10], the expected magnetic moment for the $J_{\text{eff}} = 1/2$ state is 1 μ_{B} in the ionic limit. Crawford *et al.* [3] proposed that a canted antiferromagnetic state could explain these observations. In this case, the ferromagnetic moment would represent only a small fraction of the total magnetic ordering temperature of the SIO-214 thin film on STO measured by us via superconducting quantum interference device (SQUID) magnetometry of $T_N \approx 228$ K is similar to the bulk value of 250 K [36] (see Fig. 7.1.1). The small discrepancy in transition temperature is most probably due to epitaxial strain effects or finite-size effects.



Figure 7.1.2: HRXRD measurements of the SIO-214 thin film on SrTiO₃ (STO) substrate.

Structural properties The structural quality of the SIO-214 thin film has been measured via high-resolution X-ray diffractometry (HRXRD) utilizing 2θ - ω and ω scans. The 2θ - ω scan shown in Fig. 7.1.2(a) reveals a prominent reflection of the thin film and the substrate indicating a high crystallinity of our film and no presence of other Sr_{n+1}Ir_nO_{3n+1} phases. The small symmetrical oscillations in intensity around the thin film reflection caused by a finite size of the thin film (Laue oscillations) indicate a coherent growth over the whole thickness, which points to a high crystalline quality. To further investigate the crystalline quality of the SIO-214 thin film we have performed a rocking curve (ω scan) around the SIO-214 (0 0 12) reflection. We have fitted the obtained data with a two-Gaussian model (see blue curve in Fig. 7.1.2(b)). The thin high peak with a full width at half maximum (FWHM) of 0.0155° demonstrates an excellent crystalline quality of the thin film. The component with a larger FWHM of 0.1194° points to a higher mosaicity due to structural imperfections most probably in the thin film layer close to the STO substrate.

Strain effects Previous studies have shown that the physical properties of materials can be significantly altered by strain effects induced by growing them on substrates with different lattice parameters. In the case of Sr_2IrO_4 , its growth on a $SrTiO_3$ (STO) substrate has been found to cause strain effects that alter its lattice parameters and, in turn, its physical properties [38].



Figure 7.1.3: Reciprocal space map of SIO-214 thin film and STO substrate. The black dashed line indicates the centered growth of SIO-214 on STO substrate.

To investigate the epitaxial strain of the SIO-214 thin film on STO we have performed reciprocal space map around the SIO-214 (2 2 16) reflection (Fig. 7.1.3). The (2 2 16) reflection is located centrally below the STO (1 0 3) substrate reflection with the same in-plane q_{h00} value. This indicates that the SIO-214 thin film is fully strained on the STO substrate. The different Miller indices (h k) hereby indicate that the SIO-214 thin film is grown on the diagonal of the (0 0 1)-oriented STO substrate. At the ID20 beamline of the European Synchrotron Radiation Facility (ESRF), we precisely aligned the SIO-214 thin film with respect to the scattering plane defining the orientation matrix (UB matrix) of the sample. From this alignment, the lattice constants of the SIO-214 thin film are derived.

Substrate	a = b (Å)	<i>c</i> (Å)	T (K)	$arepsilon_{xx}$	ε_{zz}
SIO-214	5 407	25 708	205	00%	0%
bulk [3]	5.497	20.190	290	070	070
STO	5.511	25.700	120	0.25%	-0.38%

Table 7.1.1: Lattice constants and calculated strain values of the SIO-214 thin film on a STO substrate. The lattice constants are derived from the alignment of the SIO-214 at the ID20 beamline at the ESRF at 120 K before the RIXS measurement. These values are compared to bulk values of SIO-214 at 295 K [3].

Table 7.1.1 summarizes the lattice constants of the SIO-214 thin film grown on a STO substrate as compared to those of bulk SIO-214. The in-plane (ϵ_{xx}) and out-of-plane strain (ϵ_{zz}) are given relative to the bulk values. Table 7.1.1 shows that there is a small but significant strain in the sample grown on STO substrate. The lattice parameter a of Sr₂IrO₄ grown on STO substrate is slightly larger than that of the bulk sample, indicating tensile strain along the a axis (in-plane strain), while the lattice parameter c is slightly smaller, indicating compressive strain along the c axis (out-of-plane strain). The magnitude of the strain is relatively small, with the strain along the a axis being only 0.25% and the strain along the c axis being -0.38%.

These strain effects have been found to have significant impacts on the physical properties of SIO-214 grown on STO substrate. For example, it has been shown in Ch. 7 that the strain leads to changes in the magnetic properties of Sr_2IrO_4 with the magnetic ordering temperature being shifted to higher values.

7.1.2 RIXS data

In the following subsection, we will discuss the RIXS data of the Sr_2IrO_4 thin film on $SrTiO_3$ (STO) substrate. The measurements have been conducted at T = 20 K and T = 120 K. It is important to note that the temperature difference does not influence the magnon dispersion much as will be shown in Part II, Ch. 8.

Figure 7.1.4 shows the results of RIXS measurements at 20 K with different in-plane momenta Q, i.e. different (h k) values along the $(0, \pi)$ direction at l = 24. One can distinguish solid black lines, which correspond to the experimental data, blue lines derived from the fitting of the experimental data, dashed red lines indicate the energy of the magnon peak, and vertical dashed black lines mark the position of the elastic line accordingly. The blue line inherits either two-Gaussian or three-Gaussian models. The first peak is considered to be the elastic line, which was shifted to zero energies. The second one is responsible for magnetic excitation [39]. A third peak was observed at some (h k) values and seems to have a non-dispersive nature.

Following the red dashed line, a dispersive nature in both the left and upper graphs of the magnon excitations can be observed. Despite the good visibility of peaks we have fitted them with Gaussian models and achieved an error $\Delta E \approx 10 \text{ meV}$, which is less than the energy resolution of the ID20 beamline, which is around $\Delta E \approx 26 \text{ meV}$.



Figure 7.1.4: RIXS data of the SIO-214 thin film measured at the ID20 beamline with different inplane momenta Q, i.e. different (h k) values at a fixed l = 24 along the $(0, \pi)$ direction at T = 20 K. Black lines represent the experimental data, blue lines are fitted to the data using Gaussian peak functions, red dashed lines track the energy position of magnon excitations, and the vertical black dashed line at zero energy is the elastic line.

The bottom single plot was only needed to better cover the local extremum of spin wave dispersion relation which we discuss in Part II, Ch. 8. We can see some "shoulders" on the high energy side of each magnon excitation possibly contributing to the multimagnon continuum.



Figure 7.1.5: RIXS data of the SIO-214 thin films measured at the ID20 beamline with different in-plane (hk) values, i.e. different in-plane momenta Q along the $(\pi/2, \pi/2)$ direction at T = 20 K. Black lines represent the experimental data, blue lines are fitted to the data using Gaussian peak functions, red dashed lines track the energy position of the magnon excitation, and the vertical black dashed line at zero energy is the elastic line.

Figure 7.1.5 shows the RIXS data along the in-plane $(\pi/2, \pi/2)$ direction measured at T = 20 K again at different momenta (h k) and Q values with l = 24. The magnon peaks are homogeneous with equally broad peaks and lesser noise. The left and right panels are pretty identical demonstrating the identical in-plane momentum using different (h k) values.

After extracting the energy of the magnon excitations from the RIXS data of Sr_2IrO_4 thin films grown on STO substrate, we would like to compare the thus obtained spin wave dispersion relation to the dispersion reported by different papers before continuing with the simulation of our data. In contrast to other reports on RIXS using SIO-214 single crystals, we have used an epitaxially strained SIO-214 thin film, which could modify the magnon dispersion of SIO-214. We would like to analyze if the spin wave dispersion of SIO-214 provided by other papers is in agreement with our data. Figure 7.1.6 takes into account five different publications with the same fitting model Eq. (8.4) from Part II, Ch. 8 but with different coupling strengthens as well as anisotropies. Table 7.1.2 provides an overview of these values.

Coupling	Kim single crystal [39]	Pincini bulk [40]	Clancy (iso.) bulk [41]	Clancy (aniso.) bulk [41]	Vale bulk [42]
J_1	$60\mathrm{meV}$	$57\mathrm{meV}$	$62\mathrm{meV}$	$65\mathrm{meV}$	$57\mathrm{meV}$
J_2	$-20\mathrm{meV}$	$-16.5\mathrm{meV}$	$-19\mathrm{meV}$	$-19\mathrm{meV}$	$-18\mathrm{meV}$
J_3	$15\mathrm{meV}$	$12.4\mathrm{meV}$	$13\mathrm{meV}$	$13\mathrm{meV}$	$14\mathrm{meV}$
α	0	0.05	0	0.02	0.08

Table 7.1.2: Values of each coupling strengthens and anisotropy factor provided by different papers for SIO-214. The detailed overview can be found in Part II, Ch. 8.

