Master’s thesis in physics

Topological phases in pyrochlore iridates

Topologische Phasen in Iridaten mit Pyrochlorstruktur

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Chapter 1.

Introduction

In the last decade there was one special material that has attracted a lot of attention in science after its discovery in the year 2004. When its discoverers got a Nobel prize in 2010 it also became famous among public: graphene. This material consists of a monolayer of carbon atoms, which are arranged in a honeycomb lattice. It became so popular that people have started to speculate about the realization of science fiction like space elevators etc. [1]

This is strongly related to the extraordinary properties the material offers. Prof. James Hone from the Columbia state university describes it like this: “It would take an elephant, balanced on a pencil, to break through a sheet of graphene the thickness of Saran Wrap.” [2]. This refers to the enormous mechanical stability. It is even possible to show some kind of self-healing effect in graphene which leads to the repair of damaged structures [3]. There are further properties that made it also popular for electronic or combined applications. Beside the mechanical stability graphene is a very good conductor (conductivity of graphene: $\sigma = 0.96 \times 10^6 /}\Omega cm$, which is higher than for copper $\sigma = 0.60 \times 10^6 /\Omega cm$ [4]). It also offers a very high electron mobility ($\mu_{el} = 200,000 cm^2/Vs$ [4], where typical metals have a mobility $\mu_{el,met} \approx 50 cm^2/Vs$) which can be used for applications that depend on a fast response of the electronic system.

There is today a lot of research going on in this field, for example considering supercapacitors. “A full micro-supercapacitor [...], has a volumetric energy density of approximately 6.3 mW/\text{cm}^3 (a value comparable to that of 4 V - 500 \mu Ah thin-film lithium batteries) while maintaining a power density more than two orders of magnitude higher than that of batteries, as well as a long cycle life.” [5]
Chapter 1. Introduction

There are other applications as well which often make use of the mechanical stability or the electronic properties (or both in combination) of graphene. Current research topics include graphene based field effect transistors [6, 7], salt water filters [8], graphene antennas [9], touchscreens [10], loudspeakers [11], frequency multipliers [12] etc.

This is only possible due to the special physics that happens in graphene which is strongly coupled with its special band structure [13]. Considering the band structure, graphene offers a two dimensional linear dispersion of the conduction as well as of the valence band close to the Fermi energy. Since graphene has a vanishing bandgap and the conduction band minimum and the valence band maximum appear at the same point in \( k \)-space, those bands touch each other. The Fermi energy for the ground state is located at this touching point, which is called “Dirac point”. The conical shape of the band structure at these Dirac points lead to the name “Dirac cone”. The linear dispersion leads to electrons behaving like massless particles in that very region, comparable to photons but with a lower speed. Due to the honeycomb lattice of graphene it hosts six of these Dirac points in its Brillouin zone.

However there is one main problem: it is a two dimensional system. First, this makes it hard to produce, and second, this offers a “weak” direction that is the out of plane direction [13]. In this direction there exist neither the mechanical stability nor the electronic properties, as the out-of-plane direction does not offer the same highly symmetrical honeycomb lattice. As the system relies strongly on the sixfold symmetry also small perturbations can destroy all of the desired properties for the in-plane direction.

In the last few years there were some theoretical and experimental reports that predicted that there may exist analogous systems in three dimensions [14–16]. There the points where valence band and conduction band touch each other are not called Dirac nodes but Weyl nodes. These are said to be absolutely robust to any perturbation [17]. There is the hope that a material containing such nodes will have extraordinary physical properties like graphene - but also in a third spatial dimension.

This, according to theory, requires a special symmetry like it is the sixfold honeycomb in graphene. For the so called Weyl semimetals the pyrochlore structure is a promising symmetry, especially when considering iridates in pyrochlore structure. However, there is only very little literature on these materials presenting contradictory results (e.g. cf. Ref. [18–24]). One candidate for a Weyl semimetal is \( \text{Nd}_2\text{Ir}_2\text{O}_7 \) which these publications mainly focus on.
In a previous bachelor’s thesis \cite{25} on Nd$_2$Ir$_2$O$_7$ that was done in our institute last year, a metal to insulator transition was found in polycrystalline Nd$_2$Ir$_2$O$_7$ at a temperature of (32.7 ± 0.4) K from magnetotransport and magnetization measurements. However, for thin films of Nd$_2$Ir$_2$O$_7$ this could not be confirmed, any fabricated films were electrically insulating. Another bachelor’s thesis \cite{26} that ran parallel to this master’s thesis was focused on Pr$_2$Ir$_2$O$_7$. According to the literature \cite{27} this material system does not show a metal to insulator transition but is metallic over all the available temperature range down to very low temperatures. In the bachelor’s thesis \cite{26}, however, again for thin films an insulating behavior was found.

This thesis is therefore organized in two parts. The first part, following a short theoretical introduction, covers polycrystalline Nd$_2$Ir$_2$O$_7$ and Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$, where we substitute neodymium with praseodymium in order to manipulate the properties of Nd$_2$Ir$_2$O$_7$. The second part will be a continuation of thin films of Nd$_2$Ir$_2$O$_7$, following the conclusions of the previous bachelor’s thesis \cite{25}. In both parts, stoichiometric, structural, magnetic and electric properties of the fabricated samples will be discussed.
Chapter 2.

Theory

This chapter is a short introduction into the theoretical background. It will discuss why Nd$_2$Ir$_2$O$_7$ is an interesting material system, why it is a candidate for a Weyl SemiMetal (WSM), and why praseodymium substitution could provide interesting results. To start with, we will compare Dirac nodes which are present in graphene and Weyl nodes existing in a WSM. Then we will discuss the pyrochlore structure, which is a candidate for a structure that may provide a Weyl semimetal. The third section will cover the theoretical background and recent experimental data concerning the material systems discussed in this thesis.

2.1. From 2D Dirac nodes to 3D Weyl nodes

The honeycomb lattice in graphene provides the system with a sixfold symmetry (Fig. 2.1 (a)). The system can also be described with two hexagonal sublattices ((α) and (β), indicated with dots and squares in Fig. 2.1 (a)) which allows to handle the electronic structure more comfortably. Applying a tight-binding model on the two sublattices results in the following Hamiltonian (cf. Refs. [28, 29]):

$$H = -t \sum_{<i\alpha, j\beta>} \left[ c_{i\alpha}^\dagger c_{j\beta} + c_{j\beta}^\dagger c_{i\alpha} \right].$$  (2.1)

The sum runs over nearest neighbors on the lattice sites $i$ and $j$ in sublattices α and β. The corresponding annihilation and creation operators for an electron on site $i$ in sublattice α are $c_{i\alpha}$ and $c_{i\alpha}^\dagger$, respectively, for $j$ and β applies the same. $t$ is a hopping amplitude, which is used to described the probability for an electron to switch orbits, therefore it can be identified with a parameter arising from the kinetic energy of the electrons. However, Eq. (2.1) neglects effects like Spin Orbit Coupling (SOC) (which is weak for light atoms like carbon) and Coulomb repulsion.
Figure 2.1.: Comparison between Dirac nodes and Weyl nodes. (a) Honeycomb lattice in graphene, the two sublattices are marked by circles and squares. (b) Typical Dirac node with the Dirac cone representing the linear dispersion. Six of these Dirac nodes exist within the Brillouin zone of graphene, located at the \(K\)-points. (c) Pyrochlore structure, a hot candidate for a Weyl semimetal (WSM). Ions are labeled with the corresponding Wyckoff-positions, discussed in the following section (also cf. Tab. 2.1). (d) Corresponding dispersion. There are two pairs of nodes, located at \(k_{x,y} = 0\) and separated by \(k_z = k_0 \pm \pi/d\) with a layer thickness \(d\) of a model system. (a), (b), and (d) are taken from Ref. [28], (c) is taken from Ref. [30].
2.1. From 2D Dirac nodes to 3D Weyl nodes

In the limit of small kinetic energies, Eq. (2.1) can be rewritten as an effective Hamiltonian $H_{\text{eff},2D}$:

$$H_{\text{eff},2D} = v_F (k_x \sigma_x + k_y \sigma_y) .$$

Here $v_F$ is the Fermi velocity, $k_i$ are the spatial components of the reciprocal wave vector $k$, and $\sigma_i$ are the Pauli matrices. This linearized equation holds in proximity to any Dirac node. Due to the special form of Eq. (2.2) electrons can be treated like massless, relativistic Dirac particles where the speed of light is replaced by the Fermi velocity of the electrons [28, 31].

Eq. (2.2) has consequences regarding symmetry operations. While $H_{\text{eff},2D}$ is not invariant under time reversal transformation and parity transformation, it is invariant under the product of both. Time reversal symmetry leads to a suppression of scattering effects that would usually originate at any non-magnetic impurities. This suppression results in a strongly increased conductivity [14, 28]. However, magnetic impurities must be considered by additional terms proportional to $\sigma_x$, $\sigma_y$ or $\sigma_z$. They result in a breaking of time reversal symmetry [17, 28]. Especially perturbations proportional to $\sigma_z$ cannot be treated with the given $H_{\text{eff},2D}$ as $\sigma_z$ is not included in the Hamiltonian. This causes to open a gap between conduction and valence band, thus destroying the 2D Dirac node. In summary, the 2D Dirac node is sensitive to perturbations and can easily be destroyed by, e.g., scattering from magnetic impurities.

For a three dimensional system with an effective Hamiltonian $H_{\text{eff},3D}$ of the form

$$H_{\text{eff},3D} = v_F (k_x \sigma_x + k_y \sigma_y + k_z \sigma_z)$$

any local perturbation is proportional to a combination of the three Pauli matrices and thus can be included because the equation already contains all three Pauli matrices. The perturbation will just shift the location of a 3D Weyl node (which is the 3D equivalent of a 2D Dirac node) in the Brillouin zone [13, 28, 32, 33]. A material that hosts such nodes is called “Weyl semimetal” (WSM) and represents a topological insulator with zero bandgap [28, 32, 34]. Any Weyl semimetal always shows an even number of such nodes. This is a result of the fact that these nodes are objects with chirality and thus always come in pairs. The only way to destroy a Weyl node is to eliminate two of them, meaning to remove the separation in $k$-space [13, 28]. This makes such a pair of nodes extremely stable and robust to perturbations [33].

To describe any suitable candidates for a WSM the effective Hamiltonian Eq. (2.3) is not sufficient. Therefore an explicit Hamiltonian is needed that describes the contributing energy terms [32]:
\[
H = H_t + H_\lambda + H_U
= \sum_{i,j,\alpha,\beta,} t_{ij,\alpha\beta} c_{i\alpha}^\dagger c_{j\beta} + h.c. + \lambda \sum_i L_i \cdot S_i + U \sum_{i,\alpha} n_{i\alpha}(n_{i\alpha} - 1).
\] (2.4)

\(H_t\) is the kinetic energy (cf. Eq. 2.1), \(H_\lambda\) describes the spin-orbit coupling, and \(H_U\) considers the Coulomb energy. \(c_{i\alpha}\) is the creation operator for the creation of an electron in orbital \(\alpha\) at a lattice site \(i\), \(c_{i\alpha}\) is the corresponding destruction operator. \(n_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha}\) is the occupation number of orbital \(\alpha\) of an atom \(i\). \(t_{ij,\alpha\beta}\) is the hopping amplitude, representing the kinetic energy when an electron moves from orbital \(\alpha\) at \(i\) to \(\beta\) at \(j\). \(\lambda\) denotes the spin-orbit-coupling (SOC) parameter connecting the spin \(S\) and the orbital angular momentum \(L\). \(U\) describes the Coulomb repulsion. Hund’s interaction is considered significantly weaker than \(U\) and is therefore omitted.

Figure 2.2.: Phase diagram for electronic materials, depending on the strength of spin-orbit coupling (SOC) \(\lambda/t\) and Coulomb repulsion \(U/t\). Weyl semimetals reside in the very center of the phase diagram with an average SOC and electron interaction strength. The diagram considers the different contributions in Eq. (2.4). Abbreviations: top. = topological, ins. = insulator (taken from Ref. [32]).
2.1. From 2D Dirac nodes to 3D Weyl nodes

Different states of materials are characterized by $U$, $\lambda$ and $t$ (cf. Fig. 2.2). Different atoms provide different combinations for the values of these parameters.

The Coulomb repulsion $H_U$, parametrized by $U$, is mainly influenced by the size of an orbital. For large orbitals, electrons can reduce their Coulomb energy by maintaining larger distances from each other. This can be seen when comparing elements with the same angular momentum but increasing principal quantum numbers: When going from $3d$ elements to $4d$ or $5d$ the extent of an orbital increases strongly.

The opposite applies for $\lambda$. This parameter scales proportionally to $Z^4$ where $Z$ is the number of protons in the atom. Therefore the strength of the SOC increases drastically from $3d$ to $5d$.

The hopping amplitude $t_{ij,\alpha\beta}$ is determined by the overlap of the corresponding orbitals, i.e., the distance of the atoms in a material. Other factors influencing $t_{ij,\alpha\beta}$ can be neglected [32].

It is advantageous not to discuss the absolute strength of the involved terms of Eq. (2.4) but only the relative strength of the parameters, namely $U/t$ and $\lambda/t$ (cf. Fig. 2.2). The interesting area here is where both, $U/t$ and $\lambda/t$, are not too strong and not too weak. This is where the WSM reside. To create such a WSM atoms with a medium atomic weight must be considered as they not only offer a sufficient Coulomb repulsion but also a SOC which is not too strong. Suitable compounds are predicted for $4f$ and $5d$ elements in a pyrochlore structure [21, 33, 35]. In this thesis only compounds containing iridium in a 227-pyrochlore structure will be discussed (“pyrochlore iridates”). For various such compounds a thermally induced phase transition from an insulating state to a metal-like state has been reported [24].

The next section is focused on the pyrochlore structure and the physical properties of the pyrochlore iridates.
2.2. Pyrochlore structure and pyrochlore iridates

The pyrochlore structure is considered a suitable candidate to form a so-called “topological insulator” (TI) (cf. Fig. 2.2) according to theoretical calculations [36]. However, just a topological insulator state is not enough to form a Weyl semimetal, which is in fact a TI with zero bandgap (cf. previous section). Amongst them are iridates with pyrochlore structure [37] which will be discussed in this thesis. Therefore the pyrochlore lattice shall be discussed. A material that crystallizes in a pyrochlore structure follows the formula \( A_2B_2O_6X \). The crystal is cubic, its space group is \( Fd\overline{3}m \) (227).

![Figure 2.3: Elements which are known to form a cubic pyrochlore oxide phase with \( A^{3+} \) and \( B^{4+} \) ions according to Ref. [35], following the chemical formula \( A_2B_2O_7 \). However, most of them are no candidates for a WSM.](image)

Here, only oxidic \( A_2B_2O_7 \) compounds are interesting, meaning the \( X \) site is solely occupied with \( O^{2−} \). In the case of \( A_2B_2O_7 \) only two ionic combinations are possible: 3+ and 4+, or 2+ and 5+ for \( A \) and \( B \). The latter combination is more uncommon, most known compounds (also the compounds in this thesis) prefer the first one (cf. Fig. 2.3) [35]. For this thesis only pyrochlores following the formula \( A_2^3+Ir_2^{4+}O_7^{2−} \) shall be considered where \( A^{3+} \) is a lanthanide ion, here neodymium and praseodymium are used.

Despite the fact that there are 7 oxygen atoms involved in one formula unit they are different regarding their symmetry in the crystal (cf. Tab 2.1).
Table 2.1.: Overview over the coordination, the Wyckoff positions, and the minimal coordinates of the ions in the pyrochlore structure $A_2B_2O_6X$. In the framework of this thesis, compounds $A_2B_2O_7$ with $X = O^{2-}$ are used. $x$ denotes one degree of freedom for the oxygen at position O which is not completely fix $\text{[30, 35]}$.

<table>
<thead>
<tr>
<th>position</th>
<th>ion</th>
<th>coordination</th>
<th>Wyckoff position</th>
<th>minimal coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Nd$^{3+}$, Pr$^{3+}$</td>
<td>8</td>
<td>16d</td>
<td>$\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$</td>
</tr>
<tr>
<td>B</td>
<td>Ir$^{4+}$</td>
<td>6</td>
<td>16c</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td>O</td>
<td>O$^{2-}$</td>
<td>4</td>
<td>48f</td>
<td>$x$, $\frac{1}{8}$, $\frac{1}{8}$</td>
</tr>
<tr>
<td>X</td>
<td>O$^{2-}$</td>
<td>4</td>
<td>8b</td>
<td>$\frac{3}{8}$, $\frac{3}{8}$, $\frac{3}{8}$</td>
</tr>
</tbody>
</table>

Figure 2.4.: (a) Tetrahedral network of Ir$^{4+}$ (blue, B-site) and Nd$^{3+}$ (green, A-site) (taken from Ref. [35]). (b) Octahedral network (taken from Ref. [30]), every oxygen (red) octahedron is centered around an Ir$^{4+}$-site as shown in (c), where also the ideal octahedral arrangement is indicated (pale red) (taken from Ref. [32]).
The oxygen O at position 48\(f\) can move slightly, depending on the atoms on other lattice sites (cf. Tab. 2.1). For \(x = 0.3125 = 5/16\) the sixfold coordination at the B-site (Ir) forms a perfect octahedron, for \(x = 0.375 = 3/8\) it creates a perfect cube around the A-site (16\(d\)). Typical real values are \(0.320 \leq x \leq 0.345\) [35]. Comparing these values with the perfect ones leads to the assumption that typically the deviation from a perfect cubic coordination is much stronger than from a perfect octahedron [35]. These octahedra are shown in Fig. 2.4 (b) and (c).

The arrangement of all the oxygen atoms around the A site leads to a distinguished direction in the crystal, which is the (111) axis [35]. This is illustrated in Fig. 2.5. There, the B and A sites each form an interpenetrating network of coplanar triangular and kagomé layers. Each network is structured in a system of corner sharing tetrahedra (cf. Fig. 2.4 (a)).

![Figure 2.5: (111) direction of the pyrochlore structure: (a) General arrangement of triangular and kagomé layers (taken from Ref. [35]). (b) Arrangement and relative positions with respect to the cubic symmetry, clearly visible as layers, as well as the tetrahedra network of Ir\(^{4+}\) (blue), indicated by gray lines. The Nd\(^{3+}\) ions are marked with green color.]

All those special arrangement details in the pyrochlore structure lead to geometric frustration at room temperature, meaning it is not possible to minimize the interaction energy for all lattice sites at the same time, because in these compounds the magnetic moments do not couple ferromagnetically but anti-ferromagnetically. This has influence on the magnetic and the electronic properties [24, 35].
2.3. Pyrochlore iridates $A_2\text{Ir}_2\text{O}_7$ with $A = \text{Nd, Pr}$

The material system $A_2\text{Ir}_2\text{O}_7$ where the $A$-(16$d$)-site contains neodymium or praseodymium have gathered a lot of interest in the last few years. However, the physical properties are discussed controversially. There is an older publication by Yanagishima and Maeno suggesting a change in behavior from metallic to non-metallic in the $A$ series that is induced by different ionic radii of $A$ atoms on the 16$d$-site (cf. Fig. 2.6 (a)) [38]. In the recent years, there was also a temperature induced Metal to Insulator Transition (MIT) discovered for several lanthanides (cf. Fig. 2.6 (a)). Ueda et al. [21] and Matsuhira et al. [24, 39] published similar results, but Disseler et al. [18] report results contradictory to the other groups. The praseodymium compound is found to be metallic all over the accessible temperature range [27].

![Figure 2.6.](image)

Figure 2.6.: (a) $Ln_2\text{Ir}_2\text{O}_7$ series for pyrochlore iridates. For ionic radii larger than for Sm, the MIT temperature drops drastically. The MIT is predicted to vanish at a quantum critical point before reaching the ionic radius of praseodymium ions. The black line indicates the separation between magnetic insulators (= magnetic ins.) and (non-)metals. (b) Electronic structure for rhodium doped neodymium iridate $\text{Nd}_2(\text{Ir}_{1-x}\text{Rh}_x)_2\text{O}_7$. It shows different phases of the material system depending on the doping level [21].

