Doctoral Thesis

Controlling multiferroic properties via strain: an X-ray diffraction and absorption study

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Controlling multiferroic properties via strain: an X-ray diffraction and absorption study

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

presented by

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Abstract

Recent years have seen an increasing interest in multiferroics, materials with multiple memory phenomena ("ferroic" phenomena), and specifically those which are both magnetic and ferroelectric. This interest is especially due to a sub-family of materials in which the electric polarization is caused by- and is intrinsically coupled to the magnetic order (type-II multiferroics). These materials exhibit exceptionally large magnetoelectric coupling, making it feasible to manipulate the magnetic order by electric fields. This is a key ability for future spintronic applications, due to the higher efficiency in applying voltages (for electric fields) rather than currents (for magnetic fields), which are the present standard tool for manipulating magnetic memory (digital bits).

A vital ingredient in type-II multiferroics is magnetic frustration between competing magnetic interactions of similar strength. The frustration is relaxed by breaking inversion symmetry in the crystal, allowing ferroelectricity to form alongside the magnetic ground state. If this material class is to be utilized in future technologies, we must learn to manipulate and enhance its memory effects. Epitaxial strain is a promising route to manipulate these materials, as both ferroic effects are strongly linked to the crystal structure. In this study we demonstrate the feasibility of manipulating ferroic properties using strain. We observe strain-induced changes in magnetic modulation, ferroelectric crystal distortion, coercive fields and even the magnetic structure itself. We explore the effects of epitaxial strain on two types of multiferroic materials:

- Orthorhombic (perovskite) manganites of type $R\text{MnO}_3$, in which $R$ represents a rare earth ion.
- Cobalt Chromite, CoCr$_2$O$_4$, a spinel structured crystal, well-known as a ferrimagnet.

$o$-$R\text{MnO}_3$ perovskites ($R =$ heavier rare earth, $o$- denotes orthorhombic structure) have a rich phase diagram in which the magnetic structure depends strongly on the $R$ ion. Lighter ions ($R =$ Dy and Tb) are known to exhibit cycloidal spin structures, which have been heavily studied. The heavier ions ($R =$ Ho, Tm, Yb, Lu) are believed to acquire a commensurate $↑-↑-↓-↓$ spin structure ("E-type"), resulting in significantly larger electric polarization values than in the lighter $R$ ions, reaching values of $> 1\mu C/cm^2$. These enlarged values are caused by symmetric exchange striction, and are the main motivation in studying these materials. In this work we study epitaxial films of these materials with heavy $R$ ions, for which no single crystals are known to exist. We use resonant soft X-ray diffraction (RSXD) to follow the magnetic order of the Mn $3d$ electrons and the $R$ ions’ $4f$ electrons. We use non-resonant X-ray diffraction (XRD) to follow the ferroelectric (FE) crystal distortion. We found that epitaxial strain controls both multiferroic properties: the FE crystal distortion and the magnetic order. We guide ourselves mainly with the aid of the magnetic modulation vector. Unlike bulk, most films do no exhibit a commensurate magnetic modulation, even for materials with the heaviest $R$ ions (e.g. $o$-LuMnO$_3$). We point to the fact that the $R$ ion is not a good measure for the describing material’s phase diagram, and argue that the existence of an $ab$ cycloid can reconcile the conflicting
observations between bulk and film samples. *Our study shows clear evidence that both ferroic properties in the o-RMnO$_3$ family are strongly coupled to the lattice.* The results of this work have been partially published, in Windsor et al. Phys. Rev. Lett. 113, 167202 (2014) and Windsor et al. Phys. Rev. B 91, 235144 (2015).