Firstly, it is worth mentioning that values provided by Kim *et al.* [39], as one of the first publications on RIXS on single-crystalline SIO-214, are derived from a phenomenological theory and empirical data. It has been stated that the exchange constants $J_1 = 60 \text{ meV}$, $J_2 = -J_1/3 = -20 \text{ meV}$, $J_3 = J_1/4 = 15 \text{ meV}$ fit the experimental data best. The black line which shows the calculated spin dispersion using these values is slightly off from our data. The green line representing the spin wave dispersion published by Clancy *et al.* [41] provides also a mode, which does not fully fit our data. They are both suitable for our two points near 0 meV at $(0, \pi)$ and in proximity to (0, 0), but deviate from other Q points. This gives us a clue that a finite anisotropy has to be taken into account. Spin dispersion relations provided by Vale *et al.* [42] or Pincini *et. al* [40] which are taking into account an anisotropy in the easy-plane between first neighbors of the Ir⁴⁺ ions reveal in Fig. 7.1.6 that this model is in best agreement to our experimental data. A finite anisotropy factor results in a gap at $(0, \pi)$ and (0, 0) decrease the slope of the dispersion in the $(\pi/2, \pi/2)$ direction, which fits better to our data.



Figure 7.1.6: Spin wave dispersion relations of SIO-214 provided by different authors depicted as color solid lines. The extracted energy loss of magnon excitations of our RIXS data measured at different temperatures is plotted as solid and open symbols with error bars.

Additional peaks with weak dispersion We have spotted some additional peaks in our RIXS data at low energy loss close to the elastic line, which show only a weak dispersion as it can be seen in Fig. 7.1.7. Interesstingly, these peaks do only appear for measurements with (h k) values larger than (50) in the $(0, \pi)$ direction and larger than (40) in the (π, π) direction, but are not visible for measurements in the $(0, \pi)$ direction with h < 5 as well as for h < 4 in the (π, π) direction. The main difference between these measurements at different (h k) values but the same in-plane momentum Q is the intensity of the elastic line (see Fig. 7.1.4 top left

and top right panel). Therefore, these peaks might be correlated to the elastic line. Additional measurements have to be carried out to clarify the origin of these additional peaks.



Figure 7.1.7: RIXS data of SIO-214 measured at the ID20 beamline along $(0, \pi)$ and $(\pi/2, \pi/2)$ direction at T = 20 K (black lines). Additional shoulders close to the elastic line are visible, which are fitted by a single Gaussian peak function (purple lines).

7.2 Resonant inelastic X-ray scattering on Sr₃lr₂O₇ thin films

In the following section the structural and magnetic properties, as well as resonant inelastic Xray scattering (RIXS) data of the Sr₃Ir₂O₇ (SIO-327) thin films used for RIXS experiments are discussed. The SIO-327 thin films are fabricated by pulsed laser deposition (PLD) on a (0 0 1)oriented SrTiO₃ (STO) and (0 0 1)-oriented (LaAlO₃)_{0.3}(Sr₂TaAlO₆)_{0.7} (LSAT) substrate at substrate temperature of 600 °C in the oxygen atmosphere with a pressure of 75 µbar using a laser fluence at the polycrystalline target of 2 J/m² and a repetitive rate of the excimer laser of 2 Hz.





Figure 7.2.1: SQUID magnetometry measurements of the SIO-327 thin films grown on STO and LSAT substrates. The magnetization is normalized to the magnetization at 100 K. Two transitions can be observed: the onset of a weak ferromagnetic component at $T_{\rm C} \approx 260$ K as well as a further upturn of the magnetization at $T^* \approx 220$ K which is attributed to a spin-reorientation transition.

Magnetic properties SIO-327 is a bilayer iridate compound that exhibits bulk properties similar to those of the single layer compound SIO-214. Cao *et al.* first reported that $Sr_3Ir_2O_7$ is barely an insulator and exhibits weak ferromagnetism in the basal plane below a transition temperature T_C of approximately 285 K with a second transition occurring at $T^* \approx 260$ K, attributed to a spin-reorientation [7]. Our SQUID magnetometry measurement (Fig. 7.2.1) carried out at $\mu_0 H = 0$ T delivers values around 260 K and 220 K, accordingly. The deviation from the bulk value might be explained by strain effects and/or finite oxygen vacancies within the SIO-327 thin films. Interestingly, only one transition temperature is visible in the SIO-327 thin film grown on a LSAT substrate.

The magnetic moment reported at 150 K in an applied field of 7 T is less than 0.003 μ_B/Ir , much smaller than the corresponding magnetic moment in Sr₂IrO₄ ($\mu_{FM} \approx 0.07\mu_B/Ir$) [37]. The effective moment deduced from a high-temperature Curie-Weiss fit the magnetic susceptibility in a field of 7 T was reported to be 0.67 μ_B/Ir , comparable to the value of 0.5 μ_B/Ir found in SIO-214 [36]. These results indicate a similar microscopic magnetism in the Sr-based layered iridates but a different origin of the weak ferromagnetic components in the two compounds.

The peculiar temperature dependence of magnetization in SIO-327 and the differences among various studies suggest that the weak ferromagnetism could originate from an extrinsic moment produced by defects rather than a canting mechanism, as in the single-layer counterpart. The



canting picture is, in fact, inconsistent with the observed magnetic and crystal structure [10].

Figure 7.2.2: HRXRD measurements on SIO-327 thin films grown on (**a**) a STO substrate as well as (**b**) a LSAT substrate.

Structural properties The structural quality of the SIO-327 thin films have been measured via high-resolution X-ray diffractometry (HRXRD) utilizing 2θ - ω scans as well as rocking curve. The 2θ - ω scans shown in Fig. 7.2.2 reveal reflections of the SIO-327 thin films and the substrates indicating high crystallinity of our films and no presence of other Sr_{n+1}Ir_nO_{3n+1} phases. To investigate the crystalline quality of the SIO-327 thin films we have performed rocking curves around the SIO-327 (0 0 10) reflection (see Fig. 7.2.2). We have fitted the rocking curves of both SIO-327 thin films grown on STO and LSAT substrates with a two-Gaussian model. The thin high peaks with FWHMs of 0.0200° and 0.0137°, respectively, demonstrate the excellent crystalline quality of both thin films. The broad component with FWHMs of 0.0839° and 0.2519°, respectively, point to possible imperfections, increasing the mosaicity of the SIO-327 thin films.



Figure 7.2.3: Rocking curves around the SIO-327 (0 0 12) reflection of the SIO-327 thin films on (a) a STO substrate and (b) a LSAT substrate. The blue curves represent a fit to the data using a two-Gaussian fit function revealing a full width at half maximum (FWHM) of the rocking curves of 0.0200° and 0.0137° , respectively.

Strain effects We have also investigated the strain state of the Sr₃Ir₂O₇ thin films grown on STO and LSAT substrates. Table 7.2.1 summarizes the lattice constants measured at the ID20 beamline at the ESRF. The results show that the in-plane lattice constants a, b of Sr₃Ir₂O₇ grown on LSAT are reduced, while the out-of-plane lattice constant c is increased leading to strained components ε_{xx} and ε_{zz} values of -0.80% and 1.78%, respectively. On the other hand, the Sr₃Ir₂O₇ thin film grown on STO shows a smaller reduction of the in-plane lattice constants and also a smaller increase of the out-of-plane lattice constant c, which results in ε_{xx} and ε_{zz} values of -0.26% and 0.48%, respectively. These findings demonstrate that the different substrates lead to different strain states, which significantly influence the lattice parameters of the SIO-327 thin films.

Substrate	a = b (Å)	c (Å)	T (K)	$arepsilon_{xx}$	ε_{zz}
SIO-327	3 806	20.870	200	0%	0%
bulk [7]	3.890	20.079	300	070	070
LSAT	3.865	21.250	20	-0.80%	1.78%
STO	3.886	20.980	20	-0.26%	0.48%

Table 7.2.1: Lattice constants of the SIO-327 thin films grown on STO and LSAT substrates measured at the ID20 beamline of the ESRF. Strain components are relative to bulk values.

The difference of the in-plane lattice constant a, b of the two SIO-327 thin films grown on LSAT and STO substrates as shown in Table 7.2.1 has also been investigated using reciprocal space maps using a HRXRD lab source (see Figs. 7.2.4 and 7.2.5). In these measurements, a small deviation of the position of the $(1\ 0\ 15)$ reflections with respect to the respective substrate can be observed. However, the small intensity of the thin film reflection hinders a detailed



evaluation of the in-plane strain state of the SIO-327 thin films.