In 2012, Ueda et al. [21] showed by rhodium doping of $\text{Nd}_2\text{Ir}_2\text{O}_7$ ($\text{Nd}_2(\text{Ir}_{1-x}\text{Rh}_x)_2\text{O}_7$) that it is possible to create a band structure where the Fermi energy lies at the touching point of conduction and valence band. This state is identified as a Weyl semimetal state as the dispersion there is linear.
For \( \text{Nd}_2\text{Ir}_2\text{O}_7 \), Ueda \textit{et al}. and Matsuhira \textit{et al}. report a MIT at 32 K and at 33 K, respectively \([21, 39]\). This was proven by magnetotransport and magnetization measurements. In magnetotransport, the appearance of a minimum of the resistivity is reported, in magnetization a splitting between field-cooled and zero-field-cooled measurements is observable (cf. Fig. 2.7). This is explained by changing the ordering of the \( \text{Ir}^{4+} \) magnetic moments from a frustrated anti-ferromagnetic order in the metallic state to an anti-ferromagnetic order in the insulating state (cf. Fig. 2.8 (a)-(c)) \([23, 32, 40, 41]\).

\[ \text{Figure 2.7.: Identification of the MIT in } A_2\text{Ir}_2\text{O}_7 \text{ via (a) magnetotransport and (b) magnetization measurements / (taken from Ref. [24]).} \]

In the framework of this master’s thesis polycrystalline \( \text{Nd}_{2-x}\text{Pr}_x\text{Ir}_2\text{O}_7 \) iridates as well as \( \text{Nd}_2\text{Ir}_2\text{O}_7 \) thin films are investigated. The \( A_2\text{Ir}_2\text{O}_7 \) with \( A = \text{Nd} \) and \( \text{Pr} \) are of particular interest since \( \text{Nd} \) and \( \text{Pr} \) are neighbors in the periodic table, meaning they are very similar considering electronic configuration and ionic radii. However, a metallic behavior down to mK temperatures is present in the \( \text{Pr} \) compound, while the \( \text{Nd} \) compound shows a clear metal to insulator transition at around 35 K. Thus, this thesis deals with praseodymium substituted \( \text{Nd}_2\text{Ir}_2\text{O}_7 \), resulting in \( \text{Nd}_{2-x}\text{Pr}_x\text{Ir}_2\text{O}_7 \) with \( 0 \leq x \leq 2 \). This should influence the transition temperature of the MIT as well as the magnetic and magnetotransport properties, if they just depend on the ionic radii.
2.3. Pyrochlore iridates $A_2Ir_2O_7$ with $A = \text{Nd, Pr}$

Figure 2.8.: Magnetic structure: (a) shows the so called “all-in all-out” configuration which is considered the anti-ferromagnetic phase that exists below the MIT temperature, exemplarily represented by the Nd$^{3+}$ ions and moments. In (b) the mutual influence of the two tetrahedral networks is shown. For ferromagnetic or anti-ferromagnetic order the direction of one color set of arrows reverses directions, retaining the “all-in all-out” (=AIAO) structure. (Both figures from Ref. [23]). (c) Schematic phase diagram (compare Fig. 2.2) for the special case of a pyrochlore lattice. Two possible anti-ferromagnetic (=AF) order variations are shown, insulating (=I) phases are marked by shaded color. ((SM = (semi-)metal, WSM = Weyl semimetal, TI = topological insulator ) The vertical line and the stars indicate the change of the electronic structure, which is shown in (d). The Weyl point is marked by a red circle. (Both figures from Ref. [32]).
Part I.

Polycrystalline Nd$_{2-x}$Pr$_x$Ir$_{2+\delta}$O$_7$
Chapter 3.

Nd$_2$Ir$_2$O$_7$ bulk material

In this chapter, the preparation of polycrystalline Nd$_2$Ir$_2$O$_7$ bulk samples as well as their physical properties will be discussed. The first section deals with the fabrication of polycrystalline powder via a solid state reaction. In the following sections, the fabricated samples will be characterized by several methods. First, we present Energy Dispersive X-ray (EDX) data to investigate the chemical composition of the samples. Section 3 focuses on X-ray powder diffraction to study the structural properties. The fourth section is dedicated to the magnetic properties of the samples. The temperature dependent magnetization and magnetic field dependent magnetization will be investigated using SQUID magnetometry. Section 5 contains magnetotransport measurements and is divided in several subsections, investigating the resistivity in different measurement geometries. This includes temperature dependent and magnetic field dependent resistivity measurements as well as the corresponding magnetoresistances, and Hall measurements. This last section summarizes the results.

3.1. Fabrication

The basis for the polycrystalline samples fabricated in the framework of this thesis is a polycrystalline powder that is produced by a solid state reaction. The chemical substances used to form the compound are Nd$_2$O$_3$ and Ir metal.

The reaction equations is:

\[
\text{Nd}_2\text{O}_3 + 2 \text{Ir} + 2 \text{O}_2 \rightarrow \text{Nd}_2\text{Ir}_2\text{O}_7
\]

To perform the reaction, the solid substances are ground into powder and then heated up to a certain temperature with a heating rate of 10$^{\circ}$C/h in oxygen atmosphere. At this temperature the powder is kept for 10 h before it is cooled down to room temperature. After that the product is ground and the heating process is repeated. This is done several times with increasing temperature from 900$^{\circ}$C up to 1125$^{\circ}$C ("batch 1") and 1000$^{\circ}$C ("batch 2"), respectively.\[1\] For transport measurements and

\[1\]The samples were produced by Astrid Habel and Karen Helm-Knapp in the WMI crystal laboratory.
for the Pulesd Laser Deposition (PLD) a pressed powder sample is essential. To produce those the powder is pressed into a thin cuboid rod (cf. Fig. 3.1) or a flat cylinder, respectively, in the final heating step.

![Figure 3.1.: Polycrystalline pressed Nd$_2$Ir$_2$O$_7$ powder rod.](image)

### 3.2. Energy dispersive X-ray (EDX)

Energy Dispersive X-ray (EDX) (cf. App. A.9) spectroscopy is a means to determine the composition of a sample. It is used in order to investigate whether the stoichiometric composition has changed during the fabrication process. This may happen due to the fact that metal atoms may be volatile at high temperatures even below the melting point.

The measurement shown in figure 3.2 was carried out using a polycrystalline Nd$_2$Ir$_2$O$_7$ sample of batch 1 fabricated at 1125 °C, henceforth referred to as “Nd$_2$Ir$_2$O$_7$ poly” (see for list of samples in Tab. B.1 in the appendix). The atomic composition is determined to be 47% neodymium and 53% iridium when not considering the oxygen content, which cannot be properly measured with this method. For the determination the $L$-edges were used. The measurement also shows the $K_\alpha$ line of iron, which may probably be caused by the EDX setup itself.

Within the accuracy of the measurement, which is several percent [25, 42], it was possible to confirm that there is no considerable Nd or Ir loss during the fabrication process. This shows that the chosen procedure in the solid state reaction is suitable for fabricating further samples.
3.3. X-Ray powder diffraction (XRPD)

To investigate the crystalline quality of the Nd$_2$Ir$_2$O$_7$ samples, X-Ray Powder Diffraction (XRPD) (cf. App. A.3) was carried out for both samples (batch 1 and 2). XRPD on polycrystalline powders usually needs a higher beam intensity than for thin films to detect a reasonable number of counts at the detector. Therefore, the monochromator has to be removed from the beam line to increase the primary intensity. This results in a non-monochromatic beam with Cu-K$_{\alpha 2}$ ($\lambda = 0.154439$ nm) and Cu-K$_{\alpha 1}$ ($\lambda = 0.154056$ nm) radiation (Ref. [43]), which causes additional reflections at slightly higher 2$\theta$ angles compared to monochromatic Cu-K$_{\alpha 1}$ radiation only.

Figure 3.3 shows the result of the XRPD measurement of the Nd$_2$Ir$_2$O$_7$ poly sample. Included in the same graph is a simulation done with PowderCell 2.4, using parameters from literature. In particular, the $x$-value of the 48f-position (cf. Sec. 2.2) and the lattice constant $a$ were set to $x = 0.33$ [44] and $a = 10.383$ Å [45], respectively. As obvious from Fig. 3.3, the calculated peak positions very well coincide with the observed peak position. However, PowderCell is not able to simulate the peak intensities well and cannot determine the lattice constant.
Therefore, we also apply the Rietveld refinement method (cf. App. A.4) using the FullProf Software Suite. This software can determine the lattice constant from the measured data and also the $x$-value of the oxygen ion which is an important structural parameter of the unit cell as it describes the deviation from a perfect oxygen octahedron around each iridium ion (cf. Sec. 2.2).

As shown in Fig. 3.3 (a), the result of the Rietveld simulation indicates very clearly that there are no parasitic phases as the peaks fulfill the requirements given by the simulation. It suggests a lattice constant of $a = 10.3737$ Å and a trigonal compression for the measured value $x = 0.3375$ compared to the ideal value of $x_{\text{ideal}} = 0.3125$. However, both values are in good agreement with literature values ($x = 0.33$ [44], $a = 10.383$ Å [45], $a = 10.3768$ Å [44], and $a = 10.3677$ Å taking a linear extrapolation from data in Ref. [18]).

Figure 3.3.: XPRD pattern of the Nd$_2$Ir$_2$O$_7$ poly sample and pattern simulated with the program PowderCell.

The Nelson-Riley (cf. App. A.4) approach is a second method to precisely determine the lattice constant under a given symmetry. In Fig 3.4 (b) the linear extrapolation $NR \rightarrow 0$ yields a cubic lattice constant of $a = 10.3674$ Å. For the evaluation we used the reflections labeled in Fig. 3.3.
Comparing both lattice constants, determined by the Rietveld refinement and the Nelson-Riley approach both provide very similar lattice constants and are therefore both suitable for further use. For the corresponding sample of batch 2 similar results are obtained, which are not shown here. This means both samples are structurally identical, and only the physical properties of the sample of batch 1 will be discussed in the following sections.

\[
NR = \frac{\cos^2(\pi \cdot 2\theta/360)}{\sin^2(\pi \cdot 2\theta/360)} + \frac{\cos^2(\pi \cdot 2\theta/360)}{2\theta/2}.
\]

The linear extrapolation \(NR \to 0\) yields a lattice constant of \(a = 10.3674\) Å.

Figure 3.4.: Determination of the lattice constant: (a) X-ray powder diffraction pattern of \(\text{Nd}_2\text{Ir}_2\text{O}_7\) poly with Rietveld refinement with the software FullProf. The blue line is shifted by -160 for sake of clarity. (b) Lattice constant as a function of the Nelson-Riley number \(NR = \frac{\cos^2(\pi \cdot 2\theta/360)}{\sin^2(\pi \cdot 2\theta/360)} + \frac{\cos^2(\pi \cdot 2\theta/360)}{2\theta/2}\). The linear extrapolation \(NR \to 0\) yields a lattice constant of \(a = 10.3674\) Å.
3.4. Magnetic properties

To investigate the magnetic properties of the Nd$_2$Ir$_2$O$_7$ poly sample, a SQUID magnetometer (cf. App. A.7) is used. The samples are placed in the magnetometer and a constant field of $\mu_0 H = 100$ mT is applied to magnetize the sample. The sample temperature is swept from 2 K up to 250 K. The cooling process is either done under field-cooled (FC) conditions by applying a field of $\mu_0 H = 7$ T or zero-field-cooled (ZFC) conditions.

As the SQUID software calculates the magnetization in units of emu/g it is necessary to convert it to standard units using the density to rescale it to the volume. The density used is $9.341 \text{ g/cm}^3$, which is calculated by FullProf using the data from the XRD measurement.

$$
\text{Nd}_2\text{Ir}_2\text{O}_7
$$

Figure 3.5.: Magnetization as a function of temperature recorded for field-cooled (FC) and zero-field-cooled (ZFC) conditions for the Nd$_2$Ir$_2$O$_7$ poly sample. There is a strong splitting between ZFC and FC curves for low temperatures observable, which might be related to the onset of a long range magnetic ordering.

The result can be seen in Fig. 3.5 (a). It clearly shows a significant splitting of the magnetization as a function of temperature recorded for FC and ZFC conditions, starting between 34 K and 35 K. Instead of determining the splitting temperature by subtracting the curves, here the first derivative is used. By taking the first derivative of the two curves it is possible to correct for non equally distributed data points. This provides a splitting temperature of $T_{\text{split}} = 34.4$ K.
3.4. Magnetic properties

The splitting of those curves is an indication for the existence of a long range magnetic order below $T_{\text{split}}$. The curves are in good agreement with available literature data [20] [21]. There are further means to detect long range order phenomena, which will be used in the following sections to confirm the data acquired so far.

Figure 3.5 (b) shows magnetic field dependent magnetization curves for various temperatures, recorded for Nd$_2$Ir$_2$O$_7$ poly. The measurements are in agreement with Ref. [20], they do not agree with the findings of Disseler et al. [19]. From these data, it is possible to exclude a ferromagnetic ordering phenomenon as all the measured curves have zero magnetization for zero field. This supports the data of other groups who claim that there is an anti-ferromagnetic all-in all-out ordering of the Ir$^{4+}$ ions below $T_{\text{split}}$ (cf. Sec. 2.3) [21] [23].

It is not possible to observe any hysteretic effects directly below $T_{\text{split}} = 34.4$ K between the up-sweep and down-sweep curves in Fig. 3.5 (b). However, below 10 K a small hysteretic effect can be seen. This coincides with a change of the curvature in Fig. 3.5 (a) at approximately $T_{\text{crit}} = (8.0 \pm 2.0)$ K. There is literature that suggests an ordering of Nd$^{3+}$ moments in the very same temperature region. For example Guo et al. determine the ordering temperature of the Nd$^{3+}$ moments to 9 K by muon spin relaxation [41], while inelastic neutron diffraction experiments suggest the ordering temperature to be $(15.0 \pm 5.0)$ K [23].

The appearance of hysteretic effects below 10 K and not below $T_{\text{split}} = 34.4$ K might be explained by the much higher magnetic moment of Nd$^{3+}$ ions compared to Ir$^{4+}$ ions (cf. Refs. [22] [23]).

In total, the SQUID magnetometry measurements suggest a long range anti-ferromagnetic order of the Ir$^{4+}$ ions with a Neel temperature of $T_N = T_{\text{split}} = 34.4$ K, which is in agreement with existing literature on Nd$_2$Ir$_2$O$_7$. Furthermore, a second temperature $T_{\text{crit}} = (8.0 \pm 2.0)$ K can be determined, at which the Nd$^{3+}$ ions get magnetically ordered.
3.5. Magnetotransport

Several magnetotransport measurements were carried out in the Nd$_2$Ir$_2$O$_7$ poly sample in the framework of this thesis, using a four point measurement geometry (“van der Pauw”, cf. App. A.5). The main purpose is to determine the metal insulator transition temperature $T_{MI}$ (cf. Sec. 2.3).

Measurements were done in several different measurement configurations:

- Magnetic field applied in-plane (parallel to the sample surface) parallel to the current direction in van der Pauw geometry (“ippj”).

- Magnetic field applied in-plane (parallel to the sample surface) perpendicular to the current direction in van der Pauw geometry (“ipnj”).

- Magnetic field applied out-of-plane (perpendicular to the sample surface) perpendicular to the current direction in Hall geometry (“oop hall”).

![Figure 3.6.](image)

Figure 3.6.: Schematic picture of the contact placement. The arrow direction denotes positive magnetic field for in-plane measurements.

The sample size is approximately $4 \times 4 \times 0.6 \text{mm}^3$. The electrical contacts to perform the magnetotransport measurements were made by sputtering using a shadow mask, resulting in the geometry shown in Fig. 3.6. In the case of the Nd$_2$Ir$_2$O$_7$ poly sample the distance between the contacts was $d = 2 \text{mm}$ and each contact diameter
3.5. Magnetotransport

was \( w = 0.5 \text{ mm} \). As the samples had a resistance in the order of \( 1 \Omega \) at room temperature we applied a current and measured the corresponding voltage. To get reasonable results, the first task is to check for ohmic contacts (independent of the measurement geometry). This means it is necessary to obtain the \( I-V \) characteristic. Figure 3.7 shows the result for the \( \text{Nd}_2\text{Ir}_2\text{O}_7 \) poly sample taken at 2 K as the highest resistance is expected at low temperatures.

![Figure 3.7: \( I-V \) curve for the \( \text{Nd}_2\text{Ir}_2\text{O}_7 \) poly sample, taken at 2 K. The vertical blue lines indicate the current value used for the following transport measurements. The ohmic region ends at an absolute current of approximately 25 mA where the linear fit and data do not converge anymore.](image)

The measurement clearly shows an ohmic region where the \( I-V \) characteristic is linear, i.e., heating effects in the sample can be neglected for currents \( I \leq 25 \text{ mA} \). For the following measurements a current of \( I = 20 \text{ mA} \) was applied across the sample. For this current value the sample is still ohmic and yet not at the edge of the ohmic region, and the high current provides reasonable voltages in the conducting region as well.
In general two different types of measurements are done:

- $\rho(T)$: temperature dependent resistivity by measuring $V(T)$ in the temperature range of 2 K to 300 K at discrete magnetic fields of 0 T and ±15 T.

- $\rho(H)$: magnetic field dependent resistance by measuring $V(H)$ in magnetic field ranges of $-15$ T to 15 T at discrete temperatures between 2 K and 70 K.

To realize this measurements the sample was mounted on a chip carrier system (cf. Fig. 3.8) is system makes it easy to perform measurements in the different geometries within a minimum of time and also guarantees the contacts on the sample to stay the same all over the time and therefore prevents errors due to bad contact.

Figure 3.8.: Contacted polycrystalline pressed Nd$_2$Ir$_2$O$_7$ powder sample mounted on a chip carrier.

### 3.5.1. $V(T)$ measurements

This type of measurement was done in the following steps:

1. Set the magnetic field to zero.
2. Set sample temperature to 100 K for 1 minute to clear any remanent effects (anti-ferromagnetic ordering predicted below approximately 34 K, cf. Sec. 2.3 and 3.4).
3. Set the magnetic field to the target field (0 T, $-15$ T, or 15 T).
4. Apply current during cooling of the sample down to 8 K and the Variable Temperature Insert (VTI) down to 5 K. Keep the temperature stable for 5 minutes to establish thermal equilibrium.

5. Cool the sample down to 2 K and the VTI down to 1.6 K and keep temperature for 1 minute to establish thermal equilibrium.

6. Start measurement while heating the sample with a rate of 2 K/min and the VTI with 0.33 K/min.

7. Start closing needle valve at helium inlet step by step after reaching 15 K.

The measurement sequence requires a precisely controlled helium level inside the VTI as too much helium causes measurement anomalies and technical problems when reaching the boiling point of liquid helium. This could be resolved by keeping the time short in which the sample has a temperature below 4.3 K. Also the VTI heating rate was set lower than the heating rate of the chip-carrier to evaporate the collected helium in the VTI very slowly at a point where the sample already is much warmer than 4.3 K to prevent effects generated by the cooling effect of the evaporated helium gas. By using the parameters given in the list above, the evaporation temperature in the VTI is reached when the sample temperature is around 16 K. First experiments revealed the need to close the needle valve step by step because closing the needle valve at a fixed temperature abruptly changes the pressure in the VTI, which leads to pressure change related effects in the measurements.

**Resistivity $\rho(T)$**

As mentioned above the resistivity versus temperature $\rho(T)$ is not measured directly but is calculated by

$$\rho(T) = \frac{V(T)}{I} \cdot \frac{w \cdot t}{d},$$

(3.1)

where $d$ is the distance between the centers of opposing contacts, $w$ the diameter of a contact and $t$ the sample thickness (cf. Fig. 3.6).

As described in Ref. [46], correction factors have to be taken into account due to the finite size of the contacts as well as the distance of the contacts with respect to the periphery of the sample. However, because all measurements (also in the following sections) are done in the same way there will be no correction carried out as every measurement has the same relative correction factors which cancel when considering, e.g., magnetoresistance, which is a relative value of measured data.
Chapter 3. Nd$_2$Ir$_2$O$_7$ bulk material

The results of the $\rho(T)$ measurement are shown in Fig. 3.9 comparing different current directions with a magnetic field applied in-plane (ippj and ipnj). $\rho_{NM}$ hereby denotes the current direction from contact $N$ to $M$, e.g. the resistivity $\rho_{21}$ is determined by applying a current $I_{21}$ from the contact 2 to contact 1 and measuring the voltage $V_{34}$ between contacts 3 and 4.

Measurements with the current parallel to the magnetic field direction (cf. $\rho_{21}$ and $\rho_{43}$) behave in the same manner, but they are off by a factor of around 2.4 to $\rho(T)$ measurements for directions perpendicular to the magnetic field. A bad contact cannot be the reason for this behavior. Also the magnetic field cannot be the cause since the measurements without field should give the same result independent of the current direction because the sample was cooled down without an applied field (ZFC). This leads to the assumption that not all the directions in the sample are equivalent, probably due to structural reasons. As the resistivity of both directions just differ by a constant factor, for the following measurements one direction was chosen: drive current over contacts 1 and 2 and measure the 4-point voltage at contacts 4 and 3.

![Figure 3.9.](image)

**Figure 3.9.** (a) Resistivity $\rho_{NM}(T)$ for different current directions with the magnetic field applied in-plane. Parallel directions coincide, perpendicular directions are off by a constant factor. (b) Resistivity curves split under the influence of a magnetic field, shown explicitly for $\rho_{21}(T)$.