The second system we study is CoCr$_2$O$_4$. CoCr$_2$O$_4$ has recently gained much attention due to the discovery of electric polarization and exceptionally strong magnetoelectric coupling in its conical magnetic state. Unlike most type-II multiferroics which are antiferromagnets, this material exhibits a macroscopic magnetic moment $M$ alongside its electric polarization $P$. The strong magnetoelectric coupling is evidenced by the fact that $M$ and $P$ switch in tandem (switching one drives a switch in the other). A strong competition exists between Co$^{2+}$ and Cr$^{3+}$ ions, which carry the same number of unpaired 3$d$ electrons, producing a ferromagnetic arrangement, and a conical magnetic order at lower temperatures. Coupled systems of this kind are expected to be easily manipulated, as the frustration can be lifted or altered by tipping the equilibrium state in favor of one ground state or another. In this study, the magnetic moments of the Co and the Cr ions are followed using X-ray magnetic circular dichroism, in reflection mode and in transmission mode. In the latter case we use the X-ray excited optical luminescence (XEOL) of the substrate. The conical order is followed using RSXD at the Co L edges (the Cr L edges are too low in energy to access any reflection). This is an indicator of the multiferroic phase, and it is the only present evidence that these films are indeed multiferroic, as their electric polarization has not been measured to date. We focus mainly on one strained state, and found that magnetic anisotropy is greatly enhanced by strain, while the conical (multiferroic) phase appears as expected from bulk. Furthermore, from RSXD measurements on other strain states we find that strain facilitates different ground state behaviors, previously reported for bulk.
Zusammenfassung

Das wissenschaftliche Interesse an multiferroischen Materialien, also Materialien, die mehr als einen ferroischen Speicherzustand aufweisen, hat in den vergangenen Jahren stark zugenommen. Insbesondere Materialien mit sowohl magnetischer als auch ferroelektrischer Ordnung sind von grossem Interesse, da es hier eine Untergruppe von Materialien gibt, in der die ferroelektrische Polarisation durch die magnetische Ordnung hervorgerufen wird und daher intrinsisch mit ihr gekoppelt ist – sogenannte Multiferroika vom Typ-II. Diese Materialien zeigen eine aussergewöhnlich starke magnetoelektrische Kopplung, die es ermöglicht, magnetische Ordnung durch elektrische Felder zu beeinflussen. Dies ist eine der Schlüsseleigenschaften für zukünftige Anwendungen in der Spintronik, da es anstelle der Verwendung von Strompulsen (im Falle von magnetischen Feldern), die heute standardmässig eingesetzt werden um magnetische Speicher (digitale Bits) zu verarbeiten, die Verwendung von Spannungspulsen (im Falle von elektrischen Feldern) erlaubt und daher eine höhere Effizienz verspricht.


- Orthorhomische Perovskit-Manganate des Typs $RMnO_3$, wobei $R$ für ein Ion der seltenen Erden steht
- Cobalt-Chromat, $CoCr_2O_4$, ein Kristall mit Spinel-Struktur und ferrimagnetischen Eigenschaften

$o-RMnO_3$ Perovskite ($R$: Ion einer seltenen Erde, $o$: orthorhombische Gitterordnung) besitzen ein komplexes Phasendiagramm, in dem die magnetische Ordnung stark vom $R$-Ion abhängt. Leichtere Ionen ($R$= Dy und Tb) führen in $o-RMnO_3$ zu spin-zykloidalen Spin-Ordnungen, die bereits ausgiebig in der Literatur untersucht wurden. Für schwere Ionen ($R$ = Ho, Tm, Yb, Lu) wird angenommen, dass die Spin-Ordnung $↑-↑-↓-↓$ kommensurabel ist und dem Typ „E“ entspricht, was im Vergleich zu den leichten Ionen zu deutlich höheren Werten der elektrischen Polarisation mit Werten bis zu $>1\mu C/cm^2$ führt. Diese erhöhten Polarisationswerte sind auf die symmetrische Austausch-