Figure 7.2.4: Reciprocal space map of the SIO-327 thin film on a STO substrate. The vertical black dashed line indicates the center of the STO $(1\,0\,3)$ substrate reflection.



Figure 7.2.5: Reciprocal space map of the SIO-327 thin film on a LSAT substrate. The vertical black dashed line indicates the center of the LSAT $(1\ 0\ 3)$ substrate reflection.

7.2.2 RIXS data

In the following subsection, we will discuss the RIXS data of the $Sr_3Ir_2O_7$ thin films on $SrTiO_3$ (STO) and $(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.7}$ (LSAT) substrates. The measurements have been conducted at T = 20 K and T = 120 K for the SIO-327 thin film on LSAT and only at T = 20 K for the film on STO at the ID20 beamline. One must confess that the temperature difference did not significantly alter the magnon positions, as it will be shown in Part II, Ch. 8.

The Fig. 7.2.6 shows the RIXS data measured at $(h \ k \ l)$ reflections for different in-plane momenta along $(\pi/2, \pi/2)$ direction at l = 24 for the SIO-327 thin film grown on both LSAT and STO substrates. The solid black lines represent the experimental data, while the blue lines fit the data using two Gaussian peak functions. The first peak is considered as the elastic line and has been shifted to zero energy. The second peak is interpreted as magnon excitations. All plots show the dispersive nature of magnon excitations indicated by the red dashed line. The magnon peaks were easily identified and fitted with the Gaussian function.


Figure 7.2.6: RIXS data measured with different in-plane momenta along $(\pi/2, \pi/2)$ direction with l = 24 (a), (b) at T = 20 K and T = 120 K of the SIO-327 thin film grown on LSAT, and (c) at T = 20 K grown on STO. Black lines represent the experimental data, blue lines are fitted to the data using Gaussian peak functions, the red dashed line tracks the position of the magnon, and the black vertical dashed line at zero energy is the elastic line.

In the SIO-327 thin film grown on STO (Fig. 7.2.6(c)) we can resolve magnon excitations at the Γ -point in contrast to the SIO-214 thin film. The difference in spin wave dispersion relation between them will be discussed in Ch. 8. But it is worth noting that the peak at Q = (0, 0) is barely visible, leading to a larger energy uncertainty of the magnon excitation. Other magnons at higher Q's are better resolvable, but nonetheless, the energy error is $\Delta E \approx 20 \text{ meV}$.

We have also conducted measurements along the $(5\ 0\ 2)$ reflection of SIO-327 to compare our data with the data published by Moretti Sala *et al.* [43]. By the time of writing this thesis, the process of manufacturing Sr₃Ir₂O₇ thin films is very demanding, which is why there is not so much research related to SIO-327. As shown in Fig. 7.2.7, different peaks can be resolved. According to the publication feature **A** is the elastic line, feature **B** is a transverse excitation of superposition of degenerate acoustic and optical magnons, feature **C** is assigned to the multimagnon continuum, and feature **D** is ascribed to longitudinal excitations.



Figure 7.2.7: RIXS data measured at $Q = (5 \ 0 \ 2)$ at $T = 20 \ K$ of the SIO-327 thin film grown on LSAT (black solid symbols) and STO (black open symbols) substrates along with data adapted from Ref. [43] (solid blue line). According to Ref. [43] the peaks are labeled as **A** (elastic line), **B** (transverse magnon excitations), **C** (multimagnon continuum), and **D** (longitudinal magnon excitations).

Despite worse energy resolution, one can see the shift of our data to smaller energies. Both **B** and **D** features were shifted approximately 20 meV to the left, which brings us to the conclusion that strained epitaxial or finite size effects play a significant role on the energy position of magnon excitations.



Figure 7.2.8: Spin wave dispersion relations of feature **B**, **C**, and **D** of SIO-327 provided by Moretti Sala *et al.* [43]. The extracted energies of these features of our RIXS data measured at different temperatures of SIO-327 thin films grown on LSAT and STO substrates are plotted as points with error bars. Feature **B** and **D** are transverse and longitudinal modes, **C** is assigned as multimagnon continuum, which is **B** shifted up by 85 meV.

It has been reported that SIO-327 have transverse and longitudinal magnon modes. Feature **B** is a transverse mode and was interpreted as the superposition of almost degenerate acoustic and optical magnons and has been constructed based on Eq. (8.6). Feature **D** is a longitudinal mode and most likely has nontrivial dependence of its intensity on momentum transfer (strong dependency on the out-of-plane component of **Q**). Feature **C** here is the lower boundary of the two-magnon continuum and is feature **B** shifted up by a 85 meV gap. Looking at our data in Fig. 7.2.8 we only have a few data points for features **C** and **D**, therefore we will concentrate only on feature **B** or the transverse mode $S_{xx}(\omega, Q) + S_{yy}(\omega, Q)$. We see some downward inclination near Γ -point.

Additional peaks with weak dispersion We also observe some odd peaks in the RIXS data at low energy loss of the $Sr_3Ir_2O_7$ thin film on LSAT with weak dispersion as shown in Fig. 7.2.9. The cause of these additional peaks close to the elastic line is unclear and needs to be investigated in further measurements.



Figure 7.2.9: RIXS data measured along the $(\pi/2, \pi/2)$ direction at T = 20 K and T = 120 K of the SIO-327 thin film grown on LSAT. Black lines represent the experimental data, purple lines are fits of the additional peak close to the elastic line using a Gaussian peak function, red dashed lines highlight the dispersion of these additional peaks, and the vertical dashed line indicates zero energy.

7.3 Summary

This chapter has discussed the findings of resonant resonant inelastic X-ray scattering (RIXS) on Sr_2IrO_4 (SIO-214) and $Sr_3Ir_2O_7$ (SIO-327) thin films fabricated on STO and LSAT substrates. To this end, we first discussed the structural and magnetic properties of the samples used for the RIXS experiment.

For the Sr_2IrO_4 thin film, high-resolution X-ray diffractometry (HRXRD) measurements were used to assess the structural quality of the thin film. The results showed that the thin film had excellent crystalline quality with low mosaicity and coherent growth along the out-of-plane direction. Furthermore, the thin film is found to be fully strained. The lattice parameters of the SIO-214 thin film grown on STO determined from reciprocal space mappings as well as during the alignment of the SIO-214 samples at the beamline ID20 at the ESRF were slightly different from the SIO-214 literature values, revealing the presence of epitaxial strain effects. It was found that the SIO-214 sample has a tensile in-plane strain and compressive out-of-plane strain.

The RIXS measurements of the SIO-214 thin film grown on STO carried out at the beamline ID20 at the ESRF at different in-plane momenta at T = 20 K and T = 120 K revealed magnetic excitations in the thin film. The analysis showed a dispersive nature of these excitations. The RIXS data were fitted with Gaussian functions to extract the energy loss of the magnon excitations. The thus obtained spin wave dispersion relation has been compared to literature data on single-crystalline bulk samples. Small but finite deviations have been observed, which will be explained in the next chapter. However, some additional peaks have been observed, close to the elastic line for some (h k)-values. The origin of these peaks needs to be investigated in future experiments.

For the Sr₃Ir₂O₇ thin films, similar investigations were conducted. The HRXRD measure-

ments indicated excellent crystalline quality for the thin films grown on both STO and $(LaAlO_3)_{0.3}(Sr_2TaAlO_6)_{0.7}$ (LSAT) substrates. Furthermore, a compressive in-plane and tensile out-of-plane strain has been found for both samples.

RIXS measurements at different in-plane momenta of the SIO-327 thin films also revealed magnetic excitations with clear dispersion. Furthermore, RIXS data at a specific momentum transfer (with $(h \ k \ l) = (5 \ 0 \ 2)$) were conducted and compared to the work by Moretti Sala *et al.* [43]. The complexity of the magnetic excitations in Sr₃Ir₂O₇ was evident, and the influence of possible epitaxial strain as well as possible finite size effects was found in the comparison to Moretti Sala *et al.* [43]. These RIXS data are further analyzed using SpinW in the next chapter.

Chapter 8

Simulation of spin wave dispersion relations

Spin waves, also known as magnons, are collective excitations of the magnetic moments in a crystal lattice. These excitations play a crucial role in understanding the magnetic properties of materials, including their magnetic ordering and dynamics. Recently, resonant inelastic X-ray scattering (RIXS) has emerged as a powerful experimental technique for studying spin waves in complex materials, such as transition-metal oxides. To analyze and interpret RIXS data, theoretical simulations of spin waves are often needed.