In Fig. 3.9 (b), a change of the temperature dependence of the resistivity is visible. The resistivity changes from a metallic behavior to an insulating behavior below ap-
proximately 35 K. This temperature dependence is in agreement with Refs. \[20, 21\] but in disagreement with Ref. \[18\], which might be caused by a difference in fabrication. Furthermore, a clear splitting between the measured $\rho(T)$ curves at 0 T and $\pm 15$ T is observable. The strength of the splitting can be determined by taking the difference $\Delta \rho(T) = \rho_{0T}(T) - \rho_{15T}(T)$ where $\rho_{15T}(T) = (\rho_{+15T}(T) + \rho_{-15T}(T))/2$ is the averaged value of the $+15$ T and $-15$ T curve. The difference $\Delta \rho(T)$ is displayed in Fig. 3.10 (a). Splitting effects start below a temperature of 35 K with first a drop in difference below zero and then a strong increase starting below 31 K. This indicates a large magnetoresistance below 35 K.

![Figure 3.10](image)

**Figure 3.10:** Evaluation of the $\rho_{21}(T)$ curves. (a) Difference between the $\rho(T)$ curves measured with an applied magnetic field of $\pm 15$ T and 0 T. The curves measured at $\pm 15$ T are averaged to the $\rho_{15T}(T)$ curve. Notable deviation from 0 starts below 35 K. (b) First derivative of $\rho_{0T}(T)$ under ZFC condition with respect to the temperature. Applied fitting methods to find the absolute minimum of the $\rho_{0T}(T)$ curve between 33.3 K and 34.3 K.

Figure 3.10 (b) exemplarily shows the first derivative with respect to the temperature of $\rho_{21}$, measured at zero field. It shows that the minimum in resistivity is located between 33.3 K and 34.3 K, depending on the used temperature region for the linear fit (cf. Fig. 3.10 (b)). This is also valid for measurements under applied field conditions. From the resistivity versus temperature measurements, the temperature of the metal to insulator transition can therefore be set to $(33.8 \pm 0.5)$ K. The temperature of the metal to insulator transition $T_{MI}$ is thus in good agreement with the Neel temperature $T_N = 34.4$ K of the anti-ferromagnetic ordering in the previous section.
Another feature in the $\rho(T)$ curves, visible in Fig. 3.9, is a small kink, located at around $(11.0 \pm 0.2)\,\text{K}$, which can be suppressed by a high magnetic field. This temperature is in the same region as $T_{\text{crit}} = (8.0 \pm 0.2)\,\text{K}$ for the onset of the hysteretic behavior in the $M(H)$ curves discussed in the previous section. Therefore, the kink in the $\rho(T)$ curve might also be explained by the ordering of the Nd$^{3+}$ ions.

**Magnetoresistance $MR(T)$**

According to the common definition of the magnetoresistance ($MR$) we define

$$MR = \frac{\rho(T, \mu_0 H = \pm 15\,\text{T}) - \rho(T, \mu_0 H = 0\,\text{T})}{\rho(T, \mu_0 H = 0\,\text{T})}. \quad (3.2)$$

To calculate the temperature dependent magnetoresistance $MR(T)$, the averaged $\pm 15\,\text{T}$ data set from above ($\rho_{15\text{T}}$) and also the $0\,\text{T}$ data set ($\rho_{0\text{T}}$) is used (cf. Fig. 3.11).

![Figure 3.11.: Magnetoresistance ($MR$) as a function of the temperature $T$. $MR(T)$ for the 4 possible current directions. A maximum appears at $32.2\,\text{K}$. The crosses indicate data points extracted from $MR(H)$ measurements discussed in the next paragraph.](image)

From Fig. 3.11 it is obvious that there is no current direction dependent $MR$. This means the relative splitting of the $\rho_{NM}$ curves (cf. Fig. 3.9) is the same for every data set. Matsuhira et al. [22] report a small positive magnetoresistance for a temperature
of 40 K and a large negative magnetoresistance of up to -79 for discrete temperatures below 25 K. For 40 K (and above) we observe the same behavior, yet we see a positive magnetoresistance down to 25 K, where it switches its sign (cf. Fig. 3.10). However, we do not observe a large negative magnetoresistance at low temperatures. An explanation for this is that at 15 T we are still in a regime where minor loops occur. This is reasonable as Matsuhira et al. seem to enter the magnetic saturation regime at around 50 T. As obvious from Fig. 3.11 a maximum of the magnetoresistance appears at 32.2 K. This is again an indication for the onset of a magnetic ordering phenomenon at this temperature.

3.5.2. \( V(H) \) measurements

This type of measurement is done in the following way:

1. Remove any applied magnetic fields and set sample temperature to 100 K for 1 minute to clear any magnetic order in the sample.

2. Set sample temperature to target temperature.

3. Apply current and wait at target temperature for at least 5 minutes to establish thermal equilibrium.

4. Start measurement.

The current is switched from positive to negative values (same absolute value) at each step to eliminate heating effects.

- The magnetic field was varied from 0 T \( \Rightarrow \) 15 T \( \Rightarrow \) -15 T \( \Rightarrow \) 15 T.

- For \(-3 \text{T} \leq \mu_0 H \leq 3 \text{T}\) the step size is 0.1 T, else 0.25 T.

- The sweep rate of the magnetic field between measurements was set to 1 T/min.

- The delay between setting field / current switching and measurement was set to 5 seconds.

Like before, the current is set fixed and the voltage is measured at each magnetic field step. An exemplary result is shown in Fig. 3.12 (a). The chosen curve is taken at 15 K. This temperature is suitable for demonstration as all effects that will be described in the next paragraph are visible and the curve has the typical behavior for the material system.
Figure 3.12.: Voltage measured with respect to the magnetic field $V(H)$ at a temperature of 15 K. (a) Voltage curves for positive and negative current $I = \pm 20$ mA. (b) Averaged voltage $(V_+ - V_-)/2$ provides a data set eliminating heating effects. The numbers at the arrows indicate time sequence of the measurement. The dashed line shows that the curve is not fully symmetric but has also an antisymmetric part. (c) Symmetric part of $V(H)$: $(V_+ + V_-)/2$. (d) Antisymmetric part of $V(H)$: $(V_+ - V_-)/2$.

Figure 3.12 (b) shows the averaged positive and negative current measurement (shown in (a)), i.e., half of the sum of the absolute voltages. This provides better results especially at higher temperatures that are typically noisy due to small temperature effects since this method eliminates heating effects. The curve contains 5 branches that are also described in Ref. [22]. Qualitatively the curve shows the same behavior as in Ref. [22]. The part labeled 1 is the initial up-sweep which shows a drop...
in voltage (and hence also in resistivity) for low to moderate magnetic fields, but then increases for high fields. The parts labeled 3 and 5 contain a local minimum, which is not visible in the corresponding figure in Ref. [22]. This, however, seems to be a temperature dependent effect in our measurement in contrast to Ref. [22]. The curves do neither show a shift of the maximum nor the initial sweep up behavior as it is shown in measurements by Ueda et al. in Ref. [20].

The average voltage can be symmetrized and antisymmetrized by calculating the sum, respectively difference of the voltages at positive \( V_{\uparrow} \) and negative \( V_{\downarrow} \) fields and dividing the sum by 2. For the calculation, the initial magnetic field sweep from 0 T to 15 T (labeled 1 in Fig. 3.12) is not taken into account. The results are shown in Fig. 3.12 (c) and (d). Very recently, Ueda et al. published similar results of the magnetoresistance in Nd\(_2\)Ir\(_2\)O\(_7\), which is composed of a symmetric and antisymmetric part [20]. However, they observed a clear shift of the up- and down-sweep with respect to zero magnetic field, which is often observed in conventional ferromagnets. Furthermore, they discovered a sign change of the antisymmetric part and related this to switchable anti-ferromagnetic domains at high magnetic fields. At the moment this is an open question if the sign change of the antisymmetric part as well as the hysteretic effects visible in the symmetric part in Fig. 3.12 (c) is caused by switchable anti-ferromagnetic domains.

Furthermore, the curvature of the measured \( V(H) \) curves changes drastically with temperature. Not only does the magnitude of the effect decrease with increasing temperatures, but also the curvature changes from concave to convex. This will be discussed in the next section on the basis of the magnetoresistance.

### Magnetoresistance \( MR(H) \)

From the symmetric part of \( V(H) \) (cf. Fig. 3.12 (c)), it is possible to extract the magnetic field dependent magnetoresistance. It is defined as:

\[
MR = \frac{\rho(T = T_0, \mu_0H) - \rho(T = T_0, \mu_0H = 0 \text{ T})}{\rho(T = T_0, \mu_0H = 0 \text{ T})}
\]

where \( T_0 \) is a fixed temperature. The value at 0 T is the value from the symmetrized curve in Fig. 3.12 (c), not the value before the first up-sweep, because the hysteretic behavior would cause an arbitrary value at zero field, and thus not provide zero.

Figure 3.13 shows the magnetoresistance \( MR(H) \) for different temperatures. Again very obvious is the hysteretic behavior, the change in curvature, and magnitude of the \( MR \), all depending on the temperature. Most noticeable is the change of the
behavior at around 35 K. At this temperature, the $MR$ changes sign and exhibits a quadratic behavior without hysteretic effects as expected for normal metals. In Fig. [3.11] the crosses indicate data points calculated by using the initial 0 T value together with the averaged $\pm 15$ T. In this case, it is correct to use this value because in the $V(T)$ measurement the 0 T curve was taken after zero-field cooling. The results are consistent with the $MR(T)$ measurements.

![Figure 3.13. Magnetoresistance $MR$ as a function of the applied magnetic field in Nd$_2$Ir$_2$O$_7$ for several temperatures.]

**Hall measurement**

For the Hall measurement, a current is driven diagonally through the sample and the voltage is measured over the other diagonal which is perpendicular to the current direction due to the chosen square geometry of the sample. The sample is cooled to 5 K in zero field and then a magnetic field of 15 T is applied in out-of-plane direction. First, the current $I_{13}$ is applied between contact 1 and 3 and the voltage $V_{24}$ is measured between 2 and 4. This is done for positive and negative currents. Then, the current is applied between contact 2 and 4 and the voltage $V_{13}$ is measured between 1 and 3. This results in 4 data sets. As there may be hysteretic effects the down-sweep and the up-sweep are treated separately. We calculate the voltage difference between positive and negative field direction $V_{\pm}$ for every current direction. The results are then added up and divided by 8:
3.5. Magnetotransport

\[ V_{\text{Hall}} = \frac{(V_{13} - V_{13}) + (V_{31} - V_{31}) + (V_{24} - V_{24}) + (V_{42} - V_{42})}{8} \]. \hspace{1cm} (3.4)

Figure 3.14 shows the result of the Hall effect measurement. Noticeable are the extrema at magnetic fields of approximately ±1.6 T and ±7.5 T.

In literature, there is only one report on the Hall effect in Nd$_2$Ir$_2$O$_7$ et al. [19]. However, in this publication the data are extracted from the antisymmetric part of ordinary resistivity measurements where the Hall effect is generated by a misalignment of the sample. We do not observe the same behavior as described in Ref. [19]. However, there are some similar features like local minima and maxima. The reason for the magnetic field dependence of the Hall voltage is still unclear and further experiments have to be carried out.

Figure 3.14.: Hall effect measurement at 5 K, up-sweep and down-sweep show hysteretic behavior.
3.6. Summary and conclusion

The successful fabrication of single-phase Nd$_2$Ir$_2$O$_7$ as a polycrystalline bulk material was demonstrated. The high structural quality could be confirmed by XRPD. For Nd$_2$Ir$_2$O$_7$ the literature value ($a = 10.3677$ Å) which is obtained by linearly extrapolating the published values in Ref. [18] to 300 K is very close to our measured value ($a = (10.370 \pm 0.004)$ Å). Our value is, however, significantly smaller than the values described in other publications ($a = 10.383$ Å [45], $a = 10.3768$ Å [44]). EDX data show the existence of the correct phase in the sample, proving the correct stoichiometry between iridium and neodymium.

Magnetization measurements suggest the existence of a long range magnetic ordering below a critical temperature $T_{\text{split}} = 34.4$ K and the onset of an additional ordering phenomenon in a temperature regime around $T_{\text{crit}} = 8$ K. This is supported by magnetotransport data which yield $T_{\text{MI}} = 32.2$ K, which is close to $T_{\text{split}}$, and $T_{\text{kink}} = (11.0 \pm 0.2)$ K, which is close to $T_{\text{crit}} = (8.0 \pm 0.2)$ K. Our measured values agree well with other reports [21, 23, 24, 39].

The appearance of a hysteretic behavior in the $M(H)$ curve below $T_{\text{crit}}$ (but not below $T_{\text{split}}$) is a first indication that the ordering at $T_{\text{crit}}$ is related to the Nd$^{3+}$ moments, and the ordering at $T_{\text{split}}$ is related to the Ir$^{4+}$ moments. This can be concluded from the fact that the Nd$^{3+}$ moments are much larger than the Ir$^{4+}$ moments [22, 23]. This is, however, in strong contrast to Disseler et al. [18] who state that the Nd$^{3+}$ moments remain in a paramagnetic state for temperatures down to 1.48 K and the Ir$^{4+}$ moments cause the effects they observe in a temperature regime around 10 K. Disseler et al. also do not observe a transition at $T_{\text{MI}}$.

In the magnetotransport section, several methods are presented to obtain a value for the metal to insulator transition temperature $T_{\text{MI}}$. We extracted $T_{\text{MI}}$ in two different ways from the $\rho(T)$ measurements. We also calculated the magnetoresistance $MR(T)$ which showed a maximum in the corresponding temperature region, and $MR(H)$ where we observe a sign change as well as a change to a quadratic behavior around $T_{\text{MI}}$. These facts support the assumption that there exist two ordering temperatures in the compound which are related to ordering of the two sublattices. The origin of the results of the Hall measurement cannot be resolved from the available data. There is only one reference in the literature [19] to compare. Further studies are needed to reveal which mechanisms cause the observed behavior of the Hall voltage.
Chapter 4.

Pr as substituent for Nd in the compound Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$

In this chapter the preparation, the structural, the magnetic, and the transport properties of polycrystalline samples of Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ with different substitution levels $x$ will be discussed. The first section discusses the difference between the solid state reactions between the neodymium pyrochlore iridate and pyrochlore iridates with praseodymium as substitute for neodymium. In section 2 the results of the EDX analysis of the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ compounds are presented. In the third section, XRPD data are shown, and section 4 focuses on the magnetic properties of the fabricated samples. The fifth section is dedicated to magnetotransport, we will discuss how the resistivity and magnetoresistance can be manipulated via praseodymium substitution. In section 6, we describe our findings provided by iridium doping of praseodymium iridate. This last section summarizes the results.

4.1. Fabrication

The fabrication is carried out in the same way as for the Nd$_2$Ir$_2$O$_7$ compound described in the previous chapter. Again, two batches of samples were fabricated. Batch 1 and batch 2 were fabricated using a maximum temperature of 1125$^\circ$C and 1000$^\circ$C, respectively. For the praseodymium substitution, Pr$_6$O$_{11}$ is used as starting oxide material. The compound formula differs strongly from Nd$_2$O$_3$, i.e., the valence of neodymium in Nd$_2$O$_3$ is different compared to praseodymium in Pr$_6$O$_{11}$. This has to be taken into account. We find

$$2 \text{Pr}_6\text{O}_{11} + 12 \text{Ir} + 10 \text{O}_2 \rightarrow 6 \text{Pr}_2\text{Ir}_2\text{O}_7$$

and modify the reaction equation for the Nd compound

$$6 \text{Nd}_2\text{O}_3 + 12 \text{Ir} + 12 \text{O}_2 \rightarrow 6 \text{Nd}_2\text{Ir}_2\text{O}_7.$$
Chapter 4. Pr as substituent for Nd in the compound Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$

It is now easy to find a reaction equation for the substituted system by weighting the formulas with \((x)\) and \((2 - x)\), respectively

\[
(2 - x) \cdot (6 \text{Nd}_2\text{O}_3) + (x) \cdot (2 \text{Pr}_6\text{O}_{11}) + (24 - 2x) \text{O}_2 + 24 \text{Ir} \rightarrow 2 \cdot (6 \text{Nd}_{2-x}\text{Pr}_x\text{Ir}_2\text{O}_7)
\]

which can be simplified to

\[
(2 - x) \cdot (3 \text{Nd}_2\text{O}_3) + (x) \text{Pr}_6\text{O}_{11} + (12 - x) \text{O}_2 + 12 \text{Ir} \rightarrow 6 \text{Nd}_{2-x}\text{Pr}_x\text{Ir}_2\text{O}_7.
\]

In the framework of this thesis, 4 praseodymium substituted samples Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ were fabricated at 1125°C with different praseodymium contents: \(x = 0.5\), \(x = 1\), \(x = 1.5\) and \(x = 2\). They are named “Nd$_{1.5}$Pr$_{0.5}$Ir$_2$O$_7$ poly”, “NdPrIr$_2$O$_7$ poly”, “Nd$_{0.5}$Pr$_{1.5}$Ir$_2$O$_7$ poly”, and “Pr$_2$Ir$_2$O$_7$ poly”, respectively. The presented results will mainly focus on these samples, however, some results for the set fabricated at 1000°C will be included, where necessary.

4.2. Energy dispersive X-ray analysis (EDX)

In this section we present the Energy Dispersive X-ray (EDX, cf. App. A.9) analysis data acquired for the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ samples. Figure 4.1 shows the EDX spectra. For neodymium and praseodymium, the corresponding X-ray emission edges are very close to each other because their atomic number only differs by 1.

Table 4.1.: Results of the EDX measurements. The table also includes the values for Nd$_2$Ir$_2$O$_7$ determined in the previous chapter. For samples containing both, neodymium and praseodymium, the results may be inaccurate as discussed in the text.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nd (atomic %)</th>
<th>Pr (atomic %)</th>
<th>Ir (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$_2$Ir$_2$O$_7$ poly</td>
<td>47.0</td>
<td>-</td>
<td>53.0</td>
</tr>
<tr>
<td>Nd$<em>{1.5}$Pr$</em>{0.5}$Ir$_2$O$_7$ poly</td>
<td>43.1</td>
<td>9.9</td>
<td>47.0</td>
</tr>
<tr>
<td>NdPrIr$_2$O$_7$ poly</td>
<td>32.9</td>
<td>20.6</td>
<td>46.5</td>
</tr>
<tr>
<td>Nd$<em>{0.5}$Pr$</em>{1.5}$Ir$_2$O$_7$ poly</td>
<td>15.4</td>
<td>36.6</td>
<td>48.0</td>
</tr>
<tr>
<td>Pr$_2$Ir$_2$O$_7$ poly</td>
<td>-</td>
<td>50.2</td>
<td>49.8</td>
</tr>
</tbody>
</table>

The atomic ratios are listed in Tab. 4.1. The Pr$_2$Ir$_2$O$_7$ sample shows nearly a 1:1 ratio for lanthanides and iridium. Samples containing both, neodymium and iridium, do not provide the proper ratios of neodymium and praseodymium. This is caused by the aforementioned fact that the edges of both are very close to each other, which
4.2. Energy dispersive X-ray analysis (EDX)

Figure 4.1.: Energy dispersive X-ray (EDX) measurements for (a) Nd$_{1.5}$Pr$_{0.5}$Ir$_2$O$_7$, (b) NdPrIr$_2$O$_7$, (c) Nd$_{0.5}$Pr$_{1.5}$Ir$_2$O$_7$, and (d) Pr$_2$Ir$_2$O$_7$. Emission lines are marked with colored arrows.

means it is harder to determine the exact peak positions. However, the lanthanide to iridium ratio is reasonable.

We assume that typical errors of this measurement series are in the range of a few percent for Pr$_2$Ir$_2$O$_7$ as well as for Nd$_2$Ir$_2$O$_7$, and in the range of several percent for Nd$_{1.5}$Pr$_{0.5}$Ir$_2$O$_7$, NdPrIr$_2$O$_7$ and Nd$_{0.5}$Pr$_{1.5}$Ir$_2$O$_7$. Therefore, the EDX measurements provide no significant results concerning the stoichiometry of the latter three samples. The EDX measurement results of Nd$_2$Ir$_2$O$_7$ and Pr$_2$Ir$_2$O$_7$, however, suggest that the fabrication process does not lead to a significant loss of iridium. Therefore, we may assume that the stoichiometric composition of our samples is acceptable for further studies.
Chapter 4. Pr as substituent for Nd in the compound Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$

4.3. X-ray powder diffraction (XRPD)

X-ray Powder Diffraction (XRPD, cf. App. A.3) is again used to determine the lattice constants of the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ samples.

Figure 4.2.: X-ray powder diffraction pattern for the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ poly samples from 31.5° to 65°, showing 4 reflections and their shift to lower angles with increasing praseodymium content. The blue vertical reference lines correspond to the peak positions of Nd$_2$Ir$_2$O$_7$, the black dashed lines indicate Rietveld refinements for the corresponding graphs. For Pr$_2$Ir$_2$O$_7$, the data of the sample fabricated at 1000°C (batch 2) is shown as the sample fabricated at 1125°C (batch 1) showed parasitic phases.