Das zweite untersuchte System ist CoCr₂O₄. CoCr₂O₄ wurde in jüngster Zeit viel Beachtung geschenkt aufgrund der Entdeckung von elektrischer Polarisation und einer aussergewöhnlich starken magnetoelektrische Kopplung im spin-konisch-geordneten Zustand bei tiefen Temperaturen. Im Gegensatz zu der Mehrzahl der Multiferroika vom Typ II, die antiferromagnetisch sind, besitzt CCO sowohl eine ferroelektrische Polarisation P als auch ein makroskopisches magnetisches Moment M. Die starke magnetoelektrische Kopplung wurde durch ein gleichzeitiges Umschalten von P und M gezeigt (das Umschalten der einen Grösse verursacht das Umschalten der anderen). Aufgrund der stark konkurrierenden magnetischen Momente der Co²⁺ und Cr³⁺-Ionen, die dieselbe Anzahl von ungepaarten 3d Elektronen besitzen, entsteht unterhalb der Curie-Temperatur zuerst eine ferrimagnetische Ordnung und daraus eine konische Spin-Ordnung bei noch tieferen Temperaturen. Bei solchen gekoppelten Systeme ist anzunehmen, dass sie leicht zu beeinflussen sind, da die Frustration der magnetischen Wechselwirkungen durch kleine Veränderungen des Gleichgewichtszustandes in die Richtung des einen oder des anderen Grundzustands verändert oder aufgehoben werden kann. In der hier vorgestellten Arbeit werden die magnetischen Momente der Co und der Cr Ionen mit Hilfe des magnetischen zirkularen Dichroismus sowohl in Reflexion als auch in Transmission gemessen. Im letzteren Fall wurde die Roentgen-stimulierte optische Lumineszenz (X-
Preface

This thesis is the product of four year’s work in the Swiss Light Source, a synchrotron radiation facility in the Paul Scherrer institute in Switzerland.

X-ray diffraction experiments comprised the bulk of my experimental work during this period. Of these experiments, most utilized an in-vacuum diffractometer designed for use with soft X-rays (the “RESOXS” station). The second tool extensively used was a (2+3) circle diffractometer designed for hard X-ray diffraction (the “Surface Diffraction”, or SD station). I feel fortunate to claim today that I am experienced in conducting soft and hard X-ray diffraction experiments, at least to the extent that I have successfully helped and tutored many colleagues in this line of work.

Also of great importance was the use of a high magnetic field absorption/transmission end station, designed for use with soft X-rays (“XTreme”). Though my work with XTreme was not nearly as extensive as with the RESOXS or SD, the results of these experiments constitute a major part of chapter 5. I feel fortunate to have gained experience with this technique.

In this line of work it is well-understood that results are usually published in scientific Journals, in addition to a more detailed account in theses. This redundancy limits the number of thesis readers, and usually means that the only readers of the thesis are those who intend to reproduce some aspect of the scientific work. To account for this redundancy, the scientific results of this work are discussed in detail in their chapters, but an attempt was made to distill all technical and methodological aspects from them. These are presented separately in appendices, and in a generalized format which I hope can be used as an efficient manual for readers wishing to adopt them. This approach is especially true for chapter 4. It is my hope that this approach will benefit the work of a future reader.

"שומ דבר איטי צומם בול פורושה.
(נהם מרשלב)"
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1 Introduction

Many materials exhibit some form of memory effect. The most common example is that of magnets. The magnetization of loadstones has been used for navigation purposes since ancient times (i.e. they remember the north), for example those mentioned by Homer date to the seventh or eighth century B.C. [1]. In modern technology, hysteresis effects, i.e. those associated with memory, are everywhere. Most notably they exist as digital memory and in electronic sensors or switches. The main drive behind the ongoing study of ferromagnets and ferroelectrics is mainly the prospect of improving memory devices: making storage devices denser, faster, and energy efficient. A major advance along these lines was the discovery of Giant Magnetoresistance (GMR), for which the 2006 Nobel prize in physics was awarded. This effect increased the sensitivity of readout heads in hard drives by orders of magnitude, allowing individual magnetic bits to reduce in size. This translated into a dramatic increase in hard drive density in the late 1990s. However, as technology approaches the fundamental limits on miniaturization, new challenges appear. These include the obvious challenges associated with reading, writing and the stability of memory of just a few atoms, as well as new challenges such as leakage currents and overheating.