The SpinW package is a widely used software tool for simulating spin waves in magnetic systems. It is built on top of the MATLAB environment and provides a user-friendly interface for generating magnetic models using mean field theory, calculating spin-wave spectra, and spin-spin correlation function. SpinW has been used in a variety of studies, ranging from investigating the magnetic properties of single crystals to simulating spin waves in thin films and heterostructures [44].

In this chapter, SpinW has been applied to study the spin wave dispersion relation of epitaxial strained Sr_2IrO_4 and $Sr_3Ir_2O_7$ thin films. The obtained spin-wave spectra of these materials have been compared to experimental data obtained from RIXS measurements.

8.1 Linear spin wave theory

Linear spin wave theory (LSWT) is a widely used method for describing the dynamics of magnetic systems, including the spin wave dispersion relation. The basic idea of LSWT is to approximate the Hamiltonian of the system as a quadratic form around a particular spin configuration. The quadratic terms in the Hamiltonian then give rise to harmonic oscillations, which can be identified as spin waves. The spin waves can be described by their dispersion relation, which relates their frequency to their wavevector [44].

In the SpinW package, the LSWT is implemented using the Holstein-Primakoff transformation, which maps spin operators onto bosonic creation and annihilation operators. The Hamiltonian is then written in terms of these bosonic operators, which can be treated using standard techniques from quantum mechanics. The resulting equations can be solved numerically to obtain the spin wave dispersion relation [44].

The LSWT Hamiltonian for a magnetic system with Heisenberg interactions can be written as:

$$\mathcal{H} = \sum_{mi,nj} \mathbf{S}_{mi}^T \cdot J_{mi} \cdot \mathbf{S}_{nj} + \sum_{mi} \mathbf{S}_{mi}^T \cdot A_i \cdot \mathbf{S}_{mi} + \mu_B \mathbf{H}^T \sum_{mi} g_i \mathbf{S}_{mi}$$
(8.1)

where indices m and n are indexing the crystallographic unit cell (running from 1 to L), while i and j label the magnetic atoms inside the unit cell (running from 1 to N), **S** are magnetic moments, A describes the magnetic anisotropy, **H** is the external magnetic field column vector, μ_B is the Bohr magneton, and J are exchange interactions including anisotropic and antisymmetric (Dzyaloshinskii-Moriya) exchange interactions [45]:

$$J_{S} = \begin{bmatrix} J_{x} & 0 & 0\\ 0 & J_{y} & 0\\ 0 & 0 & J_{z} \end{bmatrix}, \quad J_{A} = \begin{bmatrix} 0 & D_{z} & -D_{y}\\ -D_{z} & 0 & D_{x}\\ D_{y} & -D_{x} & 0 \end{bmatrix}$$
(8.2)

where J_i and D_i are directional components of coupling strengthens between atoms and DMI constants respectively.

By diagonalizing Eq. (8.1), we can obtain the spin wave frequencies and eigenvectors for a given magnetic system. The eigenvalues of the diagonalized Hamiltonian describe the dispersion relation and the spin-spin correlation function:

$$S^{\alpha\beta}(\mathbf{k},\omega) = \frac{1}{2\pi\hbar} \int dt e^{-i\omega t} \langle S^{\alpha}(\mathbf{q},0) S^{\beta}(-\mathbf{q},t) \rangle$$
(8.3)

where $\langle S^{\alpha}(\mathbf{q},t) \rangle$ is the expectation value of the spin component operator and related to the Fourier transform of the eigenvectors of the Hamiltonian at wavevector \mathbf{q} [44].

Diagonalizing the Hamiltonian can be done using the SpinW package, which provides a convenient interface for constructing the Hamiltonian and calculating the spin wave dispersion relation (Fig. 8.1.1).



Figure 8.1.1: Data transfer diagram in SpinW. The spin waves can be simulated by inputting firstly bond lengthens, symmetries, as well as exchange constants J between interested magnetic structures, anisotropies A, and dependent g-factors. Then the magnetic structures can be generated by SpinW using a mean field optimization. Finally, combining diagonalized Hamiltonian with manually defined magnetic structures and applying LSWT one obtains spin wave dispersion relation and spin-spin correlation function. Figure taken from Ref. [44].

Henceforth to simulate spin waves using SpinW, the following steps can be followed:

- 1. **Define the system**: Start by specifying the relevant parameters of the system, including the bond lengths, symmetries, and exchange constants (represented by the symbol J) between the magnetic structures of interest. These exchange constants describe the interactions between neighboring magnetic moments. Additionally, anisotropies (represented by the symbol A) and dependent g-factors can be taken into account. These parameters provide the necessary input to describe the magnetic properties of the system.
- 2. Generate magnetic structures: Using the specified parameters, SpinW employs a meanfield optimization method to generate magnetic structures. Mean-field theory treats the interactions between magnetic moments in an average or mean way, providing a starting point for the calculation. The optimization process aims to find the lowest energy state consistent with the input parameters and constraints.
- 3. Diagonalize the Hamiltonian: Once the magnetic structures are generated, SpinW proceeds to diagonalize the Hamiltonian. The Hamiltonian describes the energy of the system and includes terms related to the exchange interactions, anisotropies, and external fields. Diagonalization involves finding the eigenvalues and eigenvectors of the Hamiltonian matrix, which correspond to the energy levels and associated wave functions of the system.
- 4. Calculate spin-spin correlation function: With the diagonalized Hamiltonian and the generated magnetic structures, one can calculate the spin-spin correlation function. This

correlation function provides information about the statistical relationship between the spin components at different positions and times. By examining this correlation function, one can gain insights into the spin dynamics and collective behavior of the system.

5. Apply LSWT: LSWT is a perturbative approach commonly used to study spin waves in magnetic systems. By treating small deviations from the magnetic ground state as excitations or spin waves, LSWT allows for the calculation of the spin wave dispersion relation. This relation describes how the spin waves propagate through the system as a function of their wavevector and frequency.

8.2 Magnetic structures of Sr₂IrO₄ and Sr₃Ir₂O₇

The magnetic properties of Sr_2IrO_4 can be described by a two-dimensional anisotropic Heisenberg Hamiltonian. This Hamiltonian takes into account the nearest-neighbor (J_1) , secondnearest-neighbor (J_2) , and third-nearest-neighbor (J_3) magnetic exchange interactions, as well as an anisotropic in-plane (x - y plane term) represented by the parameter α . The introduction of this anisotropy in the system causes a distinction between the magnetic modes associated with in-plane and out-of-plane spin fluctuations. The in-plane magnon mode remains without a gap explained by Kim *et al.* [39], while the out-of-plane mode acquires a spin gap at the center of the magnetic zone [40, 42, 46]. The Hamiltonian is given by [41]:

$$\mathcal{H} = \sum_{\langle i,j \rangle} J \left[S_i^x S_j^x + S_i^y S_j^y + (1-\alpha) S_i^z S_j^z \right] + \sum_{\langle \langle i,j \rangle \rangle} J_2 \vec{S}_i \cdot \vec{S}_j + \sum_{\langle \langle \langle i,j \rangle \rangle \rangle} J_3 \vec{S}_i \cdot \vec{S}_j$$
(8.4)

Here, the first term represents the interaction between nearest-neighbor spins, with the x, y, and z components of the spins denoted by S. The second term accounts for the interaction between second-nearest-neighbor spins, and the third term represents the interaction between third-nearest-neighbor spins which are summed by i and j indices. The values of J_1, J_2 , and J_3 determine the strength of these interactions. The anisotropic easy-plane term, controlled by the parameter α , introduces an anisotropy in the z-component interaction of neighboring spins. This term reflects the preference of the spins to align in the x-y plane rather than the z-direction.

The magnetic structure of SIO-214, as shown in Fig. 8.2.1(a), can be understood by considering the interplay between these exchange interactions and the anisotropic easy-plane term in the Hamiltonian. The coupling between the nearest (J_1 , red lines), second-nearest (J_2 , green lines), and third-nearest (J_3 , blue lines) neighbor spins results in an antiferromagnetic in-plane spin-ordering.



Figure 8.2.1: Magnetic structures of SIO-214 and SIO-327. Scales are not considered. The *a* and *b* directions of the unit cells are scaled by 1.25 for visualization. The unit cell itself is shown by the black dashed line. Ir atoms are shown as red balls with red arrows displaying the direction of the magnetic moments. J_1 , J_2 , J_3 , and J_4 interactions are indicated with red, green, blue, and cyan lines respectively. As well as the antisymmetric exchange Dzyaloshinskii–Moriya interaction (DMI) in SIO-327 is depicted with red arrows between atoms.