Figure 4.2 shows the results of the XRPD measurement. Again the Rietveld method and Nelson-Riley approach (cf. App. A.4) were applied to derive the lattice constants. The results of both methods are shown in Fig. 4.3 as a function of the praseodymium substitution level $x$. The expected linear behavior is confirmed. The Nelson-Riley approach is applied for the samples of batch 1 and 2, while the Rietveld refinement is used only for the samples of batch 2. The linear fit is calculated for the lattice constants obtained by the Nelson-Riley approach. It shows that the lattice constants fulfill Vegard’s law [47] and thereby proves that there is no phase separation.

For Pr$_2$Ir$_2$O$_7$, the lattice constant ($a = 10.410$ Å) is larger than the literature value for a single crystal ($a = 10.396$ Å [48]). However, it is in agreement with literature values of polycrystalline Pr$_2$Ir$_2$O$_7$ ($a = 10.406$ Å in Refs. [42, 45]).
4.4. Magnetic properties

The magnetization of the praseodymium containing samples is measured with a SQUID magnetometer following the same procedures as for Nd$_2$Ir$_2$O$_7$ (cf. Sec. 3.4). The results are shown in Fig. 4.4.

The absolute value of the magnetization increases with increasing praseodymium content. For Pr$_2$Ir$_2$O$_7$, the magnetization has increased by a factor of 2 compared to Nd$_2$Ir$_2$O$_7$ (cf. Fig. 3.5 (a)). The increase is not completely linear but seems to be stronger for lower concentrations of praseodymium.

All the magnetization curves show a splitting of the magnetization versus temperature curves measured under ZFC and FC conditions. However, the magnitude of the splitting decreases by a factor of 2 compared to Nd$_2$Ir$_2$O$_7$. In relative terms, this is a reduction by a factor of 4 as the absolute magnetization value has increased by 2.
Chapter 4. Pr as substituent for Nd in the compound Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$

Figure 4.4.: Magnetization versus temperature of (a) the Nd$_{1.5}$Pr$_{0.5}$Ir$_2$O$_7$ poly sample, (b) the NdPrIr$_2$O$_7$ poly sample, (c) the Nd$_{0.5}$Pr$_{1.5}$Ir$_2$O$_7$ poly sample, and (d) the Pr$_2$Ir$_2$O$_7$ poly sample. From (a) to (d) the splitting decreases while the total magnetization increases. The splitting temperature, however, does not change significantly from (a) to (c).

The temperature $T_{\text{split}}$ at which the splitting occurs is almost independent of the substituent concentration (cf. Fig. 4.5). This is surprising as other properties like lattice constant and the magnetization change noticeably with the substituent concentration.

There is no literature on the magnetization of Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ compounds. Matsuhira et al. report a shift of the metal to insulator transition temperature $T_{\text{MI}}$ to lower values for Nd$_{1.4}$Pr$_{0.6}$Ir$_2$O$_7$ [22]. Considering the correlation between $T_{\text{MI}}$ and the
4.4. Magnetic properties

onset of the long range magnetic ordering, we also would have expected a change of the temperature at which the splitting of the FC and ZFC curve occurs. Ueda et al. discuss magnetization data for rhodium doped Nd$_2$Ir$_2$O$_7$ samples, where for low doping rates the position of the splitting point between ZFC and FC curves remains unchanged [21].

We also observe a change in the slope for samples with $0 \leq x < 2$ that occurs $T_{\text{crit}} = (8.0 \pm 2.0)$ K identical to the value described in Sec. 3.4. As we do not observe a significant change of the slope for Pr$_2$Ir$_2$O$_7$ this suggests that the ordering of the Nd$^{3+}$ ions is responsible for the change of the slope.

However, as shown in Fig. 4.5, $T_{\text{split}}$ strongly deviates for the Pr$_2$Ir$_2$O$_7$ sample ($x = 2$) in comparison to the samples with $0 \leq x < 2$. As described in Sec. 2.3, the magnetic behavior of Pr$_2$Ir$_2$O$_7$ is different from Nd$_2$Ir$_2$O$_7$. In particular, Pr$_2$Ir$_2$O$_7$ does not show long-range order.

Figure 4.5.: Temperature $T_{\text{split}}$ of the splitting of the magnetization versus temperature measured under FC and ZFC conditions in the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ samples. The dashed line is a guide to the eye.
Chapter 4. Pr as substituent for Nd in the compound Nd<sub>2</sub>xPr<sub>x</sub>Ir<sub>2</sub>O<sub>7</sub>

4.5. Magnetotransport

Magnetotransport measurements were also carried out on the praseodymium containing compounds. The measurement geometry is the same as shown in Fig. 3.6. The current direction is chosen to be from contact 1 to contact 2, and the voltage is measured from contact 3 to 4.

In contrast to the Nd<sub>2</sub>Ir<sub>2</sub>O<sub>7</sub> poly sample these samples are smaller. The sample size for the series with praseodymium substituting neodymium is around 2.5 × 2.5 × t mm<sup>3</sup> and the size of the contacts d = 1 mm and w = 0.5 mm. The thickness t of the samples varies from 0.78 mm to 0.48 mm with increasing praseodymium concentration.

To investigate the ohmic nature of the contacts, first I-V characteristics were taken. Fig. 4.6 exemplarily shows the behavior for the NdPrIr<sub>2</sub>O<sub>7</sub> poly sample and the Pr<sub>2</sub>Ir<sub>2</sub>O<sub>7</sub> poly sample. The other samples show a similar behavior.

Using the same measurement setup as for the Nd<sub>2</sub>Ir<sub>2</sub>O<sub>7</sub> poly sample, also V(T) and V(H) curves were taken with the same parameters, applying a current of 20 mA uniformly for all measurements. This current value is in the ohmic region of the sample and therefore well suited (cf. vertical lines in Fig. 4.6).

Figure 4.6: I-V curve for (a) the NdPrIr<sub>2</sub>O<sub>7</sub> poly sample, and (b) the Pr<sub>2</sub>Ir<sub>2</sub>O<sub>7</sub> poly sample, taken at 2 K. For simplicity, the same current (20 mA) as for the Nd<sub>2</sub>Ir<sub>2</sub>O<sub>7</sub> poly sample in the previous chapter (indicated by the vertical lines) will be used for the following magnetotransport measurements.
4.5.1. $V(T)$ measurements

In this section the temperature dependence of the resistivity and the magnetoresistance will be discussed.

**Resistivity $\rho(T)$**

The temperature dependent voltage $V(T)$ data are converted into the temperature dependent resistivity $\rho(T)$ according to Eq. (3.1). The $\rho(T)$ curves of the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ samples measured with zero magnetic field and $\mu_0 H = \pm 15$ T, respectively, are shown in Fig. 4.7.

![Graphs showing temperature dependent resistivity for different samples](image)

Figure 4.7.: Temperature dependent resistivity for (a) the Nd$_{1.5}$Pr$_{0.5}$Ir$_2$O$_7$ poly sample, (b) the NdPrIr$_2$O$_7$ poly sample, (c) the Nd$_{0.5}$Pr$_{1.5}$Ir$_2$O$_7$ poly sample, and (d) the Pr$_2$Ir$_2$O$_7$ poly sample.
All the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ curves show a change of the $\rho(T)$ behavior at around 35 K. However, the resistivity at $T = 2$ K strongly decreases when increasing the praseodymium content. This might be explained by a closing of the bandgap when increasing the praseodymium concentration, as it was observed by Ueda et al. via rhodium doping of Nd$_2$Ir$_2$O$_7$ [21]. Furthermore, the curves show a splitting of the $\rho(T)$ measured at 0 T and $\pm 15$ T comparable in behavior to the Nd$_2$Ir$_2$O$_7$ poly sample (cf. Fig. 3.9). However, the strength of the splitting effect drastically decreases with increasing praseodymium concentration. Therefore, the magnetoresistance strongly decreases with the praseodymium content.

The behavior of the Pr$_2$Ir$_2$O$_7$ poly compound is quite different. Figure 4.8 (a) shows an enlarged view of the behavior below 35 K of the Nd$_2$Ir$_2$O$_7$ poly sample and the Pr$_2$Ir$_2$O$_7$ poly sample for comparison. While the neodymium compound (as well as all other compounds with a non-zero neodymium concentration) shows a monotonous increase of the resistivity for decreasing temperatures, the resistivity of Pr$_2$Ir$_2$O$_7$ contains a local maximum at 4.5 K. Literature reports suggest that the minimum in resistivity is related to the Kondo effect, which does appear in this compound, but not in the neodymium compounds [27]. However, a phase transition in the examined temperature region (2 K - 300 K) is not reported [27]. Figure 4.8 (b) shows a diagram from Ref. [27]. The same qualitative behavior of the temperature dependent resistivity $\rho(T)$ for Pr$_2$Ir$_2$O$_7$ is visible.

Figure 4.8.: Temperature dependent resistivity of (a) the Pr$_2$Ir$_2$O$_7$ poly sample and the Nd$_2$Ir$_2$O$_7$ poly sample in direct comparison. The behavior is completely different. (b) The figure from Ref. [27] shows a similar behavior of $\rho(T)$ for the Pr$_2$Ir$_2$O$_7$ compound.
Another observation is the absolute value of the resistivity. Pr$_2$Ir$_2$O$_7$ shows metal-like behavior, which also involves a lower resistivity than in the neodymium compounds. We find a resistivity of $\rho(300 \text{ K}) \approx 7 \text{ m}\Omega \text{ cm}$, which is close to the value $\rho(298 \text{ K}) = 6.6 \text{ m}\Omega \text{ cm}$ of Ref. [45], but higher than the value of $\rho(300 \text{ K}) \approx 2 \text{ m}\Omega \text{ cm}$ published in Ref. [27] which was found for a single crystal. The difference may be related to the grain boundaries in polycrystalline material. However, the Nd$_{0.5}$Pr$_{1.5}$Ir$_2$O$_7$ sample seems to have a much lower resistivity than expected in the entire temperature region (cf. Fig. 4.9 (a)). This might be explained by the difficulty to exactly determine the distance $d$ and the width $w$ of the contacts as well as the thickness $t$ of the sample. To eliminate these uncertainties we normalized the temperature dependent resistivity to the value at 100 K. As shown in Fig. 4.9 (b), the temperature dependence of $\rho(T)/\rho(100 \text{ K})$ shows the expected increase of resistivity with decreasing praseodymium content.

![Figure 4.9.](a) Temperature dependent resistivity $\rho(T)$ of the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ compounds. (b) $\rho(T)$ normalized to $\rho(100 \text{ K})$.

Furthermore, the measurements indicate that the metal insulator transition temperature $T_{\text{MI}} = T_{\text{min}}$ remains unchanged (cf. Fig. 4.10). The minima in resistivity lie within a small temperature window of about 1 K around $T_{\text{min}} = 35 \text{ K}$ for all the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ samples except for Pr$_2$Ir$_2$O$_7$. Therefore, it is possible to say that the behavior of the materials is different than expected.

Matsuhira et al. [22] report a shift of the metal to insulator transition temperature to lower values for Nd$_{1.3}$Pr$_{0.7}$Ir$_2$O$_7$, which is in disagreement with our data. However, the lower resistivity at $T < T_{\text{MI}}$ compared to the Nd$_2$Ir$_2$O$_7$ compound is similar to the behavior of our Nd$_{1.5}$Pr$_{0.5}$Ir$_2$O$_7$ sample.
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Figure 4.10.: The diagram shows the temperatures $T_{\text{min}}$ of the minimal resistivity $\rho(T)$ of the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ compounds as well as the temperature $T_{\text{kink}}$ of the kink. Horizontal lines indicate the averaged value for all samples except for the Pr$_2$Ir$_2$O$_7$ compound, which shows a different behavior.

Very hard to see is another feature in the curves in Fig. 4.7 which was already discussed in the previous chapter. All curves contain a very small kink at $T_{\text{kink}} \approx 11$ K (except for Pr$_2$Ir$_2$O$_7$) that can be suppressed by a magnetic field. The position of the kinks can be extracted from the first derivative. Figure 4.10 shows the temperatures where these kinks occur. The change in curvature at such a kink is probably associated with an ordering of Nd$^{3+}$ moments, which is in good agreement with the available literature [23, 41]. For Pr$_2$Ir$_2$O$_7$ the reason for the appearance of a kink is not clear as it has the opposite curvature and may thus be related to different physics. Thus, this is a strong indication that the ordering phenomenon is not related to the iridium moments, but to the neodymium moments as stated by Disseler et al. [18].

**Magnetoresistance** $MR(T)$

From the $\rho(T)$ data measured at $\mu_0H = 0$ T and $\mu_0H = \pm 15$ T, it is again possible to extract the temperature dependent magnetoresistance $MR(T)$. The results are plotted in Fig. 4.11. The plots include the data of the Nd$_2$Ir$_2$O$_7$ poly sample for comparison. Figure 4.11 (b) offers an enlarged view around the maxima in magnetoresistance. Up to a praseodymium substitution rate of 50% in this sample series, a distinct maximum in the magnetoresistance is found. For 75% praseodymium, the maximum is small but
still detectable, whereas in pure $\text{Pr}_2\text{Ir}_2\text{O}_7$ the maximum completely vanishes. However, the position of the maximum does not change during the substitution series but varies slightly around the value of the $\text{Nd}_2\text{Ir}_2\text{O}_7$ poly sample. We can also observe that the low temperature magnetoresistance for the $\text{Nd}_{2-x}\text{Pr}_x\text{Ir}_2\text{O}_7$ samples is ordered correctly regarding the praseodymium content. We note that there is a larger deviation concerning the temperature where $\text{MR}(T) = 0$ for $\text{Nd}_{1.5}\text{Pr}_{0.5}\text{Ir}_2\text{O}_7$ (cf. Fig. 4.11 (b)). This may be explained with a temperature drift during the measurement as data in the next section will suggest.

Up to now, there is no literature available that discusses the magnetoresistance $\text{MR}(T)$ for $\text{Nd}_2\text{Ir}_2\text{O}_7$ samples with praseodymium substitution. However, from the data presented by Matsuhira et al. [22] for $\text{Nd}_{1.4}\text{Pr}_{0.6}\text{Ir}_2\text{O}_7$ we can conclude a large negative magnetoresistance for discrete temperatures of 4.2 K and 1.4 K and a vanishing magnetoresistance for 25 K. The former two data sets concur with our findings, the latter one does not. Concerning this point, we refer again to the next section where this will be discussed on the basis of further data.

![Magnetoresistance MR as a function of temperature for Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ samples. The orange line in both figures indicates the metal to insulator transition temperature $T_{\text{MI}}$ of the Nd$_2$Ir$_2$O$_7$ poly sample. Crosses indicate data from $V(H)$ measurements (cf. Sec. 4.5.2). Figure (a) shows the whole temperature range, figure (b) the range from 16 K to 80 K.](image)
4.5.2. \( V(H) \) measurements

\( V(H) \) measurements are carried out for the \( \text{Nd}_{2-x}\text{Pr}_x\text{Ir}_2\text{O}_7 \) samples in the same way as discussed for the \( \text{Nd}_2\text{Ir}_2\text{O}_7 \) compound. The same algorithm is used for the evaluation, which first averages positive and negative current measurements and then (anti-) symmetrizes the curves as described in the previous chapter.

Magnetoresistance \( MR(H) \)

The magnetoresistance \( MR(H) \) is shown in Fig. 4.12 for the \( \text{Nd}_{2-x}\text{Pr}_x\text{Ir}_2\text{O}_7 \) poly samples. There are three effects visible.

First, the curvature changes. Figure 4.12 reveals that the magnetoresistance as a function of the magnetic field is a superposition of a positive and negative magnetoresistance. The ratio between the positive and negative magnetoresistance changes with the praseodymium concentration. While for samples with a low praseodymium content \( (x < 1.5) \) the negative magnetoresistance dominates, for higher praseodymium concentration the positive component gets significant. The effect appears to be strongest at low temperatures. In the temperature region between 15 K and 25 K the effect vanishes. Most remarkable is the fact that in the \( \text{Pr}_2\text{Ir}_2\text{O}_7 \) poly samples the magnetoresistance does not change sign between 35 K and 50 K as the \( \text{Nd}_{2-x}\text{Pr}_x\text{Ir}_2\text{O}_7 \) samples with finite neodymium content do.

The second effect to notice is the hysteretic effect. In neodymium containing samples there is always a hysteretic effect measured. The strength of the hysteretic behavior decreases with decreasing praseodymium substitution and vanishes for \( \text{Pr}_2\text{Ir}_2\text{O}_7 \).

The absolute value of the magnetoresistance is the third point of interest. It strongly decreases with increasing praseodymium concentration. This supports the data of the resistivity \( \rho(T) \) measurement where the splitting of the \( \rho(T) \) curves measured at \( \mu_0H = 0 \) T and \( \pm 15 \) T also decreases for higher praseodymium content (cf. Figs. 4.7 and 4.11).

The data can again be compared to the \( MR(T) \) measurement by including the starting values of the measurement and calculating the magnetoresistance. The results are included in Fig. 4.11 (cf. crosses in Fig. 4.11) and support the data taken before. There is, however, a discrepancy between data for \( \text{Nd}_{1.5}\text{Pr}_{0.5}\text{Ir}_2\text{O}_7 \). The values retrieved in
the $MR(H)$ measurement are more reliable as they stem from several separate measurements. There may be some kind of drift on the temperature dependent data that provides different results. When considering the data gathered during this $MR(H)$ measurement for the Nd$_{1.5}$Pr$_{0.5}$Ir$_2$O$_7$ sample, the data is in agreement with the data presented by Matsuhira et al. [22] for 25 K for their Nd$_{1.4}$Pr$_{0.6}$Ir$_2$O$_7$ sample.

Figure 4.12.: Magnetoresistance $MR$ as a function of the external field $H$ of the Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ samples, showing (a) the Nd$_{1.5}$Pr$_{0.5}$Ir$_2$O$_7$ poly sample, (b) the NdPrIr$_2$O$_7$ poly sample, (c) the Nd$_{0.5}$Pr$_{1.5}$Ir$_2$O$_7$ poly sample, and (d) the Pr$_2$Ir$_2$O$_7$ poly sample.
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4.6. Iridium doping

There is literature [42] which states that iridium loss can change the behavior of Pr$_2$Ir$_2$O$_7$ due to site stuffing effects where praseodymium takes some of the free slots at missing iridium sites. This may happen if there is an iridium loss due to the volatile nature of iridium. To investigate this behavior two Pr$_2$Ir$_{2+\delta}$O$_7$ samples with different iridium content were fabricated. The fabrication process follows Sec. 4.1, the maximum temperature during the process is 1000 °C (“batch 3”).

The sample with $\delta = -0.1$ is expected to show site stuffing effects as there definitely is less iridium inside. For Ir$^{4+}$ in octahedral coordination (6 bonds) the ionic radius is 0.625 Å [49], for Pr$^{4+}$ it is 0.85 Å and for Pr$^{3+}$ a value of 0.99 Å is reported [49]. It is not clear whether the iridium site is occupied with Pr$^{4+}$ or Pr$^{3+}$ as both can exist in octahedral coordination and both are part of Pr$\textsubscript{6}$O$_{11}$ (equivalent to: Pr$_2$O$_3 \cdot 4$ PrO$_2$). Because of the different ionic radii a change towards larger lattice constant should be observed in both cases. The sample with an excess of iridium ($\delta = +0.1$), however, allows to investigate whether it is possible to correct for small iridium losses.

![X-ray powder diffraction (XRPD) of polycrystalline samples of Pr$_2$Ir$_{2.1}$O$_7$ and Pr$_2$Ir$_{1.9}$O$_7$. The dashed lines are the corresponding Rietveld refinements. In both samples parasitic phases consisting of Pr$_6$O$_{11}$ (orange lines) and PrO$_2$ (purple lines) are detected.](image)

Figure 4.13.: X-ray powder diffraction (XRPD) of polycrystalline samples of Pr$_2$Ir$_{2.1}$O$_7$ and Pr$_2$Ir$_{1.9}$O$_7$. The dashed lines are the corresponding Rietveld refinements. In both samples parasitic phases consisting of Pr$_6$O$_{11}$ (orange lines) and PrO$_2$ (purple lines) are detected.
4.6. Iridium doping

After fabrication of the two samples, XRPD measurements were carried out. Fig. 4.13 shows the results. Both cases appear to have residual Pr$_6$O$_{11}$ as well as PrO$_2$, neither of them shows metallic iridium or iridium oxide phases. The lattice constant is found to be the same for both cases (10.406 Å) and does not differ from the undoped Pr$_2$Ir$_2$O$_7$ sample (10.410 Å) within the measurement uncertainty.