For continued technological advance, alternative routes must be explored. One promising route is that of multiferroics, with which this thesis deals. These are materials which exhibit multiple memory phenomena at the same time. The term “ferroic property” refers to a memory or hysteretic effect, in analogy to ferromagnetism. The immediate application for these would be multi-bit memory, i.e. one piece of material housing more than one bit of digital information. Another important approach would be to utilize the coupling between two such properties, so that the external stimulus of one ferroic property could affect that of the other. This is a central prospect for magnetoelectric multiferroics, in which ferroelectricity and magnetic order exist simultaneously, as depicted in Figure 1.1. The importance of this idea is that magnetic bits could be manipulated by voltages (electric fields), instead of currents (magnetic fields), as done today. This setting promises vastly improved energy efficiency both in terms of direct input for writing the bit, and in terms of residual heating.

![Figure 1.1 – Concept of magnetoelectric multiferroics, from Ref. [2].](image)
A subgroup of the multiferroic materials are those labelled “type-II”. These are materials in which one ferroic order drives the other. The typical case, albeit still rare, is that the magnetic ground state is reached by reducing the crystal symmetry in a way that allows ferroelectric polarization to occur. The importance of this case is that an inherently strong coupling between electric and magnetic orders is implied. Furthermore, it is clear that both orders are directly coupled to the structure of the crystal lattice. For this reason, the lattice is believed to be an effective “knob” through which the coupling between the two orders can be manipulated. This knob can be accessed by applying pressure to the material. An effective way to achieve this is through epitaxial strain, when the material is grown as a film on a substrate.

This is where the present study begins. It focuses on the microscopic properties of multiferroics under the influence of epitaxial strain. We shall focus our attention to two main cases. The first is the orthorhombic rare-earth manganites (RMnO$_3$). This family is known to possess a phase, known as the “E-type” phase, in which antiferromagnetic order induces an exceptionally strong electric polarization. The second case is that of CoCr$_2$O$_4$. This material is exceptionally unique in that it is a type-II multiferroic with a macroscopic magnetization alongside its polarization (most type-II multiferroics are antiferromagnets). Both of these cases are transition metal oxides, and place this work in the broader context of the study of highly-correlated electron systems.

To observe the effects of strain, we employ synchrotron-based techniques. The main tool in this thesis is resonant soft X-ray diffraction (RSXD), which provides direct information on the long range order of electronic states (e.g. 3d states of transition metal ions), information which is central to understanding the multiferroic behavior. Non-resonant crystal diffraction using the intense synchrotron beam allows us to follow the lowering of crystal symmetry. Finally, we employed magnetic circular dichroism to follow the magnetization of CoCr$_2$O$_4$. This is not a straightforward experiment, and our solution to the problems it posed was a non-standard approach which involved utilizing optical luminesce.

The goal of this study is to acquire information that will facilitate a fundamental understanding of the effects of strain on these multiferroics. Compared to ferromagnets, which are widely applied in industry, the study of multiferroics is in its infancy. In fact the entire field is only around two decades old. Clearly a body of knowledge is needed before any future application may appear. It is our hope that the results herein will benefit future work towards implementing technologies based on multiferroics.

The next two chapters are a brief introduction for understanding multiferroics, followed by a brief account of the techniques. Chapters 4 and 5 present the bulk of the scientific study. These are followed by a brief summary and appendixes that detail some of the concepts employed in this work.
2 Background on Multiferroics

The concept of multiferroics is problematic because, by definition, it is a combination of multiple fields. In most cases, a multiferroic material is one which exhibits magnetic and electric order simultaneously. Therefore such a material can be studied from either angle.

Such is the case in this thesis: the majority of attention is focused on the magnetic side. This chapter is a relatively brief account of the theoretical background on magnetism, ferroelectricity, and multiferroics. It is structured to provide sufficient background for the main chapters.

2.1 Magnetic order

The modern theories of magnetism have been around for many decades (some nearly a century). As such, I will not go into great detail, but only touch the basic concepts leading directly to topics relevant to this thesis.