On the other hand, in the study of the magnetic structures in $Sr_3Ir_2O_7$, a theoretical model Hamiltonian based on a pseudospin-1/2 frustrated Heisenberg model is employed. This model takes into account both intrinsic anisotropic and spin-orbit coupling effects, and its details can be found in the review by Boseggia *et al.* [10] and Jackeli *et al.* [18]:

$$\mathcal{H}_{ij} = J\mathbf{S}_i \cdot \mathbf{S}_j + J_z S_i^z S_j^z + \mathbf{D} \cdot [\mathbf{S}_i \times \mathbf{S}_j] + \mathcal{H}'$$
(8.5)

In the context of theoretical models for bilayered systems with strong spin-orbit coupling, the Hamiltonian describes the layered iridate materials. It includes terms such as isotropic Heisenberg superexchange, pseudo-dipolar interaction (PDI), Dzyaloshinskii–Moriya interaction (DMI), and anisotropic contribution from Hund's coupling. This Hamiltonian can explain the observed basal-plane canted antiferromagnetic structure and predicts a spin-flop transition as a function of the tetragonal crystal field θ . In SIO-327, the interlayer coupling prevents the complete elimination of the twist of the IrO_6 octahedra, resulting in intrinsic anisotropy. Introducing interlayer interactions enhances the PDI in the Hamiltonian, leading to the reorientation of the magnetic moments along the *c*-axis. Solving this anisotropic Hamiltonian specifically for $Sr_3Ir_2O_7$ we yield a Hamiltonian with frustration and longer-range interactions, given by [43]:

$$\mathcal{H} = J_1 \sum_{\langle i,j \rangle,l} \left[\cos(2\theta) \mathbf{S}_{li} \cdot \mathbf{S}_{lj} + 2\sin^2(\theta) S_{li}^z S_{lj}^z - \epsilon_i \epsilon_l \sin(2\theta) \left(\mathbf{S}_{li} \times \mathbf{S}_{lj} \right) \cdot \hat{e}_z \right] + J_4 \sum_i \mathbf{S}_{1i} \cdot \mathbf{S}_{2i} + J_2 \sum_{\langle \langle i,j \rangle \rangle,l} \mathbf{S}_{li} \cdot \mathbf{S}_{lj} + J_3 \sum_{\langle \langle \langle i,j \rangle \rangle \rangle,l} \mathbf{S}_{li} \cdot \mathbf{S}_{lj}$$

$$(8.6)$$

Here, the indices $\langle i, j \rangle$, $\langle \langle i, j \rangle \rangle$, and $\langle \langle \langle i, j \rangle \rangle$ refer to nearest, second-nearest, and thirdnearest neighbors within each layer just as in Eq. (8.4), labeled as l = 1, 2, 3. The parameter θ represents the relative strength of the anisotropic interactions θ of IrO₆ octahedra in each layer. The terms in the Hamiltonian can be described as follows:

- 1. The first term captures the interaction between nearest neighbors. It consists of three components:
 - a) The first component, $J_1 \sum_{\langle i,j \rangle,l} \cos(2\theta) \mathbf{S}_{li} \cdot \mathbf{S}_{lj}$, represents the isotropic exchange interaction between spins in the *x-y* plane.
 - b) The second component, $J_1 \sum_{\langle i,j \rangle,l} 2\sin^2(\theta) S_{li}^z S_{lj}^z$, accounts for the pseudodipolar interactions arising from Hund's coupling and the staggered rotation of the IrO₆ octahedra.
 - c) The third component involves the DMI and is given by $J_1 \sum_{\langle i,j \rangle,l} \epsilon_i \epsilon_l \sin(2\theta) (\mathbf{S}_{li} \times \mathbf{S}_{lj}) \cdot \hat{e}_z$ where ϵ_i and ϵ_l are parameters associated with the DMI interaction strength, and \hat{e}_z denotes the unit vector along the z-axis.
- 2. The second term, $J_4 \sum_i \mathbf{S}_{1i} \cdot \mathbf{S}_{2i}$, represents the interaction between spins in out-of-plane direction.
- 3. The third term accounts for the interaction between second-nearest neighbors and is given by $J_2 \sum_{\langle \langle i,j \rangle \rangle, l} \mathbf{S}_{li} \cdot \mathbf{S}_{lj}$.
- 4. The fourth term represents the interaction between third-nearest neighbors and is given by $J_3 \sum_{\langle \langle (i,j) \rangle \rangle, l} \mathbf{S}_{li} \cdot \mathbf{S}_{lj}$.

The complex magnetic structure of SIO-327 is shown in Fig. 8.2.1(b). The chosen coupling strengths J_1 , J_2 , J_3 , and J_4 represented by red, green, blue, and cyan lines, respectively, together with a finite DMI interaction visualized by small red arrows between atoms result in an antiferromagnetic spin-ordering with spins aligned the out-of-plane z-direction.

8.3 Simulation of spin wave dispersion relation of Sr₂IrO₄

After comparing our data to different spin wave dispersion relations provided by different publications on SIO-214 single crystals using variables shown in Table 8.3.1, it is time to find the best fit to the spin wave dispersion relation of the Sr₂IrO₄ thin film obtained from our RIXS data. To better understand the influence of each coupling constant and anisotropy of the Hamiltonian Eq. (8.4) on the spin wave dispersion relation, we have calculated the spin wave dispersion relation using different coupling strengths J_1 , J_2 , J_3 , and different anisotropy values α . The thus obtained spin wave dispersion relations are depicted in Figs. in B.1.1. While different J_l -values with l = 1, 2, 3 result in different shapes of the spin dispersion relation, a finite anisotropy α leads to a finite gap at $(0, \pi)$ and (0, 0).

Coupling	Kim single crystal [39]	Pincini bulk [40]	Clancy (iso.) bulk [41]	Clancy (aniso.) bulk [41]	Vale bulk [42]	This work best fit
J_1	$60\mathrm{meV}$	$57\mathrm{meV}$	$62\mathrm{meV}$	$65\mathrm{meV}$	$57\mathrm{meV}$	$55\mathrm{meV}$
J_2	$-20\mathrm{meV}$	$-16.5\mathrm{meV}$	$-19\mathrm{meV}$	$-19\mathrm{meV}$	$-18\mathrm{meV}$	$-19\mathrm{meV}$
J_3	15 meV	12.4 meV	13 meV	13 meV	14 meV	$13\mathrm{meV}$
α	0	0.05	0	0.02	0.08	0.07

Table 8.3.1: Values of the coupling strength J_l (l = 1, 2, 3) and anisotropy factor α of Sr₂IrO₄ provided by different publications on basis of Eq. (8.4). The values yield the best fit to our RIXS data of the SIO-214 thin film grown on STO are also displayed.

After thorough consideration of each variable and understanding how each affects the spin wave dispersion relation we have made our best fit to our RIXS data. Using the values displayed in Table 8.3.1 Fig. 8.3.1 shows the intensity of the spin-spin correlation function calculated by SpinW package, taking into account a finite energy resolution of 26 meV. Interestingly, the second-nearest neighbor coupling J_2 and third-nearest neighbor coupling J_3 are comparable to values from the publications summarized in Table 8.3.1. A more drastic difference of our data compared to the data on SIO-214 single crystals shows the first-nearest neighbor coupling $J_1 = 55$ meV, which is smaller than the values found for SIO-214 single crystals. Together with a 7% easy-plane anisotropy ($\alpha = 0.07$), we can suggest that epitaxial strain effects can play a significant role in influencing the magnetic structure of Sr₂IrO₄. Table 7.1.1 reveals that the SIO-214 thin film has a tensile in-plane strain, which increases the distance between Ir atoms and, on the other hand, decreases the coupling strength, which agrees with our findings.



Figure 8.3.1: Spin wave dispersion relation calculated using the SpinW software taking into account the energy resolution $\Delta E = 26 \text{ meV}$. The energy of magnon excitations extracted from our RIXS data on the SIO-214 thin film grown on a STO substrate is shown as green symbols. Intensity depicts the spin-spin correlation function.

8.4 Simulation of spin wave dispersion relation of Sr₃Ir₂O₇

Since there is not so much research on $Sr_3Ir_2O_7$ up to date because of the complexity in fabrication, we only consider the publication by Moretti Sala and coworkers [43] for comparison. To better understand the influence on the coupling constants as well as the anisotropy based on the Hamiltonian Eq. (8.6) on the spin wave dispersion relation, we have performed simulations with different J_l and θ -values. While a variation of J_1 and J_4 results in a shift of the spin wave dispersion, the influence of J_2 , J_3 , and θ are more complex (see Figs. B.1.2).