Since Pr$_6$O$_{11}$ and PrO$_2$ are both detected via XRPD the solid state reaction of the Pr$_2$Ir$_{2+\delta}$O$_7$ is not complete, which does not allow definite conclusions about the physical properties of these samples. However, Fig. 4.13 suggests that if there is any iridium loss in the Pr$_2$Ir$_2$O$_7$ sample, it is less than 5%.
4.7. Summary and Conclusion

It is possible to easily manipulate the lattice constant by substituting praseodymium into Nd$_2$Ir$_2$O$_7$. The lattice constant in our polycrystalline bulk samples ($a = 10.410\,\text{Å}$) is larger than expected for a single crystal of Pr$_2$Ir$_2$O$_7$. The literature value ($a = 10.396\,\text{Å}$ [48]) is significantly smaller than the lattice constant found in our measurements. However, comparing our data with literature values for polycrystalline Pr$_2$Ir$_2$O$_7$ ($a = 10.406\,\text{Å}$ in Refs. [42, 45]) our data is in good agreement.

Figure 4.14.: Nd$_{2-x}$Pr$_x$Ir$_{2+\delta}$O$_7$ series with all measured lattice constants. The lattice constants indicated by a black cross are obtained via Rietveld refinement, the other ones are derived with the Nelson-Riley approach. The linear fit is calculated from the lattice constants of batch 1 and 2 obtained via the Nelson-Riley approach. For both $x = 2$ (Pr$_2$Ir$_2$O$_7$) and $x = 0$ (Nd$_2$Ir$_2$O$_7$), the discrepancy between different literature values of the lattice constant is significant. The lattice constants obtained in our experiments, however, agree with at least one publication each. Abbreviations: DIS [18], KIM [42], LAZ [45], MIL [48], TAK [44].

All the measured lattice constants are compiled in one diagram together with available literature values in Fig. 4.14. The linear behavior indicated by the black line is calculated from the lattice constants determined via the Nelson-Riley approach for batch 1 and 2 as an averaged fit. The data also suggest that the lattice constant is not influenced by excess iridium or less iridium during the fabrication process. However,
in XRPD measurements we detected residual praseodymium oxide, but no iridium or iridium oxide in the samples. This may lead to the conclusion that during the reaction iridium may be evaporated in larger quantities than expected. With the available EDX data, it is not possible to find an accurate value for the iridium content as its measurement accuracy is not better than several percent [25, 42]. This leaves the option of modifying the fabrication process or quantifying the amount of iridium contained in the samples by other experiments.

Figure 4.15.: (a) Characteristic temperatures for Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$. $T_{\text{MI}}$ indicates the position of the minimum of $\rho(T)$, calculated via a linear fit of the first derivative. It coincides with $T_{\text{split}}$ from magnetization measurements which is the splitting temperature of ZFC and FC curves. The black dashed line is the averaged value for $0 \leq x < 2$ at $T_{\text{MI}} = 35$ K. $T_{\text{kink}}$ is the temperature of the kink in the resistivity $\rho(T)$, which coincides with the $T_{\text{crit}}$ from the slope change in magnetization measurements. The blue dashed line is the averaged value of $T_{\text{crit}}$ and $T_{\text{kink}}$ at around 9 K. (b) Metal to insulator transition temperatures which are the averaged values of $T_{\text{split}}$ and $T_{\text{MI}}$ shown in (a), and the literature values taken from Fig. 2.6 (a). For Pr$_2$Ir$_2$O$_7$ the value is set to zero as the data in (a) do not provide a consistent value. The green line separates different regions (metallic/insulating) according to Fig. 2.6 (a).

Regarding the metal to insulator transition temperatures, the results are different from the expectations. Literature suggests $T_{\text{MI}} \approx 32$ K [21, 39] for Nd$_3$Ir$_2$O$_7$ and no metal to insulator transition for Pr$_2$Ir$_2$O$_7$ [27]. Therefore, by substituting neodymium by praseodymium it was reasonable to assume that $T_{\text{MI}}$ can be manipulated depending on the substitution level (also cf. Ref. [22]). This is not confirmed by our findings. We
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identified $T_{\text{MI}}$ as a minimum in the resistivity $\rho(T)$, which coincides with a splitting temperature $T_{\text{split}}$ between ZFC and FC curves in magnetization measurements. As shown in Fig. 4.15(a), the characteristic temperatures do not behave in the same linear way as the lattice constant. This is quite surprising as Pr$_2$Ir$_2$O$_7$ shows indeed no metal insulator transition at all. Nd$_2$Ir$_2$O$_7$ shows a transition temperature in agreement with several groups [21, 39]. Thus, a general or systematic error in our experiment can be excluded.

Therefore, we have to redraw Fig. 2.6(a). The result is shown in Fig. 4.15(b). As no metal to insulator transition was found in Pr$_2$Ir$_2$O$_7$, its transition temperature is set to zero. The green line indicates the separation line between different regions as shown in Fig. 2.6(a). We could not confirm the predicted MIT temperature trend for ionic radii between Nd$^{3+}$ and Pr$^{3+}$.

Figure. 4.15(a) also shows the kink in the resistivity $\rho(T)$ at $T_{\text{kink}} \approx 11$ K that is observed in all transport measurements of neodymium containing samples. $T_{\text{kink}}$ is in good agreement with the temperature $T_{\text{crit}}$ which was obtained from temperature dependent magnetization measurements. $T_{\text{crit}}$ is the temperature at which the magnetization curves change slope. This confirms the findings of Refs. [23, 41] where it is associated with an ordering of Nd$^{3+}$ moments. This is in strong contrast to Ref. [18].

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Part II.

Thin films of Nd$_2$Ir$_2$O$_7$
Chapter 5.

Thin films of Nd$_2$Ir$_2$O$_7$

In this chapter the fabrication and characterization of epitaxial Nd$_2$Ir$_2$O$_7$ thin films on single crystalline [111]-oriented Y:ZrO$_2$ substrates are discussed. To find the optimal parameters for the deposition of Nd$_2$Ir$_2$O$_7$ thin films via Pulsed Laser Deposition (PLD) the temperature of the substrate, the pressure of the growth atmosphere as well as the laser fluence of the excimer laser at the target is varied. The resulting thin films are then characterized using X-ray and electron diffraction as well as atomic force microscopy, magnetization and transport measurements.

5.1. Fabrication of thin film samples

In a previous bachelor’s thesis [25], Nd$_2$Ir$_2$O$_7$ thin films were fabricated for the first time. Although their crystalline quality was excellent, no metallic conductance at room temperature could be achieved. Therefore the starting point for the fabrication of Nd$_2$Ir$_2$O$_7$ thin films is to use the best deposition parameters found in the previous thesis, which are shown in Tab. 5.1.

Table 5.1.: Deposition parameters used in a previous bachelor’s thesis [25] to fabricate thin films of Nd$_2$Ir$_2$O$_7$. They are referenced as “standard parameters” until changed due to newer results.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature $T_s$</td>
<td>700°C</td>
</tr>
<tr>
<td>Oxygen pressure $p_{O_2}$</td>
<td>25 µbar</td>
</tr>
<tr>
<td>Repetition rate $f$</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Laser fluence $\rho_E$</td>
<td>2 J/cm$^2$</td>
</tr>
</tbody>
</table>

As a single crystalline substrate for thin film growth we used 5 × 5 × 1 mm$^3$ and 5 × 5 × 0.5 mm$^3$ Yttria-Stabilized Zirconium oxide Y:ZrO$_2$ (YSZ) by CrysTec. The YSZ crystals are based zirconia (ZrO$_2$) doped with 9.5% yttria (Y$_2$O$_3$) [50]. YSZ exhibits
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a cubic fcc symmetry with a lattice constant of 5.12 Å [51]. In a X-Ray Diffraction (XRD), experiment the lattice constant was determined via the Nelson-Riley approach to be (5.14 ± 0.04) Å, which is in good agreement with the manufacturer’s data. The substrate is chosen because of the small lattice mismatch (approximately 0.8%) when Nd$_2$Ir$_2$O$_7$ grows on four unit cells of YSZ. In the previous bachelor’s thesis, it was shown that the (111) direction is the favored growth direction [25]. Therefore for the deposition (111) oriented YSZ substrates were used. In addition, YSZ is diamagnetic which is advantageous for magnetization measurements. A diamagnetic contribution to temperature dependent magnetization measurements can be corrected by a subtraction of a constant negative background.

The following sections will be designated to the improvement of the fabrication process of Nd$_2$Ir$_2$O$_7$ thin films on YSZ substrates.

5.1.1. Laser fluence series

The first parameter to check is the laser fluence at the target. This mainly influences the energy of the particles inside the plasma plume as well as the material transport to the sample surface. The laser fluence at the target can be set up to 5 J/cm$^2$ in the used PLD system. A recently published study on the fabrication of pyrochlore Bi$_2$Ir$_2$O$_7$ thin films [52] suggests that the laser fluence used in the previous thesis might be too high (cf. Tab. 5.1). For the growth of Bi$_2$Ir$_2$O$_7$, a laser fluence of 0.75 J/cm$^2$ was used.

To investigate the influence of the laser fluence on the crystalline properties of the Nd$_2$Ir$_2$O$_7$ thin films, we fabricated a series of Nd$_2$Ir$_2$O$_7$ thin films using a constant substrate temperature of 700 °C, an oxygen pressure of 25 µbar, a repetition rate of 10 Hz as well as a number of pulses of 50,000, while varying the laser fluence from 1.0 J/cm$^2$ to 3.0 J/cm$^2$.

Figure 5.1 shows the results of the XRD measurements carried out on these Nd$_2$Ir$_2$O$_7$ thin films. The 2θ-ω scans displayed in Fig. 5.1 (a) reveal a crystalline structure of all thin films. However, the Nd$_2$Ir$_2$O$_7$ (222) reflections of the thin films are shifted to lower 2θ values compared to the calculated 2θ angle using a cubic symmetry as well as the bulk lattice constant of $a_{\text{poly}} = 10.370$ Å, which we determined in Sec. 3.3 (cf. vertical line in Fig. 5.1 (a)). This results in a higher lattice constant $a$ than $a_{\text{poly}}$ as shown in Fig. 5.1 (c). The deviation might be explained by strain effects due to the difference in lattice constant of Nd$_2$Ir$_2$O$_7$ and the substrate YSZ of 0.8% as well as non-stoichiometric effects like oxygen vacancies or iridium deficiency.
5.1. Fabrication of thin film samples

Figure 5.1.: Laser fluence series: Nd$_2$Ir$_2$O$_7$ thin films fabricated using a constant substrate temperature $T_s = 700^\circ$C, an oxygen pressure $p_{O_2} = 25$ µbar and a repetition rate of $f = 10$ Hz while varying the laser fluence from 1.0 J/cm$^2$ to 3.0 J/cm$^2$. (a) $2\theta$-$\omega$ scans of Nd$_2$Ir$_2$O$_7$ thin films fabricated at different laser fluence. A parasitic phase is indicated by an asterisk. Furthermore, the $2\theta$ angle of the Nd$_2$Ir$_2$O$_7$ (222) reflection of the polycrystalline material is marked by the red vertical line. (b) Rocking curves around the Nd$_2$Ir$_2$O$_7$ (222) reflection. Two components are observable: A narrow one which is labeled as “peak”, and a broader one labeled as “base”. (c) Cubic lattice constant $a$, density $\rho$, roughness $r_{\text{rms}}$, thickness $d$ as well as the full width at half maximum (FWHM) of the rocking curves as a function of the laser fluence $\rho_E$. The theoretical density as well as the lattice constant of the polycrystalline material $\rho_{\text{poly}} = 9.341$ g/cm$^3$ (cf. Sec. 3.4) and $a_{\text{poly}} = 10.370$ Å (cf. Sec. 3.3) is indicated by horizontal lines, respectively. The vertical dashed line indicates the optimum laser fluence at the target.
The 2θ-ω scans further reveal a crystalline parasitic phase at around 27.6° in all Nd$_2$Ir$_2$O$_7$ thin films (cf. asterisk in Fig. 5.1(a)). However, the reflection is smallest for the Nd$_2$Ir$_2$O$_7$ thin film fabricated with a laser fluence of 2.0 J/cm$^2$.

![Figure 5.2.](image.png)

Figure 5.2.: X-ray reflectometry of the Nd$_2$Ir$_2$O$_7$ thin film fabricated using a laser fluence at the target of ρ$_E$ = 1.5 J/cm$^2$. The black dashed line indicates a curve simulated where only the lattice constant is adjusted for 2θ values between 1.5° and 2.5°. The green line is a simulation that also considers the density ρ and the roughness $r_{\text{rms}}$. The positions of the Kiessig fringes are marked with orange lines.

By utilizing X-ray reflectometry (cf. Fig. 5.2), the thickness $d$ as well as the roughness $r_{\text{rms}}$ and the density $\rho$ of the thin films can be determined by using the software LEPTOS. The thickness $d$ can be determined by adjusting the simulation to fit the Kiessig fringes (indicated with orange lines in Fig. 5.2). However, the simulation does only coincide within a small region between 1.5° and 2.5°, which provides a thickness of $d = (32.9 \pm 0.5) \text{ nm}$. The density $\rho$ mainly influences the horizontal position as well as the slope of the simulated curve. Therefore, the density $\rho$ is adjusted by fitting the simulation curve to the first decrease between 0.5° and 1.0°. The roughness $r_{\text{rms}}$ determines the slope of the curve, where the effects are strongest for high angles. After adjusting the density $\rho$ and the roughness $r_{\text{rms}}$, the fringes of the reflectometry now coincide with the simulated curve. Thus, the simulated thickness has changed to $d = (32.6 \pm 0.3) \text{ nm}$, and we find a density of $\rho = (7.15 \pm 0.10) \text{ g/cm}^3$. The deviation of the density $\rho$ from the theoretical value $\rho_{\text{poly}} = 9.341 \text{ g/cm}^3$ might be explained by
5.1. Fabrication of thin film samples

non-stoichiometric effects. However, $\rho$ only slightly changes with the laser fluence $\rho_E$ at the target used for the deposition (cf. Fig. 5.1 (c)).

As shown in Fig. 5.1 (c), a clear dependence of $d$ as well as $r_{\text{rms}}$ on the laser fluence used for the fabrication can be observed. For an laser fluence of 1.0 J/cm$^2$, the growth rate is very low resulting in a small film thickness of only 9 nm. The thickness increases to 61 nm when increasing the laser fluence to 2.0 J/cm$^2$, while it decreases again when further increasing $\rho_E$. The decrease in film thickness can be explained by back-sputtering of the material from the substrate due to the high energy of the particles in the plasma plume.

As shown in Fig. 5.1 (c) there is a strong correlation of $d$ and $r_{\text{rms}}$. For thicker films $r_{\text{rms}}$ strongly increases. This suggests that the crystalline quality gets worse by increasing the thickness. To investigate the mosaic spread and thus the crystalline quality of the Nd$_2$Ir$_2$O$_7$ thin films rocking curves around the Nd$_2$Ir$_2$O$_7$ (222) reflections were performed (cf. Fig. 5.1 (c)). Two components are distinguishable: One with a low full width at half maximum (FWHM) (labeled with “peak” in Fig. 5.1 (c)) and one with a high FWHM (labeled with “base” in Fig. 5.1 (c)). The former one indicates an excellent crystalline quality while the latter one indicates a high mosaic spread and thus a low crystalline quality. Therefore, the rocking curves suggest two different regions with different crystalline qualities in the Nd$_2$Ir$_2$O$_7$ thin film. As the component with a large FWHM is the lowest for the Nd$_2$Ir$_2$O$_7$ thin films with the lowest film thickness, i.e., fabricated with an laser fluence of 1.0 J/cm$^2$, compared to the Nd$_2$Ir$_2$O$_7$ thin films with the highest thickness, i.e., fabricated with an laser fluence of 2.0 J/cm$^2$, the results of the rocking curves as well as the roughness $r_{\text{rms}}$ suggest a high mosaic spread with a high density of defects after reaching a critical film thickness $d_{\text{crit}}$. Therefore, the Nd$_2$Ir$_2$O$_7$ thin films might grow in a columnar growth mode for $d > d_{\text{crit}}$.

However, for an laser fluence of 2.0 J/cm$^2$ the FWHM of the rocking curve is lowest. Furthermore, the growth rate is highest as well as the reflection from the parasitic phase is the smallest. We therefore determine the optimal laser fluence at the target to be 2.0 J/cm$^2$, which is identical to the value used in the previous bachelor’s thesis (cf. Tab. 5.1).

After optimizing the laser fluence, the existence of a parasitic phase leads to the conclusion that there is at least one other parameter that is not optimized. To achieve single-phase Nd$_2$Ir$_2$O$_7$ thin films in the next step the substrate temperature $T_s$ is varied using a laser fluence of 2.0 J/cm$^2$. 

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5.1.2. Substrate temperature series

Following the conclusion of the last section, the next deposition parameter, which is varied, is the substrate temperature $T_s$. The crystallinity of the thin films strongly depends on $T_s$ as the offered energy can be used by the ad-atoms to move on the substrate surface to find their correct lattice sites.

![Graphs and diagrams showing the effect of substrate temperature on various properties of Nd$_2$Ir$_2$O$_7$.](attachment:image.png)

Figure 5.3.: Substrate temperature $T_s$ series. (a) $2\theta$-ω scan. The thin films fabricated at 600°C (grown in 50 µbar oxygen atmosphere) and 700°C show parasitic phases (indicated by one and two asterisks, respectively). Finite thickness fringes are visible for Nd$_2$Ir$_2$O$_7$ thin films fabricated at $T_s \geq 750$°C. (b) Rocking curves around the Nd$_2$Ir$_2$O$_7$ (222) reflection. Two components are visible. (c) Cubic lattice constant $a$, density $\rho$, roughness $r_{\text{rms}}$, thickness $d$ as well as full width at half maximum (FWHM) of the rocking curves as a function of $T_s$. The vertical dashed line indicates the optimal substrate temperature $T_s$. 
For the substrate temperature series, Nd$_2$Ir$_2$O$_7$ thin films were fabricated at a constant oxygen pressure of 25 µbar, a repetition rate of 10 Hz, a laser fluence of 2.0 J/cm$^2$ as well as a number of pulses of 50,000, modifying the substrate temperature from 700°C to 850°C, except for the Nd$_2$Ir$_2$O$_7$ thin films grown at $T_s = 600$°C which is fabricated using an oxygen pressure of 50 µbar.

Figure 5.3(a) shows 2θ-ω scans of Nd$_2$Ir$_2$O$_7$ thin films grown at different substrate temperatures $T_s$. For thin films deposited at $T_s \leq 700$°C parasitic phases are visible. The first sample to be phase pure is fabricated at $T_s = 750$°C. For thin films using higher $T_s$ pronounced finite thickness fringes (Laue oscillations) are observable. However, the lattice constants calculated by assuming a cubic symmetry deviates from the bulk value $a_{\text{poly}}$. This is more pronounced for the sample fabricated at $T_s = 850$°C (cf. Fig. 5.3).

To investigate the crystalline quality rocking curves were taken around the Nd$_2$Ir$_2$O$_7$ (222) reflection. Figure 5.3 (b) shows the results for the thin films fabricated at $T_s \geq 700$°C. Again two components are visible. By using a substrate temperature $T_s \geq 800$°C the crystalline quality can be improved, which is demonstrated by an increase of the component with a low FWHM. However, at these substrate temperatures the thickness $d$ of the resulting Nd$_2$Ir$_2$O$_7$ layer as well as the roughness $r_{\text{rms}}$ strongly decrease (cf. Fig. 5.3 (c)).

In total, the Nd$_2$Ir$_2$O$_7$ thin film fabricated at a substrate temperature of 800°C exhibits the best crystalline quality. This value is higher than the values used in the previous bachelor’s thesis (cf. Tab. 5.1). The reason for this behavior is unclear. One possibility could be a change of the target material. The best sample produced so far under this conditions is labeled “IRZ 36” (cf. sample fabricated at 800°C shown in Fig. 5.3) and will be referenced like this and plotted in the same color in the following sections for comparative reasons.

Figure 5.4 (b) shows a 2θ-ω scan around the Nd$_2$Ir$_2$O$_7$ (222) reflection of the sample IRZ 36. Laue oscillations are clearly visible, which can be simulated by using the software LEPTOS. The simulation is adjusted to match the amplitude at low angles as they describe the value close to the decay of the signal. The graphs indicate that the intensities are quite close to the simulation for lower angles. The substrate, however, has a much sharper reflection in the spectrum but the amplitude is lower. This causes a discrepancy in amplitude for higher angles. From the simulation, a thickness of $d = (40.4 \pm 0.3)$ nm is obtained, which is close to the thickness determined by X-ray reflectometry ($d = (41.4 \pm 1.0)$ nm), which is shown in Fig. 5.4 (a). This demonstrates that the film is grown coherently over the whole thickness.
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5.1.3. Pressure series

In this section, the influence of different oxygen pressures and atmospheres on the structural properties is investigated. To this end three samples are discussed: The reference sample IRZ 36 is fabricated at 25 µbar in oxygen. Another sample is fabricated at 8 µbar while a third one is deposited in argon atmosphere at a pressure of 25 µbar.