Coupling	Moretti Sala bulk [43]	This work best fit STO	This work best fit LSAT
J_1	$26\mathrm{meV}$	$16\mathrm{meV}$	$16\mathrm{meV}$
J_2	$-15\mathrm{meV}$	$-22\mathrm{meV}$	$-28\mathrm{meV}$
J_3	$6\mathrm{meV}$	$3\mathrm{meV}$	$4\mathrm{meV}$
J_4	$90\mathrm{meV}$	$90\mathrm{meV}$	$90\mathrm{meV}$
heta	37°	54°	69°

Table 8.4.1: Values of each coupling strengthens and twisting angle factors provided by the paper and best fit of our RIXS data of SIO-327 grown on both LSAT and STO substrates.

Except for the out-of-plane coupling strength J_4 , a clear difference to the bulk values of SIO-327 has been obtained (Table 8.4.1). The antiferromagnetic coupling strength J_1 and J_3 are smaller and the ferromagnetic diagonal second-nearest neighbor coupling has become bigger in comparison to the bulk values. Moreover, a larger value of the anisotropic twisting angle θ has been found. This suggests that Sr₃Ir₂O₇ grown on both substrates is compressed in [1 1 0] direction. However, this could not be verified by measuring the lattice constants of SIO-327. HRXRD measurements summarized in Table 7.2.1 reveal a compressive in-plane strain but with equal in-plane lattice constants a and b retaining a tetragonal crystal symmetry. To further investigate this discrepancy additional reciprocal space mappings along different in-plane directions have to be carried out.



Figure 8.4.1: Spin wave dispersion relation calculated via SpinW using the exchange constants as well as the anisotropy value, which results in the best agreement between simulation and experimental data (blue solid symbols) extracted from RIXS measurements of the SIO-327 thin film grown on a STO substrate. The simulation takes into account the energy resolution $\Delta E = 26 \text{ meV}$. The intensity depicts the spin-spin correlation function.

Figure 8.4.1 shows the simulation of the spin wave dispersion relation using parameters (see best-fit values summarized in Table 8.4.1 which yield the best agreement between simulation and experimental data extracted from RIXS measurements of the SIO-327 thin film grown on a STO substrate. The data points as well as errors are in the boundaries of the resolution of the ID20 beamline. Similarly the spin wave dispersion relation of the SIO-327 thin film grown on LSAT substrate (see Fig. 8.4.2) has been simulated using SpinW and the "best-fit values" shown in Table 8.4.1. The simulation and the experimental data shown as solid symbols agree with the experimental uncertainty.



Figure 8.4.2: Simulated spin wave dispersion relation taking into account the energy resolution $\Delta E = 26 \text{ meV}$ together with the experimental data extracted from RIXS measurements at 20 K and 120 K of SIO-327 thin film grown on the LSAT substrate. The intensity depicts the spin-spin correlation function.

8.5 Summary

In this chapter, the SpinW package has been utilized to study the magnetic properties of Sr_2IrO_4 and $Sr_3Ir_2O_7$ thin films and to investigate the influence of epitaxial strain caused by substrates. The spin wave spectra in these materials were simulated using SpinW, and the results were compared to experimental data obtained from resonant inelastic X-ray scattering (RIXS) measurements.

In the previous chapter, we have compared the spin wave dispersion relation obtained from our RIXS data of the Sr_2IrO_4 (SIO-214) thin films grown on a strontium titanate (STO) substrate to spin wave dispersion relations on single crystalline SIO-214 bulk samples published by different groups. The comparison revealed that the fitting models and the used parameters can not fully explain the behavior of our data despite the low energy resolution of 26 meV of the ID20 beamline.

Considering the low energy resolution ($\Delta E \approx 26 \text{ meV}$) of the RIXS data, it was challenging to choose a specific simulation from other papers. By using the SpinW package, the influence of each coupling constant and anisotropy value on the spin wave dispersion relation was analyzed to understand their effects. The best agreement to the RIXS data was obtained by adjusting the coupling variables and incorporating a 7% easy-plane anisotropy, indicating the significant role

of a possible epitaxial strain on the magnetic structure of Sr_2IrO_4 . In particular, we have found a reduced in-plane coupling constant between first-nearest neighbor Ir^{4+} ions, which is in agreement with a finite tensile strain of the SIO-214 thin film grown on STO.

In a similar way, the spin wave dispersion relation of the $Sr_3Ir_2O_7$ thin films grown on STO and LSAT substrates have been simulated using SpinW. The downward inclination at the Γ point in the experimental data matched well with the simulated spin wave dispersion relation. The simulations suggest a compressive in-plane strain along the [110]-direction, which could not be revealed by X-ray diffraction measurements discussed in Part II, Ch. 7.1. This discrepancy needs to be investigated in future measurements.

Chapter 9 Conclusion and Outlook

Superconductivity, a captivating quantum phenomenon, has been a subject of intense scientific inquiry for over a century. This master's thesis embarked on a multifaceted exploration of unconventional superconducting materials, particularly focusing on strontium iridate (Sr_2IrO_4 and $Sr_3Ir_2O_7$) and strontium-doped neodymium nickelate ($Nd_{0.8}Sr_{0.2}NiO_3$) thin films, with an emphasis on understanding their crystalline growth and examining the effect of epitaxial strain on their magnetic properties. To get deeper insights into these properties, we have utilized advanced techniques such as resonant inelastic X-ray scattering (RIXS) and spin wave dispersion relation simulations using the SpinW package.

In the pursuit of growth optimization of $Nd_{0.8}Sr_{0.2}NiO_3$ thin films using pulsed laser deposition (PLD), an intriguing exploration was undertaken. High-resolution X-ray diffractometry (HRXRD) measurements unveiled a complex growth of neodymium nickelates, indicated by the presence of various phases of the Sr-doped Ruddlesden-Popper series $Nd_{n+1}Ni_nO_{3n+1}$ at the same time. Among these phases, the $Nd_{0.8}Sr_{0.2}NiO_3$ phase with $n \to \infty$ was successfully fabricated as a starting point for further growth optimizations. In particular, this work suggests that the precise adjustment of the oxygen gas pressure is essential to eliminate other unwanted neodymium nickelate phases.

In case of the growth optimization of Sr_2IrO_4 thin films, meticulous efforts have been carried out to find the best growth conditions, which was established using a substrate temperature of 850 °C, oxygen pressure of $25 \,\mu$ bar, 90 % transmittance of the UV laser beam, and a high excimer laser fluence at the target surface of at least $3.5 \,\text{J/cm}^2$. The resulting high-quality thin films exhibit a good crystalline quality, as evidenced by HRXRD measurements. It was further revealed that additional parameters such as the target condition as well as the substrate to target distance play a crucial role in fabricating Sr_2IrO_4 thin films with high crystalline quality, which could lead to future investigations into superconductivity in Sr_2IrO_4 .

To increase the understanding of the dependence of the magnetic properties of strontium iridate thin films on epitaxial strain as well as on finite size effects, we carried out RIXS measurements for Sr_2IrO_4 and $Sr_3Ir_2O_7$ thin films providing critical insights into their magnetic excitations. Comparisons with prior studies on single-crystalline bulk samples revealed that epitaxial strain as well as finite size effects indeed affect the magnetic exchange in these thin films. To address this, SpinW simulations were employed, yielding promising results, particularly with the incorporation of anisotropy factors. The presence of weak-dispersive excitations at low energies remained a challenge, indicating potential measurement artifacts that warrant further investigation.

In the outlook for this research, several promising avenues for further exploration emerge. Firstly, a more in-depth analysis of the additional weak-dispersive excitations observed in the RIXS data is warranted. It is essential to determine whether these features are related to measurement artifacts or hold intrinsic significance for the materials' properties. Since these excitations appear at low energies close to the elastic line, measurement strategies yielding low intensity of this elastic line are needed such as using left and right circularly polarized light for RIXS.

Additionally, future research should delve into the effects of epitaxial strain more comprehensively, possibly incorporating novel techniques to control and manipulate strain. This could lead to the discovery of new phenomena and the development of tunable material properties.

Exploring other complex oxide materials with strong spin-orbit coupling (SOC) beyond Sr_2IrO_4 and $Sr_3Ir_2O_7$ is another promising path. Investigating how these findings apply to a broader range of materials, which are similar to high-temperature cuprate superconductors, could yield valuable insights into the understanding of high-temperature superconductivity also in the limit of strong SOC.

In conclusion, this master thesis represents a contribution to the understanding of unconventional superconducting materials. It has laid the groundwork for future investigations into epitaxial strain effects and the interplay between structure and magnetism in these materials. The scientific journey continues, and the future promises exciting developments using unconventional superconducting materials.

Appendix A Further measurements

A.1 Superconducting quantum interference device magnetometry measurements on strontium iridate thin films



Figure A.1.1: Superconducting quantum interference device (SQUID) magnetometry data of a SIO thin film with the highest crystallinity revealed by high-resolution X-ray diffractometry (HRXRD) measurements shown in Fig. 4.2.2 fabricated at a substrate temperature of $850 \,^{\circ}$ C, an oxygen pressure $40 \,\mu$ bar, and a $90 \,\%$ transmittance of UV laser pulses. We can spot a magnetic ordering temperature at around $200 \,\text{K}$.

A.1 Superconducting quantum interference device magnetometry measurements on strontium iridate thin films



Figure A.1.2: Superconducting quantum interference device (SQUID) magnetometry data of SIO thin films fabricated at a substrate temperature of 850 °C, an oxygen pressure 25 μ bar, and a 90 % transmittance of UV laser pulses on STO (left panel) and LSAT (right panel). LSAT substrate is slightly paramagnetic [47] resulting in $M \sim 1/T$ behaviour influencing our SIO data (grey line on right panel). We have subtracted this paramagnetic contribution resulting in a more refined magnetization curve of SIO thin film (black line on right panel). STO is diamagnetic [47] with no paramagnetic impurities. Therefore, it is more favorable for further SQUID magnetometry measurements.

A.2 Atomic force microscopy scans



A.2.1 Strontium iridate thin films

Figure A.2.1: Atomic force microscopy (AFM) scans of strontium iridate thin films. Root mean square value for surface roughness in the bottom right corner of each scan varies between 2.1 nm- $59.7 \,\mathrm{nm}$ on scanned surfaces with the areas of $1 \,\mu\mathrm{m}^2$. The growth parameters (substrate temperature, oxygen pressure, UV laser transmittance) of the SIO thin films are indicated on the top left of each image. 91



A.2.2 Neodymium nickelate thin films

Figure A.2.2: Atomic force microscopy (AFM) scans of neodymium nickelate thin films. Root mean square value for surface roughness in the bottom right corner of each scan varies between $0.4 \,\mathrm{nm}$ -3.7 nm on scanned surfaces with the areas of $1 \,\mu\mathrm{m}^2$. The growth parameters (substrate temperature, oxygen pressure, UV laser transmittance) of the NNO thin films are indicated on the top left of each image.

Appendix B

Further SpinW simulations and codes

B.1 Comparison of coupling strengths and other variables

B.1.1 Sr_2IrO_4



Figure B.1.1: SpinW simulations of the spin wave dispersion relation of SIO-214 using the model Hamiltonian Eq. (8.4) with different coupling strengths J as well as anisotropy values α . The model by Kim *et al.* [39] was set as a background model varying only one parameter at each plot. By increasing the first nearest-neighbor coupling strength J_1 (Fig. B.1.1(a)) the maximum values of the spin wave dispersion relation are increased. A similar but opposite dependence was found while varying the second-nearest neighbor coupling J_2 (Fig. B.1.1(b)). Increasing the third nearest neighbor coupling strength J_3 (Fig. B.1.1(c)) results in changes of the slope of the spin wave dispersion relation and changes of the value at $(0, \pi/2)$. Interestingly, increasing the anisotropy value α (Fig. B.1.1(d)) yields to a finite energy gap at $(0, \pi)$ and (0, 0).



B.1.2 Sr₃Ir₂O₇



Figure B.1.2: SpinW simulations of the spin wave dispersion relation of SIO-327 using the Hamiltonian Eq. (8.6) with different coupling strengthens J as well as relative strength of the anisotropic interactions θ of IrO₆ octahedra. The model by Moretti Sala *et al.* [39] was set as a background model varying only one parameter at each plot. By increasing the first next-nearest coupling strength J_1 (Fig. B.1.2(a)) the spin wave dispersion is shifted to higher in energy. The same dependence is observed while changing the coupling strength J_4 (Fig. B.1.2(d)). Decreasing J_2 (Fig. B.1.2(b)) and increasing J_3 coupling strengths (Fig. B.1.2(c)) result to changes of the slopes. Interestingly, decreasing the relative anisotropic angle θ (Fig. B.1.2(e)) yields to closing the energy gap at the Γ -point.

B.2 SpinW code for the simulation of spin wave dispersion relations

B.2.1 SpinW code for Sr₂IrO₄

```
1 Creating a lattice
  % https://materials.springer.com/isp/crystallographic/docs/
2
      sd 1215409
3
  sr2iro4 = spinw;
4
  sr2iro4.genlattice('lat_const', [5.493 5.493 25.777],'angled', [90
5
       90 90],'sym','I 41/a c d');
6 sr2iro4.addatom('r',[0 0.25 0.05072],'S',0,'ox',+2,'label','Sr2+
      ','color','green');
7 sr2iro4.addatom('r',[0 0.25 0.375],'S',1/2,'ox',+4,'label','Ir4+
      ','color','red');
  sr2iro4.addatom('r',[0 0.25 0.95045],'S',0,'ox',-2,'label','02-'
8
      ,'color','blue');
  sr2iro4.addatom('r',[0.19372 0.44372 0.125],'S',0,'ox',-2,'label
9
      ','02-','color','blue');
10
  Plotting a lattice
11
  sr2iro4.plot('range', [1.25 1.25 1]);
12
  swplot.plotchem('atom1','Ir','atom2','0','limit',6,'color','
13
      vellow');
14
15 Defining exchange interactions
  sr2iro4.gencoupling('maxDistance',8)
16
17
 J1 = 60;
18
  J_2 = -20;
19
  J3 = 15;
20
  alpha = 0;
21
22
  sr2iro4.addmatrix('value', diag([J1 J1 (1-alpha)*J1]),'label','J1
23
      ','color','red')
24 | sr2iro4.addmatrix('value', J2, 'label', 'J2', 'color', 'green')
  sr2iro4.addmatrix('value', J3, 'label', 'J3', 'color', 'blue')
25
26
27
  sr2iro4.addcoupling('mat','J1','bond',1);
28
  sr2iro4.addcoupling('mat','J2','bond',2);
29
  sr2iro4.addcoupling('mat','J3','bond',5);
30
31
  sr2iro4.table('bond',1:5)
32
33
34 Defining magnetic structures
_{35} theta = 0;
_{36} R = [cosd(theta) -sind(theta) 0; sind(theta) cosd(theta) 0; 0 0
```

```
1];
37
  S mat = [1 -1 1 -1 -1 1 -1 1; ...
38
            0 0 0 0 0 0 0 0;...
39
            0 0 0 0 0 0 0 0 0 0 0 1;
40
41
  sr2iro4.genmagstr('mode','direct','S', R*S_mat)
42
43
  Optimize magnetic structure
44
  sr2iro4.optmagsteep('nRun',1e3)
45
46
  plot(sr2iro4,'range',[1.25 1.25 1],'atomMode','mag')
47
48
  disp('Magnetic structure:')
49
  sr2iro4.table('mag')
50
51
52 Simulating spin wave dispersion relation and plotting
      experimental data
  |Q_H_SIO = [0; 1; 0];
53
  Q_G_SIO = [0; 0; 0];
54
  Q_P_SIO = [1/2; 1/2; 0];
55
56
  sr2iro4Spec = sr2iro4.spinwave({Q_P_SIO Q_H_SIO Q_G_SIO Q_P_SIO
57
      501}, 'formfact', true, 'hermit', true);
58
  sr2iro4Spec = sw_neutron(sr2iro4Spec);
59
  sr2iro4Spec = sw_egrid(sr2iro4Spec,'component','Sperp');
60
  sr2iro4Spec.omega(isnan(sr2iro4Spec.omega)) = 0;
61
  sr2iro4Spec = sw_omegasum(sr2iro4Spec,'zeroint',le-5,'tol',le-3)
62
      ;
63
  figure
64
  sw_plotspec(sr2iro4Spec,'mode',3,'axLim',[0 5],'dE',26,'qlabel'
65
      ,{'(\pi/2,\pi/2)' '(0,\pi)' '(0,0)' '(\pi/2,\pi/2)'});
  legend('off')
66
  colorbar off
67
68
69 Finding maximum intensity
70 energy1 = transpose(sr2iro4Spec.omega(1,:));
71 energy1(isnan(energy1)) = 0;
r2 energy2 = transpose(sr2iro4Spec.omega(2,:));
73
  energy2(isnan(energy2)) = 0;
74
rs intensity1 = transpose(sr2iro4Spec.swInt(1,:));
76 intensity1(isnan(intensity1)) = 0;
m | intensity2 = transpose(sr2iro4Spec.swInt(2,:));
  intensity2(isnan(intensity2)) = 0;
78
79
80 | for i = 1:1501
```

```
if intensity1(i,:) >= intensity2(i,:)
81
            energy(i,:) = energy1(i,:);
82
       elseif intensity1(i,:) <= intensity2(i,:)</pre>
83
            energy(i,:) = energy2(i,:);
84
       end
85
  end
86
87
  momentum = transpose(1:1501);
88
89
90 plot (momentum, energy)
```