Figure 5.5 shows the result of the XRD measurements carried out on these samples. The 2θ-ω scans reveal a shift of the Nd$_2$Ir$_2$O$_7$ (222) reflection to lower 2θ angles for the Nd$_2$Ir$_2$O$_7$ thin films grown in oxygen at 8 µbar as well as of the thin film fabricated in argon compared to the reference sample IRZ 36. This results in an increase of the lattice constant for both samples (cf. Fig. 5.5(c)). Interestingly, the thickness determined by X-ray reflectometry decreases with decreasing oxygen pressure. This is unexpected since normally the growth rate increases at low oxygen pressures. This might suggest an increase of iridium loss at low oxygen pressures due to the volatile nature of iridium.

The rocking curves around the Nd$_2$Ir$_2$O$_7$ (222) reflections (Fig. 5.5(b)) also indicate that a lower oxygen pressure leads to films with lower crystalline quality. The main peaks have a comparable FWHM with IRZ 36. The same is even more true for the broad component where the FWHM increases drastically with decreasing oxygen growth pressure.

Figure 5.4: (a) Reflectometry of IRZ 36 with different fit variations to improve the agreement between experiment and simulation by varying the thickness, roughness, and density. (b) Laue oscillations around Nd$_2$Ir$_2$O$_7$ (222) and simulation to determine the crystalline thickness of IRZ 36.
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Figure 5.5 gives strong indication that an oxygen atmosphere is necessary to obtain Nd$_2$Ir$_2$O$_7$ thin films with good quality. Furthermore, a pressure of 25 µbar seems to be optimal. However, to make a definite conclusion on the best growth pressure further Nd$_2$Ir$_2$O$_7$ thin films are required.

![Graph](image)

Figure 5.5.: Pressure series. (a) 2θ-ω scan of the three Nd$_2$Ir$_2$O$_7$ thin films fabricated at 25 µbar (IRZ 36) and in 25 µbar oxygen as well as in 25 µbar argon atmosphere. The latter two samples show a shift to lower angles compared to IRZ 36. (b) Rocking curves around the Nd$_2$Ir$_2$O$_7$ (222) reflections. (c) Cubic lattice constant $a$, density $\rho$, roughness $r_{\text{rms}}$, thickness $d$ as well as full width at half maximum (FWHM) of the rocking curves as a function of the growth pressure $p$. The vertical line indicates the optimum pressure for the growth of Nd$_2$Ir$_2$O$_7$ thin films.
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5.1.4. Pulse series

As already mentioned in the previous sections, the thickness of a sample influences the quality of a sample. This is mainly due to strain relaxation effects, arising from the small misfit of substrate and film lattice constants. As discussed in the previous sections the rocking curves measured, around the Nd$_2$Ir$_2$O$_7$ (222) reflections of the thin films reveal two components with either a high or a low mosaic spread, i.e., two regimes with different crystalline qualities. However, the thickness evolution of the two regions is not clear up to now. There was only one sample in the previous series fabricated at 1 J/cm$^2$ (cf. Fig. 5.1) which is significantly thinner than the other samples. But the problem is that other parameters are varied, which might influence the crystalline quality as well. Therefore, it is not possible to conclude a correlation between thickness and quality of a sample. To this end, Nd$_2$Ir$_2$O$_7$ thin films were fabricated under the same conditions, but with different pulse numbers and a different repetition rate. The samples are divided in two series (S1 and S2) which are fabricated in the same run. However, the thin films of series S2 were fabricated 3 months later than the thin films of series S1.

Figure 5.6 shows the crystalline properties of several samples in comparison with the reference sample IRZ 36, which is fabricated with 50,000 pulses. The results are very interesting as they show no obvious correlation between the growth rate and the number of pulses, e.g. the samples with 100,000 pulses are both significantly thicker than IRZ 36, however, they are both different from each other in thickness as well as in position of the Nd$_2$Ir$_2$O$_7$ (222) reflection of the film. When considering samples that were fabricated in the same series the thickness versus pulses curve (Fig. 5.6(c)) is a line through the origin, which it should be (cf. Fig 5.6(c)). The repetition rate does not seem to influence this behavior since the thickness of the Nd$_2$Ir$_2$O$_7$ thin film fabricated at 2 Hz fits on this line. Thus, the growth rate of the Nd$_2$Ir$_2$O$_7$ thin films, which were fabricated within one series, is consistent. However, it is changed over time. This suggests that the properties of the target material might have changed with time.

The rocking curves and the 2θ-ω scans confirm the assumption which the sample fabricated at 1 J/cm$^2$ indicated: thinner samples have an increased lattice constant, but a better crystalline quality since the intensity of the broad component of the rocking curve is very low in these samples.

The Nd$_2$Ir$_2$O$_7$ (222) reflections of the thicker Nd$_2$Ir$_2$O$_7$ thin film show a shift to higher 2θ angles in the 2θ-ω scan, which corresponds to smaller lattice constants. These observations indicate that the first monolayers of the film are strongly strained,
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leading to a larger lattice constant in out-of-plane direction. Increasing the film thickness, the lattice constant tends to the unstrained single crystal value. However, the crystalline quality gets worse.

Figure 5.6.: Pulse series: The plots show two series (S1, S2) where series 2 was fabricated three months later. (a) $2\theta$-ω scan as well as (b) rocking curves around the Nd$_2$Ir$_2$O$_7$ (222) reflection of the thin films fabricated with a different number of pulses using the parameters determined in the last sections. One sample of series S2 is fabricated with 2 Hz instead of 10 Hz. (c) Cubic lattice constant $a$, density $\rho$, roughness $r_{\text{rms}}$, thickness $d$ as well as full width at half maximum (FWHM) of the rocking curves. The data points are plotted for both series S1 and S2.
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The rocking curve of the sample fabricated during series S2 with 100,000 pulses (cf. green line in Fig. 5.6 (b)) shows another feature (which is also observed in another sample, which is not discussed in this thesis). The curve has a two shoulders near the main peak. There are two possible explanations for this behavior:

First, the rocking curve around the YSZ (111) substrate reflection revealed two peaks close to each other, which indicates that the substrate consists of two inclined crystallites. These may also cause two additional reflections in the rocking curve of the thin film, which might be not resolvable due to its larger FWHM in comparison to the YSZ substrate reflection. The second possibility could be a network of misfit dislocations, which results in two additional side-peaks as described in Ref. [53].

In total, since the growth rate changed within three months, there must be at least one other parameter that influences the growth which cannot be adjusted in a controllable way by the user. This might be caused by a change of the quality of the polycrystalline target material. Another possibility could be the decrease of the energy of the excimer laser, which is caused by a degradation of the performance of the laser tube.

5.1.5. Iridium excess target

The simulations of the X-ray reflectometry discussed in the previous sections reveal a deviation of the density of Nd$_2$Ir$_2$O$_7$ thin films from the theoretically calculated one. This is probably an indication of iridium loss during the deposition. Until now there is no measurement that can quantify the iridium content with an accuracy better than several percent. In the previous bachelor’s thesis [25] EDX measurements were carried out on a thin film sample and the target material. These measurements indicate an approximate ratio of 1:1 for neodymium and iridium.

However, two Nd$_2$Ir$_2$O$_7$ thin films were fabricated using a Nd$_2$Ir$_2$O$_7$ target material with 5% excess iridium to compensate for possible iridium loss. Fig. 5.7 shows the results of these thin films. The crystalline properties of two reference samples produced in the same cycle from a stoichiometric target using the optimal parameters are also included in Fig. 5.7.

The properties of the first Nd$_2$Ir$_2$O$_7$ sample fabricated using the target with excess iridium (labeled as (α)) differs strongly from the properties of the second one (β). However, sample (α) is fabricated directly after the series S1 discussed in the previous section. By comparing the structural properties of sample (α) with the corresponding one of series S1 (red graph in Fig. 5.6 (a), (b)), a similar behavior in the 2θ-ω scan as
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well as in the rocking curve can be observed. In the following, only the properties of sample (β) will be discussed. When comparing the values with the reference samples the results are astonishingly similar. The iridium excess in the target does not seem to strongly influence the properties of the samples. There are only minor differences.

Figure 5.7.: Iridium excess target series: (a) 2θ-ω, (b) rocking curves around the Nd₂Ir₂O₇ (222) reflection as well as the corresponding dependence of (c) cubic lattice constant $a$, density $\rho$, roughness $r_{\text{rms}}$, thickness $d$, and full width at half maximum (FWHM) of the rocking curves on the iridium content of the PLD target $c_{\text{Ir target}}$. It shows two samples ((α) and (β)) fabricated from Nd₂Ir₂O₇ target (5% excess iridium), and two reference samples ((A) and (B)) which are grown under optimal conditions from a stoichiometric Nd₂Ir₂O₇ target.
There are several possible explanations. First, the iridium loss is stronger than assumed. However, this is in contradiction to the EDX results. Second, the iridium loss is not proportional to the iridium content in the target. Then, an enormous amount of additional iridium could be necessary. Third, there is only very little or no iridium loss. Then the origin of the deviation in density remains unrevealed. There might be also oxygen vacancies in the Nd$_2$Ir$_2$O$_7$ thin films. However, these vacancies cannot explain the huge difference in density since the atomic weight ratio to iridium is 1:12.

Probably a combination of these possibilities is the answer. However, without knowing the iridium concentration in the Nd$_2$Ir$_2$O$_7$ thin films with an accuracy better than at least 1% it is very difficult to exclude or confirm any of these.
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5.1.6. Summary and conclusion

To achieve a high quality of thin films several parameters need to be optimized. The optimal temperature of the substrate is $T_s = 800^\circ C$ and the optimal laser fluence is $\rho_E = 2 \text{ J/cm}^2$. Concerning the growth atmosphere, it was possible to show that a pressure of $8 \mu\text{bar}$ of oxygen is not sufficient to provide high quality films. Also, an argon atmosphere provides $\text{Nd}_2\text{Ir}_2\text{O}_7$ thin film samples inferior to samples grown in oxygen. Due to the small number of samples in the pressure series an optimal value for the pressure was not determined, however, in the previous bachelor’s thesis the influence of the oxygen pressure on the structural quality of $\text{Nd}_2\text{Ir}_2\text{O}_7$ thin films was studied in detail in the range from $10 \mu\text{bar}$ to $100 \mu\text{bar}$, but with a substrate temperature of $T_s = 700^\circ C$, where the optimal pressure was found to be $25 \mu\text{bar}$ [25]. The pressure was kept at the same value during our experiments.

We also revealed a strong correlation between the thickness of the $\text{Nd}_2\text{Ir}_2\text{O}_7$ thin film samples and their crystalline quality. The thicker the samples the higher is the mosaic spread. This is probably related to a columnar growth after reaching a critical thickness $d_{\text{crit}}$, whereas below $d_{\text{crit}}$ the thin films may be epitaxially strained. If all collected data are sorted such that only samples with a high quality, i.e. no parasitic phases and in density close together ($\rho = (8.0 \pm 0.1) \text{ g/cm}^3$), it is possible to plot the lattice constant over the film thickness (cf. Fig. 5.8). This figure suggests, even if all the data points with different parameters are left out, that the critical thickness $d_{\text{crit}}$ is in a region close to values below approximately $20 \text{ nm}$.

However, for any $\text{Nd}_2\text{Ir}_2\text{O}_7$ thin film sample we found a too small density $\rho$. It is not clear whether the thin films have the correct stoichiometry. During the growth series with iridium excess in the PLD target it was not possible to observe an influence on the thin films. The second point of uncertainty is the oxygen content as there were no methods available to quantify this value. Oxygen loss may explain a lattice constant that is different from the theoretical value. To obtain a reliable answer to the question of the origin of our observations probably much more technical effort has to be made to investigate thin film samples. This may include X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS), Atom Probe Tomography (APT), Scanning Tunneling Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS).

There are indications of way how to improve the quality of the films. There may be a window of higher substrate temperature combined with a larger pulse number that may lead to films with a lattice constant closer to the bulk material value. This may otherwise be a problem if oxygen loss is found out to be the cause for the deviation as oxygen is very light and volatile. This can probably be influenced by a slightly higher
oxygen pressure. During fabrication it turned out to be advantageous if the first layers of the film are grown with increased relaxation times (30 s during the first 10 pulse series) and annealed in oxygen atmosphere for approximately 1 minute. This may be improved further, but offers an enormous amount of parameter combinations, and therefore might be time-consuming with uncertain outcome. This is also closely connected with the number of pulses per packet which may be varied by several decades. This may influence the stoichiometry of the sample as it changes the amount of offered material.

Figure 5.8.: Collection of high quality samples, showing the cubic lattice constant $a$, obtained via the Nelson-Riley approach, versus the thickness $d$ of Nd$_2$Ir$_2$O$_7$ thin film samples. Samples with parameters different from standard ($T_\text{s} = 800^\circ C$, $p_{O_2} = 25 \mu$bar, $\rho_\text{E} = 2 \text{ J/cm}^2$) are marked. Here “E-” is for lower energy density, “T-” for lower temperature, “p-” for lower oxygen pressure and “Ir+” for higher iridium content in the target. However, even if that data points are left out it shows a clear trend. The film typically relaxes if thicker than approximately 20 nm. The orange line indicates the bulk value of $a_{\text{poly}} = 10.370 \, \text{Å}$
5.2. Physical properties of Nd$_2$Ir$_2$O$_7$ thin films fabricated under optimal conditions

In the following the structural, magnetic, and electric properties of Nd$_2$Ir$_2$O$_7$ thin films fabricated under optimal conditions are discussed.

5.2.1. Structural properties

**Reflection high energy electron diffraction (RHEED)**

During the fabrication of several samples, Reflection High Energy Electron Diffraction (RHEED) measurements were carried out (cf. App. A.2). In this section, we will present data taken in-situ during the fabrication of the reference sample IRZ 36.

Figure 5.9 shows RHEED patterns at four different stages of the growth process. The pattern displayed in Fig. 5.9 (a) was taken before the deposition process. It shows the pattern of the YSZ substrate after annealing in oxygen for 5 minutes at a substrate temperature of $T_s = 800^\circ$C before the deposition process. After 1,000 pulses, the sharp reflections changed to straight lines, which indicates an increased roughness of the surface caused by the deposition of a thin layer of Nd$_2$Ir$_2$O$_7$ (cf. Fig. 5.9 (b)). The emergence of weak intermediate lines, indicated by red arrows in Fig. 5.9 (c), is visible after approximately 3,000 pulses. The intensity of these lines raises during the deposition process. Figure 5.9 (d) shows the RHEED pattern at the end of the deposition process after 50,000 pulses.

Because RHEED provides information in the $k$-space, a halved distance in $k$-space means doubled distance in real space. Thus, the RHEED pattern suggests a 1:2 proportion of the lattice constants between the Nd$_2$Ir$_2$O$_7$ thin film and the YSZ substrate. Therefore, we can conclude that Nd$_2$Ir$_2$O$_7$ thin films grow over four unit cells of YSZ.

**$\phi$-scan**

In the previous sections on X-ray diffractometry only scans around a symmetric reflections were discussed. To investigate the in-plane orientation in more detail, $\phi$-scans around the asymmetric Nd$_2$Ir$_2$O$_7$ (10 62) as well as the YSZ (531) reflection were performed.

The samples are usually aligned in the diffractometer to compensate for misorientation of the sample such as miscut, tilted mounting etc., by using the built-in $\chi$ and $\omega$ drives. However, this results in an inclination of the built-in $\phi$-drive, which is disadvantageous for a $\phi$-scan, in which the rotation axis should be exactly along the [111]
direction of the substrate (or film). To be able to rotate the sample along the [111] axis, using the built-in $\varphi$-drive of the diffractometer, an additional 2-circle goniometer was installed. Using this extra goniometer to compensate for the misalignment instead of the built-in $\chi$ and $\omega$ drives, the built-in $\varphi$-drive rotates the sample around the [111] axis. This results in comparable intensities for all the reflections, which would not be the case if the extra goniometer would be left out.

Figure 5.9.: Reflection high energy electron diffraction (RHEED), recorded in-situ during the growth process of the sample IRZ36. (a) RHEED pattern of the substrate YSZ at $T_s = 800^\circ$C. (b) RHEED pattern after 1,000 pulses: Point-reflections have expanded to straight lines, indicating an increase in the roughness of the surface. (c) RHEED pattern after 3,000 pulses: Intermediate reflections appear (red arrows). (d) RHEED pattern after 50,000 pulses at the end of the growth process. The intermediate lines are clearly visible. Note: Due to adjustments of the camera and sample for obtaining the best possible pictures, the peak positions vary in relative position.
5.2. Physical properties of Nd$_2$Ir$_2$O$_7$ thin films fabricated under optimal conditions

In Fig. 5.10 the results are shown. The reflections of the Nd$_2$Ir$_2$O$_7$ thin film appear at the same $\varphi$-angles as the reflections of the YSZ substrate. This proves that the Nd$_2$Ir$_2$O$_7$ thin film grows with the same in-plane orientation as provided by the substrate. We can therefore assume that a Nd$_2$Ir$_2$O$_7$ unit cell grows over four YSZ unit cells.

![Graph showing Nd$_2$Ir$_2$O$_7$ (10 62) and YSZ (531) reflections at the same angles](image)

Figure 5.10: $\varphi$-scan of IRZ 36. The film as well as the substrate show 60° symmetry as expected. The Nd$_2$Ir$_2$O$_7$ (10 62) and the YSZ (531) appear at the very same angles, proving that film and substrate have the same in-plane orientation.
Reciprocal Space Mapping (RSM)

Reciprocal space maps offer the opportunity to not only probe the X-ray diffraction pattern of a sample in a one dimensional fashion, but in two dimensions in \( k \)-space. This is obtained by an array of adjacent linear \( q \)-scans. For this section, a special notation is used: \( q_{\text{LLL}} \) means \( q \)-vectors parallel to the substrate [111] direction and \( q_{\text{H0H}} \) means \( q \)-vectors parallel to the [1 10] direction. There are in general 2 different types of RSM, one is around a symmetric reflection, the other one around an asymmetric reflection. Both types provide different information.

Figure 5.11.: Reciprocal space map (RSM) around the symmetric substrate reflection YSZ (111). The \( \text{Nd}_2\text{Ir}_2\text{O}_7 \) (222) reflection is clearly visible as well as the Laue thickness fringes. The lattice constant can be determined via the \( q \)-values (Eq. (5.1)) to be \( a = 10.365 \) Å. The magenta colored dashed line indicates the [111] direction, showing all reflections are in-line.

Fig. 5.11 shows a RSM around a symmetric reflection on the \( q_{\text{LLL}} \) axis. The peak with the strongest intensity is the substrate YSZ (111) reflection. Below this reflection is the sharp \( \text{Nd}_2\text{Ir}_2\text{O}_7 \) (222) reflection. Laue oscillations are clearly visible around the \( \text{Nd}_2\text{Ir}_2\text{O}_7 \) (222) reflection. These Laue oscillations together with the main peak are on the \( q_{\text{LLL}} \)-line that contains the substrate peak and crosses \( (q_{\text{H0H}}, q_{\text{LLL}}) = (0, 0) \). This proves that the film does not grow tilted, but parallel to the substrate [111] direction. This is again an indication for a very high quality thin film growth, but it does not provide any information about in-plane properties of the sample.
Therefore, a RSM around an asymmetric reflection was recorded. Here the Nd$_2$Ir$_2$O$_7$ (10 62) and the YSZ (531) reflections are used, respectively. Figure 5.12 shows the measured RSM. First, the film peak is not on the relaxation line. This line is defined by two points: The fully relaxed state where the film has the lattice constant of a single crystal or the polycrystalline powder ($a_{\text{film}} = 10.374 \, \text{Å}$), and the fully strained state where the film has the doubled lattice constant of the substrate ($a_{\text{film}} = 2a_{\text{YSZ}} = 10.240 \, \text{Å}$). The corresponding $q$-values can be determined by:

$$\frac{q_{\text{film}}}{q_{\text{YSZ}}} = \frac{d_{\text{YSZ}}}{d_{\text{film}}} = \frac{a_{\text{YSZ}} \cdot \sqrt{10^2 + 6^2 + 2^2}}{\sqrt{5^2 + 3^2 + 1^2} \cdot a_{\text{film}}} = 2 \frac{a_{\text{YSZ}}}{a_{\text{film}}}. \quad (5.1)$$

The $q_{\text{LLL}}$-value for the fully strained case, however, must be calculated via the strain tensor. There was already an estimation done in the bachelor’s thesis [25] using the data of La$_2$Hf$_2$O$_7$ [54] due to a lack of experimental data for Nd$_2$Ir$_2$O$_7$. The following equation was used [55]:

$$\epsilon_3' = -\frac{c_{11} + 2c_{12} - 2c_{44}}{c_{11} + 2c_{12} + 4c_{44}} (\epsilon_1' + \epsilon_2'), \quad (5.2)$$

where $c_{ij}$ are components of the stiffness matrix of La$_2$Hf$_2$O$_7$ and $\epsilon_k'$ are the compression components of the strain matrix. As the determined lattice constants for Nd$_2$Ir$_2$O$_7$ in polycrystalline powder differ less than 0.02% from the value in the bachelor’s thesis [25] the calculated $q$-values, $(q_{\text{H0H}}, q_{\text{LLL}}) = (1.974, 2.961)$ for the fully relaxed case and $(\epsilon_{\text{H0H}}, q_{\text{LLL}}) = (2.000, 2.949)$ for the fullystrained case, are also used in this thesis.