B.2.2 SpinW code for $Sr_3Ir_2O_7$

```
1 Creating a lattice
  % https://materials.springer.com/isp/crystallographic/docs/
2
      sd_1611271
3
  sr3ir2o7 = spinw;
4
  sr3ir2o7.genlattice('lat_const',[3.896 3.896 20.879],'angled'
5
      ,[90 90 90],'sym','I 4/m m m');
  sr3ir2o7.addatom('r',[0 0 0.5],'S',0,'ox',+2,'label','Sr2+','
6
      color','green');
  sr3ir2o7.addatom('r',[0 0 0.3128],'S',0,'ox',+2,'label','Sr2+','
7
      color','green');
  sr3ir2o7.addatom('r',[0 0 0.09743],'S',1/2,'ox',+4,'label','Ir4+
8
      ','color','red');
  sr3ir2o7.addatom('r',[0 0 0],'S',0,'ox',-2,'label','02-','color'
9
      ,'blue');
  sr3ir2o7.addatom('r',[0 0 0.1939],'S',0,'ox',-2,'label','02-','
10
      color','blue');
  sr3ir2o7.addatom('r',[0 0.3957 0.404],'S',0,'ox',-2,'occ',0.5,'
11
      label','02-','color','blue');
12
  Plotting a lattice
13
  sr3ir2o7.plot('range',[1.25 1.25 1]);
14
  swplot.plotchem('atom1','Ir','atom2','0','limit',10,'color','
15
      yellow');
16
  Defining exchange interactions
17
18
  sr3ir2o7.gencoupling('maxDistance',10)
19
  J1 = 26;
20
  J_2 = -15;
21
_{22} J3 = 6;
_{23} | J4 = 90;
  theta = 90-37;
24
  DM = -J1 * sind(2 * theta);
25
26
```

```
27 sr3ir2o7.addmatrix('value',[J1*cosd(2*theta) DM 0; -DM J1*cosd
      (2*theta) 0; 0 0 J1*cosd(2*theta)+J1*2*sind(theta)^2],'label'
      ,'J1','color','red');
  sr3ir2o7.addmatrix('value', J2, 'label', 'J2', 'color', 'green');
28
  sr3ir2o7.addmatrix('value', J3, 'label', 'J3', 'color', 'blue');
29
  sr3ir2o7.addmatrix('value', J4, 'label', 'J4', 'color', 'cyan');
30
31
sr3ir2o7.addcoupling('mat','J1','bond',1);
33 sr3ir2o7.addcoupling('mat','J2','bond',3);
  sr3ir2o7.addcoupling('mat','J3','bond',7);
34
  sr3ir2o7.addcoupling('mat','J4','bond',2);
35
36
  sr3ir2o7.table('bond',1:7)
37
38
  Defining magnetic structures
39
  omega = 0;
40
  R = [1 \ 0 \ 0; \ 0 \ cosd(omega) - sind(omega); \ 0 \ sind(omega) \ cosd(omega)
41
      )];
42
  S_mat = [0]
               0 0 0;...
43
            0
                0 0 0;...
44
            -1 -1 1 1];
45
46
  sr3ir2o7.genmagstr('mode','direct','k',[1/2 1/2 0],'S', R*S_mat)
47
48
  Optimize magnetic structure
49
50
  sr3ir2o7.optmagsteep('nRun',1e3)
51
  plot(sr3ir2o7,'range',[2 2 1],'atomMode','mag')
52
53
54
  disp('Magnetic structure:')
  sr3ir2o7.table('mag')
55
56
57 Simulating spin wave dispersion relation and plotting
      experimental data
  Q_H_SIO = [1/2; 1/2; 0];
58
  Q_G_SIO = [0; 0; 0];
59
  Q_P_SIO = [1/2; 0; 0];
60
61
  sr3ir2o7Spec = sr3ir2o7.spinwave({Q_P_SIO Q_H_SIO Q_G_SIO
62
      Q_P_SIO 501},'formfact',true,'hermit',false);
63
  sr3ir2o7Spec = sw_neutron(sr3ir2o7Spec);
64
65 sr3ir2o7Spec = sw_egrid(sr3ir2o7Spec,'component','Sxx+Syy');
  sr3ir2o7Spec.omega(isnan(sr3ir2o7Spec.omega)) = 0;
66
  sr3ir2o7Spec = sw_omegasum(sr3ir2o7Spec,'zeroint',1e-5,'tol',1e
67
      -3);
68
69 figure
```

```
70 | sw_plotspec(sr3ir2o7Spec,'mode',3,'axLim',[0 5],'dE',26,'qlabel'
      ,{'(\pi/2,0)' '(\pi/2,\pi/2)' '(0,0)' '(\pi/2,0)'});
  legend('off')
71
  colorbar off
72
73
  Finding maximum intensity
74
  energy1 = transpose(sr3i2o7Spec.omega(1,:));
75
  energy1(isnan(energy1)) = 0;
76
  energy2 = transpose(sr3i2o7Spec.omega(2,:));
77
  energy2(isnan(energy2)) = 0;
78
79
  intensity1 = transpose(sr3i2o7Spec.swInt(1,:));
80
  intensity1(isnan(intensity1)) = 0;
81
  intensity2 = transpose(sr3i2o7Spec.swInt(2,:));
82
  intensity2(isnan(intensity2)) = 0;
83
84
  for i = 1:1501
85
      if intensity1(i,:) >= intensity2(i,:)
86
           energy(i,:) = energy1(i,:);
87
       elseif intensity1(i,:) <= intensity2(i,:)</pre>
88
           energy(i,:) = energy2(i,:);
89
      end
90
91
  end
92
  momentum = transpose(1:1501);
93
94
95 plot (momentum, energy)
```
Acronyms

- **AFM** atomic force microscopy. 91, 92
- **ARPES** angle-resolved photoemission spectroscopy. 10
- **CM** collimating mirror. 50
- **DMI** Dzyaloshinskii–Moriya interaction. 75, 78, 79
- ESRF European Synchrotron Radiation Facility. 50, 57, 65, 71
- FM focusing mirror. 50
- **FWHM** full width at half maximum. 32, 33, 56, 64, 65
- HRXRD high-resolution X-ray diffractometry. 28–31, 33, 36–40, 56, 64, 65, 71, 82, 86, 88
- **IR** infrared. 25
- **KB** Kirkpatrick-Baez mirror. 50
- LHB lower Hubbard band. 8
- **LSAT** (LaAlO₃)_{0.3}(Sr₂TaAlO₆)_{0.7}. 28–31, 36–39, 62–65, 67–72, 81–84, 89
- **LSWT** linear spin wave theory. 2, 74, 76, 77
- **MBE** molecular beam epitaxy. 18–20
- NIXS non-resonant inelastic X-ray scattering. 50, 51
- NNO neodymium nickel oxide thin film, neodymium nickelate thin film. 36–39, 92
- PDI pseudo-dipolar interaction. 78, 79
- PLD pulsed laser deposition. 1, 18–20, 23–26, 28, 29, 32, 54, 62, 86
- **RHEED** reflection high-energy electron diffraction. 25
- **RIXS** resonant inelastic X-ray scattering. 1, 44–51, 54, 55, 57–63, 67–72, 74, 80–83, 86, 87

- **SIO** strontium iridium oxide thin film, strontium iridate thin film. 10–12, 28–34, 40, 44, 88, 89, 91
- **SIO-214** Sr₂IrO₄. 4–6, 10, 11, 28–34, 54–63, 68, 71, 77, 78, 80, 81, 83, 84, 95
- **SIO-327** Sr₃Ir₂O₇. 4–7, 54, 62–72, 78, 79, 81–83, 97
- **SOC** spin-orbit coupling. 8, 9, 87
- SQUID superconducting quantum interference device. 34, 55, 63, 88, 89
- **STO** SrTiO₃. 28–32, 34, 54–58, 60, 62–72, 80–84, 89
- **UHB** upper Hubbard band. 8
- **UHV** ultra-high vacuum. 18–20
- **UV** ultraviolet. 20, 21, 23, 24, 29–31, 33, 37–40, 86, 88, 89, 91

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