We can now apply Eq. (5.1) to determine the lattice constant assuming a cubic symmetry. However, we can calculate the lattice constant from the in-plane $q$-value as well as from the out-of-plane $q$-value. If the assumption of a cubic symmetry is correct, we would expect the same result for both calculations. For the symmetric case, using the out-of-plane $q$-value, we obtain a cubic lattice constant $a = 10.365 \, \text{Å}$. For the asymmetric case, we find a cubic lattice constant of $a = 10.363 \, \text{Å}$ for the out-of-plane $q$-value, and a cubic lattice constant of $a = 10.753 \, \text{Å}$ for the in-plane $q$-value. While the lattice constants, calculated from the out-of-plane $q$-value, are close to the fully strained case (cf. Fig. 5.12), the cubic lattice constant, calculated from the in-plane $q$-value, is far off the expected value. However, because the lattice constant calculated from the out-of-plane $q$-value is close to the strained case, this behavior is strange as the film obviously is not strained compressively in-plane, but there is tensile strain where one would expect the opposite behavior. The occurrence of two different lattice constants under assumption of cubic symmetry leads to the conclusion that the assumption is wrong. This means that epitaxial strain cannot be the (only) reason for the results of these measurements. It would be reasonable to assume a rhombohedral deformation in the case of a small deformation. Attempts to apply a rhombohedral lattice which would be a deformation along the [111] direction under assumption of
constant lattice parameters for all edges have failed. Therefore, this is an indication for a lower symmetry deformation.

Figure 5.12.: Reciprocal space map around the asymmetric substrate reflection YSZ (531). The magenta colored dashed lines indicate the positions of maximal intensity of each reflection. The Nd$_2$Ir$_2$O$_7$ (10 62) reflection is very weak but clearly measurable. It is far off the expected relaxation line, indicated in orange. From the in-plane $q$-value a cubic lattice constant of 10.753 Å can be calculated. The out-of-plane $q$-value yields a cubic lattice constant of 10.363 Å. The latter value is in good agreement with the result from the symmetric RSM.
5.2. Physical properties of Nd$_2$Ir$_2$O$_7$ thin films fabricated under optimal conditions

5.2.2. Atomic force microscopy (AFM)

One sample, fabricated under standard conditions, comparable in quality with IRZ 36 but only 29 nm thin, is measured in an Atomic Force Microscope (AFM) to determine the roughness of the sample surface.

As Fig. 5.13 shows the sample is very flat. The AFM analysis determines a root mean square of the sample roughness of less than $r_{\text{rms}} = 4$ Å which is a good value if taking into account that a single unit cell of Nd$_2$Ir$_2$O$_7$ is in the order of 10 Å. The roughness equals the value found via reflectometry measurements for this sample (cf. Tab. B.2 sample IRZ 48). This is comparable with the substrate roughness of $r_{\text{rms}} \approx 1$ Å measured by CrysTec. This means the sample surface has a high quality.

![AFM image](image)

**Figure 5.13.:** Atomic force microscopy (AFM) of a thin film Nd$_2$Ir$_2$O$_7$ sample. The highest peaks are in the order of 3 to 4 unit cells. The root mean square roughness is in the order of $r_{\text{rms}} = 4$ Å.

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1AFM data for YSZ was provided by CrysTec via e-mail after request.
5.2.3. Magnetic properties

This section deals with the magnetic properties of Nd$_2$Ir$_2$O$_7$ thin films. To obtain as much signal as possible, the thickest sample was used for measurements in the SQUID magnetometer to determine the magnetization as a function of temperature under field-cooled (FC) ($\mu_0 H = 7$ T) and zero-field-cooled (ZFC) conditions. The results are shown in Fig. 5.14. For the magnetization, measured at a field of $\mu_0 H = 100$ mT, the diamagnetic background of YSZ is subtracted. The response is one order of magnitude stronger than the expected signal on the basis of the magnetic properties of bulk Nd$_2$Ir$_2$O$_7$ (cf. Sec. 3.4). However, we found paramagnetic impurities in the YSZ substrate during a reference measurement with a blank YSZ substrate. Therefore, this signal is probably mainly caused by the substrate, which causes the high magnetization values because the response is normalized to the volume of the Nd$_2$Ir$_2$O$_7$ thin film. However, no splitting of the magnetization curve versus temperature for FC and ZFC conditions is observable.

![Figure 5.14: Magnetization as a function of temperature of a thick Nd$_2$Ir$_2$O$_7$ thin film sample ($d \approx 80$ nm). No splitting of both measurements is visible. The overall magnetization is one order of magnitude larger than for bulk Nd$_2$Ir$_2$O$_7$ (cf. Fig. 3.5). The signal is mainly the paramagnetic response from impurities in YSZ.](image-url)

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5.2. Physical properties of Nd$_2$Ir$_2$O$_7$ thin films fabricated under optimal conditions

5.2.4. Electrical properties

Two samples are contacted via an IDT$^2$ structure. The IDT structure of IRZ 36 has 30 fingers of 500 µm by 5 µm at each side, with an intermediate spacing of 5 µm and the IDT structure of IRZ 40 has 90 fingers of 1800 µm by 5 µm at each side, with an intermediate spacing of 5 µm. The length refers to the intersecting parts of the finger. By using this structure, the resistance of the sample can be decreased by maximizing the cross section for transport and minimizing the transport distances.

As the samples are thin film samples they are expected to have a higher resistance than a bulk sample. Therefore by applying a fixed current this may result in high voltages and thereby damage the sample. So the measurement method is changed to a fixed voltage bias (20 V) and to measure the current in a simple 2 point geometry.

![IDT structure](image)

Figure 5.15.: IDT structure on top of the sample IRZ 40 used for the electrical transport measurements.

Figure 5.16 shows the results. These are in contradiction to the temperature versus resistivity measurement of bulk Nd$_2$Ir$_2$O$_7$ (cf. Sec. 3.5.1). In particular, the resulting resistivities are far off the bulk value. The behavior of IRZ 40 is more similar to the bulk behavior, the corresponding minimum value, however, is more than 15 K lower. As obvious from Fig. 5.16, both Nd$_2$Ir$_2$O$_7$ thin films are highly insulating in the entire

$^2$IDT = InterDigital Transducer
temperature range. This might be caused by non-stoichiometric effects like iridium loss or oxygen vacancies in the Nd$_2$Ir$_2$O$_7$ thin films.

![Magnetotransport measurement in two thin film samples.](image)

Figure 5.16.: Magnetotransport measurement in two thin film samples. The behavior of IRZ 36 is not related to bulk Nd$_2$Ir$_2$O$_7$. IRZ 40 has a similar qualitative shape like the bulk material, the values of resistivity and a small minimum (located around 10 K) in the curve, however, are far off compared to bulk Nd$_2$Ir$_2$O$_7$. 
5.2. Physical properties of Nd$_2$Ir$_2$O$_7$ thin films fabricated under optimal conditions

5.2.5. Summary and Conclusion

Though the structural properties of the Nd$_2$Ir$_2$O$_7$ thin film samples are very good it was not possible to reproduce the electric and magnetic properties of the polycrystalline material.

During the growth process the construction of a lattice with a unit cell of Nd$_2$Ir$_2$O$_7$ over 4 unit cells of YSZ is visible via RHEED. The films grow with the same in-plane orientation as provided by the substrate by using a $\phi$-scan. By means of the reciprocal space mapping we found that the Nd$_2$Ir$_2$O$_7$ thin films grow parallel to the [111] direction. The lattice constant behaves in out-of-plane direction as expected for compressive in-plane strain, however, we found tensile strain in-plane which is a strong contradiction. We could also exclude a rhombohedral deformation. Further study is needed to explain this unexpected behavior.

Magnetization may not be visible in any (future) thin film samples because the response of the substrate is found to be one order of magnitude larger. Due to the small volume of the thin film compared to the substrate (in the order of 1:10,000) the response of the film is very hard to resolve. The magnetization can only be measured when the sample is either grown on a substrate with smaller magnetic response, grown much thicker than 80 nm on YSZ, or as a single crystal.

The samples showed to be quasi-insulating. Any electrical current driven is probably related to a transport phenomenon different from the expected. This may have several reasons, e.g., leak currents on surfaces, not well insulated wiring, transport via gaseous helium, or internal resistances of the measurement devices. The samples may be insulating due to a wrong stoichiometry, strain in the sample, a non uniform conductivity tensor etc.

However, without a further specification of the thin film composition there is little chance to resolve the issues.
Chapter 6.
Summary and Outlook

6.1. Polycrystalline Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ samples

The polycrystalline Nd$_{2}$Ir$_2$O$_7$ material showed the same properties as described in literature. We fabricated the material system from Nd$_2$O$_3$ and metallic Ir powder by a solid state reaction, and confirmed the correct phase by X-ray powder diffraction. Also our EDX analysis suggests a correct stoichiometry. The lattice constant was determined to be $a = (10.370 \pm 0.004)$ Å, depending on the fit method (Rietveld refinement, Nelson-Riley approach), which is in good agreement with literature values ($a = 10.383$ Å [15], $a = 10.3768$ Å [44], and $a = 10.3677$ Å taking a linear extrapolation from data in Ref. [18]). We find a metal to insulator transition at a temperature $T_{MI} \approx 35$ K in magnetotransport measurements as well as magnetization measurements, which is related to an anti-ferromagnetic ordering of the Ir$^{4+}$ ions. At a temperature around $10$ K in magnetotransport measurements as well as in magnetization measurements, we found indications of an ordering related to the Nd$^{3+}$ ions, while we could exclude a ferromagnetic structure.

By substituting Nd$^{3+}$ ions with Pr$^{3+}$ ions (Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$) we wanted to achieve a shift in the metal to insulator transition temperature as reported in Ref. [22]. According to Vegard’s law for alloys, material parameters change linearly for similar crystal systems by substitution [47]. We were able to show a linear dependence of the lattice constant on the praseodymium concentration $x$, thus fulfilling Vegard’s law. Pr$_2$Ir$_2$O$_7$ showed a lattice constant of $a \approx 10.410$ Å which is in good agreement with the literature ($a = 10.406$ Å in Refs. [42, 45]). However, the metal to insulator transition temperature did not change for $x < 2$, though Pr$_2$Ir$_2$O$_7$ ($x = 2$) does no longer show an insulating behavior in the measured temperature region down to 2 K. We observed a decreasing splitting between field-cooled and zero-field-cooled magnetization curves as well as a decreasing magnetoresistance $MR$ for increasing praseodymium concentrations in our samples. The ratio between high and low temperature resistivity changes strongly throughout the substitution series. For all samples with $x < 2$, we found a second ordering temperature at around 11 K. This confirms the findings for Nd$_2$Ir$_2$O$_7$.
where we suggested that the ordering of the Nd\textsuperscript{3+} ions causes this observation. In our measurements, we were not able to confirm or exclude iridium loss as the iridium doping series was inconclusive.

All in all our results are in agreement with findings of Ueda \textit{et al.}, Matsuhira \textit{et al.} (cf. Refs. [20–24]), however there are some findings that do not concur, e.g. the observed behavior for the substitution series. Our results do not agree with Disseler \textit{et al.} (cf. Refs. [18, 19]).

### 6.2. Thin films of \textit{Nd}_2\textit{Ir}_2\textit{O}_7

The \textit{Nd}_2\textit{Ir}_2\textit{O}_7 thin film samples, grown on [111] oriented YSZ, overall showed a very high structural quality. During different series some parameters were varied, thus refining available parameters from previous works. We were able to show that the samples fabricated at optimal parameters ($T_s = 800^\circ$C, $p_{O_2} = 25$ µbar, $p_E = 2$ J/cm\textsuperscript{2}) have a lattice constant (under assumption of a cubic symmetry) close to the relaxed value. They grow coherently strained with the same orientation as provided by the YSZ substrate. We were able to find epitaxial strain below a critical thickness $d_{crit} \approx 20$ nm, above which thin films relax. However, we found a lattice constant of $a = 10.753$ Å (under assumption of a cubic symmetry), calculated from the in-plane component of a RSM, which is approximately 3.7% larger than the expected value despite compressive strain from the substrate. This leads to the conclusion that the crystal structure of the \textit{Nd}_2\textit{Ir}_2\textit{O}_7 thin films deviates from a cubic lattice. It also does not concur with the RHEED data, which suggest a lattice constant ratio of 2:1 for \textit{Nd}_2\textit{Ir}_2\textit{O}_7 and YSZ. The surface of the thin film samples is very smooth (typically $r_{rms} = (0.6 \pm 0.2)$ nm), which was measured via AFM and X-ray reflectometry. The reflectometry also revealed that the thin film samples have a decreased density, which might be related to the samples being not conductive. Both effects are probably related to non-stoichiometric effects like iridium loss or oxygen vacancies. The magnetization could not be evaluated due to the paramagnetic background of the YSZ substrate at low temperature. A possible iridium loss could not be proved, the use of a PLD target with excess iridium provided films with the same crystalline properties.

We found that over time the growth rate of thin films changes drastically, which could be related to changes in the PLD target. In a bachelor’s thesis [26], \textit{Pr}_2\textit{Ir}_2\textit{O}_7 thin films samples showed strong oxidation on the sample surface after several weeks of exposition to air. This may be an indication for similar processes in \textit{Nd}_2\textit{Ir}_2\textit{O}_7.
6.3. Outlook

Some points remain unclear and have to be investigated in the future.

We had no means available to precisely quantify the composition of the thin films and the polycrystalline samples, as well as the crystalline structure with atomic resolution. This is necessary because it is not clear whether iridium and neodymium/praseodymium ions are located at the correct lattice sites, or are even missing. Also we could neither confirm nor exclude oxygen vacancies as a reason for our results in the thin films, partly contradictory to literature.

For further experiments also single crystalline samples should be considered. Transport in polycrystalline samples may be influenced by grain boundaries. Effects from grain boundaries could also be visible in thin films. However, up to now it is not revealed whether the transport in epitaxial Nd$_{2-x}$Pr$_x$Ir$_2$O$_7$ thin films is anisotropic, there is still the possibility that the plane perpendicular to the [111] direction is insulating. Also strain effects may influence the transport behavior of the crystalline thin films.
Appendix A.

Experimental techniques

A.1. Pulsed laser deposition (PLD)

For fabricating thin film samples Pulsed Laser Deposition (PLD) was used. A schematic is given in figure A.1.

![Schematic of pulsed laser deposition (PLD)](image)

Figure A.1.: Schematic of pulsed laser deposition (PLD), explained in the text (taken from Ref. [56]).

PLD works as means to transfer a target material system stoichiometrically to a substrate in the following way: A high energy UV excimer laser (KrF, 248 nm) is focused on a rotating polycrystalline target, consisting of the deposition material (e.g., Nd$_2$Ir$_2$O$_7$). When a laser pulse arrives on the target it ionizes the material system detaching several atoms and thus produces a so called “plasma plume” above the
Appendix A. Experimental techniques

target. The substrate is placed inside this plume in a distance of several centimeters above the target, resulting in the deposition of some material from the plasma onto the substrate surface. The substrate can be heated from the backside via an infrared laser, which provides the deposited ions with thermal energy, allowing them to move on the substrate surface to find the correct lattice sites. If the environmental conditions in the PLD chamber are appropriate, a single crystalline layer can form on the substrate surface. To reach this goal, several parameters must be carefully adjusted by the operator of the PLD cluster:

- **Temperature:** By adjusting the power of the infrared laser the temperature of a substrate can be regulated very accurately up to $T_S = 1200^\circ C$.

- **Atmosphere:** Different gases can be let into the PLD chamber, here argon or molecular oxygen are used. The pressure can be adjusted to a certain value by choosing the gaseous flow at the inlet, and using an automatized gate valve in combination with a turbomolecular pump, which control the amount of excess gas being removed.

- **Lasing parameters:** The control program for the laser offers the possibility to choose the laser fluence at the target by resizing the UV laser spot with an automated lens system. The setup thus allows laser fluences in the range of $\rho_E = 0.5 \, J/cm^2$ to $\rho_E = 5 \, J/cm^2$. The repetition rate can be chosen up to 10 Hz. The laser can operate in 2 modes: “normal mode” where it lases with the given repetition rate throughout the given pulse number, and “packet mode” where the laser is provided with a number of packets, a number of pulses per packet, and a time value to wait between two packets.

The growth process can be monitored in-situ via RHEED, which will be explained in the following section. Further information on the used PLD system can be found in Ref. [57].
A.2. Reflection high energy electron diffraction (RHEED)

While producing thin film samples Reflection High Energy Electron Diffraction (RHEED) can be applied to monitor the growth of the sample in-situ.

Figure A.2.: Principle of the emergence of reflection high energy electron diffraction (RHEED) patterns in thin films, described in the text. Abbreviations: $e^-$ = electrons, $k_{i,j}$ = electron wave vectors, $g_\perp$ / $g_\parallel$ = in-plane lattice vectors (taken from Ref. [58]).

An electron gun is mounted at the PLD chamber. The e-beam is adjusted parallel to the desired crystal direction of the substrate, here (10\overline{1}) is used. The electrons for the e-beam are evaporated from a thin tungsten wire. To prevent the tungsten
from being burned in the oxygen atmosphere the e-gun has a differentially pumped tube which produces a lower pressure at the front end and thus preventing gas from moving from the chamber directly to the wire. The heating current is adjusted to generate an emission current of 60 mA, which then is accelerated by a voltage 15 kV to generate a sharp e-beam. By adjusting the vertical position and inclining the sample the path of the reflected electrons can be adjusted to hit a fluorescent screen, where a CCD-camera records the pattern. The pattern is generated because only such reflections are allowed that fulfill the Laue equation $\Delta k = k_s - k_i = G$. This means for an electron to be scattered, the difference $\Delta k$ of its incident wave vector $k_i$ and its scattered wave vector $k_s$ is a lattice vector $G$ of the reciprocal lattice. Figure A.2 shows the fulfillment of this condition in the (side view) and (top view) panels, where for thin films the reciprocal lattice consists of rods as also shown. The emergence of the observed pattern is illustrated in Fig. A.2 (3D view). Depending on the inclination of the sample, a set of reflections can be chosen to appear on the fluorescent screen. However, as thin films usually have a rough surface the reflections are smeared and form one dimensional, parallel lines, where the distance between the lines is the same as the distance $l$ (cf. Fig. A.2 (3D view)) between the dots.
A.3. High resolution X-ray diffraction (HRXRD), X-ray powder diffraction (XRPD)

High Resolution X-Ray Diffraction (HRXRD) is a technique to investigate structural properties like the lattice constant, crystalline quality, layer thickness and is used to identify the material phases in the sample. For polycrystalline samples X-Ray Powder Diffraction (XRPD), is used which provides information about phases in the sample and the lattice constant.

Figure A.3.: Measurement setup for high resolution X-ray diffraction. For X-ray powder diffraction the monochromator is removed (taken from Ref. [59]).

In our institute, we use a Bruker "Discover08" 4-circle X-ray diffractometer. The setup (cf. Fig. A.3) contains a X-ray source which uses the Cu-K$_\alpha$1 line with $\lambda = 0.154\,06\,0\,nm$ [43]. The X-rays are generated when electrons, accelerated via a voltage of 40 kV, hit a Cu-plate. The Cu-K$_\alpha$1 line is extracted from the spectrum by using a Goebel mirror and a germanium monochromator. The 4-circle device makes it possible to also reach reflections that originate from lattice planes which are inclined to the sample surface by inclining the sample itself.

The two measurement methods (HRXRD, XRPD) are different in the measurement setup as well as in the information they provide. Where the setup in the case of HRXRD contains a monochromator, this is removed for XRPD to increase the primary beam intensity at the cost of a secondary reflection, originating from the Cu-K$_\alpha$2 line ($\lambda = 0.154\,43\,9\,nm$ [43]). This is necessary to reveal signals with low intensity as polycrystalline powders consist of many crystallites, which provide any allowed reflections. Single crystalline samples or thin films, however, provide only reflections in one lattice direction, which can be chosen by the measurement geometry. The intensity
Appendix A. Experimental techniques

of a given reflection depends on the amount of the corresponding layers in all crystallites in the scanned area which face the same direction. This value is typically lower in polycrystalline powders than in single crystalline samples or thin films because in the first case the orientation of crystallites is equally distributed, where in thin films ideally there is only one crystallite. However, in reality in thin films there are usually several slightly tilted crystallites, which broaden measured signals but provide similar patterns like single crystals. So by increasing the primary intensity, weak reflections can still be observed.

The measurement techniques both rely on interference effects (illustrated in Fig. A.4). The equation describing all angles with constructive interference is Bragg’s equation

\[ 2d_{hkl} \sin \theta = n\lambda, \]  

(A.1)

where \( d_{hkl} \) is the spacing between two parallel layers in the lattice, \( \theta \) the angle of incidence / reflection (measured between reflecting layer and incident beam), \( n \) the order of the reflection and \( \lambda \) the X-ray wavelength. Usually we set \( n = 1 \) as higher order reflections can also be accounted for by multiplying the \( hkl \) index with an integer.

![Figure A.4.: Constructive interference following Bragg’s equation (A.1). Parallel X-rays with wavelength \( \lambda \) incide under an angle \( \theta \) on the left hand side (1, 2, 3). They are reflected by the parallel lattice planes indexed with \( hkl \), which have a distance of \( d_{hkl} \). Following Bragg’s equation the beams, which are reflected by different lattice planes, interfere. Eventually the superposition of the reflections emerges on the right hand side (1’, 2’, 3’) (taken from Ref. [60]).](image-url)
A.3. High resolution X-ray diffraction (HRXRD), X-ray powder diffraction (XRPD)

There is a set of standard scans that is used for the samples and provides different information:

- **2θ-ω-scan**: This type of measurement provides information about the phases in the sample as well as about the lattice constant. After aligning the sample on a strong (symmetric) substrate reflection (here YSZ (111)), which is necessary to correct for a miscut or tilt of the substrate, the scan tests the sample in [111] direction, which is perpendicular to the sample surface, by rotating the detector twice as much as the sample. Due to the nature of this scan, only information about the lattice constant in [111] direction can be retrieved (cf. Fig. A.5 (a), (b)). Any other direction can be probed by aligning on an asymmetric substrate reflection (cf. Fig. A.5(a), (c)).

- **rocking curve**: This scan is used to determine the crystalline quality of the thin film. After doing a 2θ-ω-scan the sample is aligned on the film reflection. By keeping the detector on a fixed position and rotating the sample (ω-scan, cf. Fig. A.5 (a), (b)) a superposition of two Gaussians can be seen, which arise from regions in the film with different crystalline quality. The full width at half maximum (FWHM) is a measure for the mosaic spread.

- **reflectometry**: A reflectometry probes the thickness $d_{\text{film}}$ of a thin film, as well as the density $\rho$ and roughness $r_{\text{rms}}$. The detector is positioned slightly off the X-ray incidence axis. Via a rocking curve the maximum reflectivity is determined. Then a 2θ-ω-scan is used to observe interference effects arising from the path difference of directly reflected beam and the beam reflected at the interface between thin film and substrate. This also obeys Bragg’s law

\[
2d_{\text{film}} \sin \theta_{\text{film}} = n\lambda, \quad (A.2)
\]

where $\theta_{\text{film}}$ is the angle between beam and sample surface. The roughness $r_{\text{rms}}$ can be considered by assuming crystallites with a Gaussian distributed thickness $d$, resulting in diffuse scattering and thus reduced intensity of the reflected beam. The density $\rho$ is determined by the square of the critical angle, which causes the first drop in intensity in reflectivity measurements (cf. Ref. 59). The reflectometry measurements were evaluated with the software LEPTOS.

- **reciprocal space mapping (RSM)**: While the techniques above only lead to information extracted from a single line a RSM reconstructs the $k$-space in a limited area. The software can couple the movement of detector and sample in such a manner that it is possible to scan along straight (not curved) lines in $k$-space ("linear $q$ scan"). This allows to produce a 3D picture that also provides information about the lateral extent of any scanned reflections. Asymmetric RSMs (cf. Fig. A.5(a), (c)) allow to investigate strain and also a in-plane lattice
constant (here: [101] direction), while symmetric RSMs (cf. Fig. A.5 (a), (b)) provide information about tilt of the film growth direction.

Figure A.5.: Measurement geometries in X-ray diffraction. (a) The scan mode of $2\theta$-$\omega$ scans and rocking curves is shown here for a symmetric scan (taken from Ref. [59]). (b) Symmetric scan geometry, used for symmetric RSM as well as $2\theta$-$\omega$ scans and rocking curves shown in (a). (c) Asymmetric scan geometry, used for asymmetric RSM. $\tau$ hereby denotes the inclination of the probed crystal layer. ((b) and (c) taken from Ref. [60]).
A.4. Determination of the lattice constant

A.4.1. Nelson-Riley approach

The Nelson-Riley approach is a method that considers systematic errors that arise from the measurement setup during $2\theta$-$\omega$ scans. The Nelson-Riley number $NR$ is calculated via (cf. Ref. [61]):

$$NR = \frac{\cos^2(\pi \cdot \frac{2\theta}{360})}{\sin^2(\pi \cdot \frac{2\theta}{360})} + \frac{\cos^2(\pi \cdot \frac{2\theta}{360})}{2\theta/2}.$$  

For every reflection with different order, e.g., (111), (222), (333) etc., the corresponding lattice constant obtained via Bragg’s law (Eq. (A.1)) is plotted over its Nelson-Riley number $NR$. The extrapolation to $2\theta-\omega \to 180^\circ$ then yields the lattice constant (cf. Ref [61]).

A.4.2. Rietveld refinement

The Rietveld method was developed by H. M. Rietveld to evaluate his neutron diffraction experiments. The method is also applicable for X-ray diffraction. The calculated intensity $y_{ci}$ has the following shape (cf. Refs. [62, 63]):

$$y_{ic} = s \sum L_k |F_k|^2 \varphi(2\theta_i - \theta_k) P_k A + y_{ib}$$

where $y_{ic}$ is the calculated intensity at the $i$-th step, $s$ is a scale factor, $k$ stands for the Miller indizes $(h, k, l)$ of a Bragg reflection, $L_k$ includes multiplicity, Lorentz and polarization factors, $F_k$ is the structure factor for the $k$-th Bragg reflection, $\varphi$ is the reflection profile function, $P_k$ a correction for preferred orientations, $A$ an absorption factor, and $y_{ib}$ the background intensity.

The refinement then is calculated via the method of least squares via (cf. Ref. [63]):

$$M = \sum W_i \left( y_{iob} - \frac{1}{c} y_{ic} \right)^2,$$

where $y_{iob}$ is the observed intensity at the $i$-th step, $W_i$ is a statistical weight and $c$ a scale factor. To reconstruct the lattice constant the calculated Bragg reflection positions are plugged in Bragg’s law with the corresponding Miller indizes.
A.5. Van der Pauw measurement technique

The van der Pauw method is an established technique for determining resistance and resistivity of bad conductors in an arbitrary shape. An accurate way to perform and evaluate measurements concerning these samples is published in van der Pauw’s original reports [46, 64].

To simplify the measurement, a square geometry is preferred to eliminate effects arising from the shape of the sample. Another reason is that in square shape all directions along edges or diagonals are equal. Like this it is easy to perform measurements along all 4 edges to investigate inhomogeneities and to correct for them by averaging.

Van der Pauw suggests different points that should be considered when measuring a homogeneous, isotropic material:

“It will be shown that the specific resistivity [. . .] of an flat sample of arbitrary shape can be measured without knowing the current pattern if the following conditions are fulfilled:

   a) The contacts are at the circumference of the sample.

   b) The contacts are sufficiently small.

   c) The sample is homogeneous in thickness.

   d) The surface of the sample is singly connected, i.e., the sample does not have isolated holes.” [64]

Figure A.6.: Contact placement in van der Pauw measurements [65].
This leads to certain shapes of a sample shown in Fig. A.6 that might be used. However, due to the sample shape and measurement setup we had to use the non-preferred rightmost geometry in Fig. A.6.

The measurements were performed in an Oxford magnet cryostat with a Nb$_3$Sn superconducting coil (maximum magnetic field: 17 T), both cooled by liquid helium. The current to the sample was supplied by a Keithley K2400 source meter which also recorded the applied two point voltage. The four point voltage (or the hall voltage, respectively) was measured by a Keithley K2010 multimeter. The sample was positioned on a dip stick in a heatable Variable Temperature Insert (VTI) in the cryostat. It has a controllable needle valve to regulate the helium flux and is pumped to evaporate incoming helium. Together with a temperature sensor and an ohmic heater at the copper sample mount the temperature of the sample can be controlled precisely.
Appendix A. Experimental techniques

A.6. Lithography of IDT structure

The investigation of the conductivity of thin film samples is difficult if they have low conductance. As the conductance scales with $A/d$ it is helpful to shorten the distance $d$ between contacts and to increase the area $A$ (perpendicular to the sample surface) where the current can flow. A way to do this is by bringing a so called InterDigital Transducer (IDT) structure made of gold (cf. Fig. 5.15) on top of the sample surface. This was done by UV-lithography.

To copy the structure from the mask to the sample surface the following steps were done:

- Cleaning the sample in a ultrasonic bath with acetone, then rinsing with isopropyl alcohol and water, drying with nitrogen
- Spin coating with photo resist “AZ 5214E”, spinning 30 seconds at 2000 rpm
- Prebaking for 70 s at 110 °C
- Exposure with mask at 36 mJ/cm²
- Reversal baking for 30 s at 119 °C
- Flood exposure with >200 mJ/cm²
- Developing in “AZ 726 MIF” for 30 s, then rinsing with water
- Sputtering with gold 100 s at 45 mA
- Lift-off process with acetone in ultrasonic bath

After that contacts were brought onto the sample by using a bonding machine which connected the sample to the chip carrier system used for mounting in different devices.
A.7. SQUID magnetometry

For magnetization measurements, a commercial SQUID (Superconducting QUantum Interference Device) magnetometer MPMS XL-7, produced by Quantum Design, was used. This magnetometer is cooled by liquid helium and shielded with liquid nitrogen, providing temperatures down to 1.8 K. The superconducting coil allows to reach magnetic fields up to $\mu_0 H = 7$ T.

As shown in Fig. A.7, the sample (thin film or polycrystalline pressed powder rod) is placed inside a plastic measurement tube and then inserted into the device. In the measurement device, there are three coils to pick up magnetic fields, where the outer two have the same number of windings (1), and the coil in the center is wound in the opposite direction with twice as many windings (2). This setup therefore cancels any external static fields as well as first order gradient fields. By moving the sample up and down with a small magnetic field (typically $\mu_0 H = 100$ mT) applied a current is induced in the coil system. The magnetization is then determined via a radio frequency SQUID, which is coupled to the pickup-system. Due to the external magnetic field, the magnetization component parallel to this magnetic field can be evaluated. For further information see Ref. [66].
A.8. Atomic force microscopy (AFM)

Atomic Force Microscopy (AFM) is used to determine the roughness of a sample surface. The principle is shown in Fig. A.8. A cantilever with a sharp tip scans the surface. The surface potential determines whether the tip is drawn to the sample surface or pushed away from the sample surface. The displacement of the cantilever is measured by determining the deflection angle of a laser beam that hits the cantilever. There are three general modes available to probe the surface: First, contact mode where the height profile is either determined by measuring the displacement of the cantilever (constant height setting) or by regulating the height of the cantilever to provide a constant cantilever displacement (constant force setting). Second, tapping mode, where the cantilever oscillates near its resonance frequency, hitting the sample surface and therefore changing the amplitude of the oscillation, which is measured. Third, non-contact mode where the cantilever also oscillates near its resonance frequency (forces modulate frequency) or slightly above (forces modulate amplitude), however, it does not hit the sample surface. The choice of the mode depends on the sample and the environmental conditions.

Figure A.8.: Schematic setup of an atomic force microscope (AFM), explained in the text (taken from Ref. [67]).
A.9. Energy-dispersive X-ray spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDX) is a means to quantify the atomic composition in a sample. In our institute a commercial setup, produced by EUMAX, is used. Primary electrons that are ejected from an electron gun (cf. Fig. A.9 (a)), accelerated by a high voltage, are focused on the sample surface with a coil system. When they hit the surface, electrons are likely to kick out core electrons, where the interaction probability is highest for core electrons with binding energies close to the kinetic energy of the incident electrons. This typically results in the interaction with K or L electrons, depending on the acceleration voltage. The free space in an atomic orbit is filled by an electron from a higher order shell, typically L or M. The difference in electron binding energy is emitted as an X-ray photon that can be detected. The binding energies strongly depend on the proton number $Z$ in an atom (or ion), and are therefore characteristic for each element. For heavy elements, separate lines for different angular momentum of involved electronic shells are observed. The method is not applicable for hydrogen and helium because they only have one shell. For light elements such as oxygen the detection of individual lines is difficult as in this energy region there are also lines that originate from occasional scattering events happening in the outer shells of heavy elements. The relative intensities of the lines is a measure for the chemical composition.

Figure A.9.: Schematic setup of an energy-dispersive X-ray spectroscope (EDX). Usually a scanning electron microscope (SEM) as shown in the picture is used to provide the e-beam. This allows to probe the surface (which was not done in this thesis) as well as the composition (taken from Ref. [68])
Appendix B.

Samples: Fabrication parameters and measured values

B.1. Polycrystalline samples

The polycrystalline samples that were fabricated in the framework of this thesis are listed in Tab. B.1.

Table B.1.: Polycrystalline samples. Abbreviations: P (powder), PP (pressed powder rod), PLD (PLD target). Temperature / time corresponds to the last heating step. The two samples marked with an asterisk are not discussed in this thesis as they showed mainly parasitic phases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Batch 1</th>
<th>Batch 2</th>
<th>Batch 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd₂Ir₂O₇</td>
<td>P 1125°C, 10h O₂</td>
<td>P 1000°C, 10h O₂</td>
<td>-</td>
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<td>PP 1125°C, 10h O₂</td>
<td>PP 1000°C, 10h O₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PLD 1125°C, 10h O₂</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>P 1000°C, 10h O₂</td>
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<tr>
<td></td>
<td>PP 1125°C, 10h O₂</td>
<td>PP 1000°C, 10h O₂</td>
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<td>PP 1125°C, 10h O₂</td>
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</tr>
<tr>
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<td>P 1125°C, 10h O₂</td>
<td>P 1000°C, 10h O₂</td>
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<td>PP 1125°C, 10h O₂</td>
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</tr>
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<td>Pr₂Ir₂O₇</td>
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<td>P 1000°C, 10h O₂</td>
<td>P 950°C, 10h O₂*</td>
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<td>PP 1125°C, 10h O₂</td>
<td>PP 1000°C, 10h O₂</td>
<td>P 950°C, 25h O₂*</td>
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<td>Pr₂Ir₁,₅O₇</td>
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<td>-</td>
<td>P 1000°C, 10h O₂</td>
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<td>Pr₂Ir₂,₁O₇</td>
<td>-</td>
<td>-</td>
<td>P 1000°C, 10h O₂</td>
</tr>
</tbody>
</table>
B.2. Thin film samples

The thin film samples that were fabricated in the framework of this thesis are listed in Tab. B.2. The evaluation of several properties is listed in Tab. B.2.

Table B.2.: Measured values of thin film samples. Abbreviations in table header: $a =$ lattice constant, FWHM peak/base = full width at half maximum of the rocking curves, $d =$ thickness of film, $r_{\text{rms}} =$ roughness, $\rho =$ density. Blank fields in the table were not evaluated, only concerns samples labeled with parasitic, sapphire or damaged in Tab. B.3.

<table>
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<tr>
<th>ID</th>
<th>$a$ [Å]</th>
<th>FWHM peak [°]</th>
<th>FWHM base [°]</th>
<th>$d$ [nm]</th>
<th>$r_{\text{rms}}$ [nm]</th>
<th>$\rho$ [g/cm$^3$]</th>
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</thead>
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<tr>
<td>IRZ 28</td>
<td>10.41</td>
<td>0.347°</td>
<td>0.509°</td>
<td>27.6 ± 0.3</td>
<td>0.65 ± 0.05</td>
<td>7.3 ± 0.1</td>
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<tr>
<td>IRZ 29</td>
<td>10.412</td>
<td>0.345°</td>
<td>0.521°</td>
<td>32.6 ± 0.3</td>
<td>0.6 ± 0.1</td>
<td>7.15 ± 0.1</td>
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<tr>
<td>IRZ 30</td>
<td>10.415</td>
<td>0.357°</td>
<td>0.682°</td>
<td>7.9 ± 0.2</td>
<td>0.5 ± 0.1</td>
<td>7.9 ± 0.3</td>
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<tr>
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<td>10.506</td>
<td>0.323°</td>
<td>0.652°</td>
<td>17.3 ± 0.1</td>
<td>0.47 ± 0.08</td>
<td>7.81 ± 0.1</td>
</tr>
<tr>
<td>IRZ 33</td>
<td>0.346°</td>
<td>0.544°</td>
<td>21.3 ± 0.1</td>
<td>0.5 ± 0.05</td>
<td>7.6 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>IRZ 34</td>
<td>10.429</td>
<td>0.320°</td>
<td>0.526°</td>
<td>63.6 ± 0.2</td>
<td>1.2 ± 0.1</td>
<td>7.75 ± 0.15</td>
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<tr>
<td>IRZ 35</td>
<td>10.416</td>
<td>0.321°</td>
<td>0.436°</td>
<td>51 ± 6</td>
<td>0.85 ± 0.05</td>
<td>8 ± 0.1</td>
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<tr>
<td>IRZ 36</td>
<td>10.415</td>
<td>0.349°</td>
<td>0.411°</td>
<td>41.4 ± 1</td>
<td>0.55 ± 0.05</td>
<td>7.9 ± 0.15</td>
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<tr>
<td>IRZ 37</td>
<td>10.409</td>
<td>0.351°</td>
<td>0.417°</td>
<td>23.6 ± 0.6</td>
<td>0.45 ± 0.05</td>
<td>7.9 ± 0.1</td>
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<tr>
<td>IRZ 38</td>
<td>10.425</td>
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<td>29.6 ± 1</td>
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<td>0.530°</td>
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<tr>
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<td>0.471°</td>
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<tr>
<td>IRZ 41</td>
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<td>0.45 ± 0.05</td>
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<tr>
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<td>0.329°</td>
<td>0.398°</td>
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<td>0.5 ± 0.1</td>
<td>8 ± 1.1</td>
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<tr>
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<td></td>
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<td>0.393°</td>
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<td>7.9 ± 0.1</td>
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<td>IRZ 47</td>
<td>10.491</td>
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<td>8.1 ± 0.2</td>
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<tr>
<td>IRZ 48</td>
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<td>IRZ 49</td>
<td>10.421</td>
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<td>0.355°</td>
<td>0.428°</td>
<td>54 ± 0.3</td>
<td>0.45 ± 0.1</td>
<td>7.95 ± 0.15</td>
</tr>
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## Appendix B: Samples: Fabrication parameters and measured values

### Table B.3: Fabrication parameters of Nd$_2$Ir$_2$O$_7$ thin film samples. Abbreviations in table header: $T_s$ = substrate temperature, $p$ = pressure, $f$ = repetition rate, $\rho_E$ = laser fluence. Column series denotes which samples are used in which series: $E$ = laser fluence, $T$ = temperature series, $P$ = pressures series, Ir = iridium series, S1/2 = pulse series, blank field = not evaluated in this thesis. Comments: parasitic = film is other phase than Nd$_2$Ir$_2$O$_7$, IR+ = PLD target contained excess iridium, Laue = thickness evaluated via Laue oscillations, sapphire = grown on sapphire, other phase than Nd$_2$Ir$_2$O$_7$, contaminated = may contain contamination, damaged = damaged during process.

<table>
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<th>ID</th>
<th>$T_s$ [°C]</th>
<th>$p$ [µbar]</th>
<th>$f$ [Hz]</th>
<th>$\rho_E$ [J/cm$^2$]</th>
<th>Series</th>
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<td>10</td>
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<td>parasitic</td>
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<tr>
<td>IRZ 38</td>
<td>800</td>
<td>25</td>
<td>200</td>
<td>10</td>
<td>T, P, Ir, S1</td>
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</tr>
<tr>
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<td>25</td>
<td>200</td>
<td>10</td>
<td>T, P, Ir, S1</td>
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<td>IRZ 47</td>
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Bibliography


[67] (University of Arkansas) Prof. J. Chakhalian. AFM and imaging of the Surface. URL http://comp.uark.edu/~jchakhal/afm-draw-1-c-1.jpg

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- My physics teachers, especially Dr. Paul Schlüter and Bernhard Martin, who got me enthusiastic about physics.
- My family who supported me during my studies, and kept everyday-life trouble out of my mind especially during the preparation of this thesis.
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