2.1.1 Simple concepts

We refer to magnetic materials when describing materials on which an external magnetic field exerts a torque. In other words, they possess a magnetic moment. The magnetic moment of an atom is described by its total angular momentum $J = L + S$, and $m = -g\mu_B J$. Here $\mu_B = |e|h/2m_e$ is the Bohr magneton and $g$ is the Lande factor. The magnetization (magnetic moment per unit volume) is related to the external magnetic field by the magnetic susceptibility (a material property), as

$$M = \chi H$$  \hspace{1cm} (2.1)

If no independent order remains when $H = 0$, the material is a paramagnet. For an arbitrary value of $J$ one can describe the paramagnetic behavior of spins as

$$M = \frac{N}{V} g\mu_B B_j(x)$$  \hspace{1cm} (2.2)

With $a = g\mu_0\mu_B H/K_B T$. When $x \ll 1$ the system is in a regime in which the magnetic field is weak compared to the temperature. In this case Eq. (2.2) simplifies, and one can obtain the Curie law:

$$\chi \propto T^{-1}$$  \hspace{1cm} (2.3)

Materials that exhibit magnetization also in the absence of an external magnetic field are ferromagnets. In these, the microscopic constituent moments remain aligned to each other. The macroscopic magnetization of a ferromagnet below its transition temperature ($T_c$) follows an order-parameter-like temperature dependence, as shown in Figure 2.1.
The susceptibility of the material above $T_C$ follows the Curie-Weiss law of the form:

$$\chi \propto \frac{1}{T - \theta}$$  \hspace{1cm} (2.4)

With $\theta < T_C$. This offset is a well-known characteristic of ferromagnets because it can be macroscopically measured. In the 1930’s materials were studied in which this offset was observed (and was negative), but no macroscopic magnetization was observed below the apparent ordering temperature. These are known today as antiferromagnets, and are central to this thesis. Within the mean-field model, directly below $T_C$ the magnetization follows a critical exponent behavior of the form $M \propto T^{\beta}$.

### 2.1.2 Exchange interaction

The proximity of dipole moments in a magnetic material is not sufficient to explain their ordering. The magnetic dipole-dipole interaction is of the order of

$$\mu_0 \mu_B^2 / a_0^3 \approx 1K$$  \hspace{1cm} (2.5)

which is too small to generate stable ordering under ambient room temperature ($\sim 300K$). An additional interaction is required. Exchange interaction is fundamental to the understanding of magnetic order. It stems from Pauli’s exclusion principle, which requires that multi-electron wave function must be antisymmetric to avoid having two electrons in the same state.

#### 2.1.2.1 Two electron exchange

In this section we derive interaction between the spins of two adjacent electrons in free space, mainly following Refs. [4] and [5]. This simple case can be generalized to $n$ electrons.

The combined wave function of the two electrons
\[ \Psi = \psi(r_1, r_2) \otimes \chi(\sigma_1, \sigma_2) \]  

(2.6)

consists of a spin component \( \chi(\sigma_1, \sigma_2) \) and a real-space component \( \psi(r_1, r_2) \). The spins can combine to give three symmetric “triplet” states \( \chi_T \), and an antisymmetric “singlet” state \( \chi_S \).

\[
\chi = \begin{cases}
\chi_S & \frac{1}{\sqrt{2}}(|\uparrow\downarrow) - |\downarrow\uparrow) \quad S = 0 \quad S_z = 0 \\
\chi_T & \frac{1}{\sqrt{2}}(|\uparrow\uparrow) \quad S = 1 \quad S_z = 1 \\
& \frac{1}{\sqrt{2}}(|\uparrow\downarrow) + |\downarrow\uparrow) \quad S = 1 \quad S_z = 0 \\
& |\downarrow\downarrow) \quad S = 1 \quad S_z = -1
\end{cases}
\]  

(2.7)

To ensure that the overall wave function must be antisymmetric due to Pauli’s exclusion principle, the spatial component \( \psi \) also needs to be formed from symmetric and antisymmetric configurations of the two possible states \( \psi_1 \) and \( \psi_2 \) (with single-electron eigenenergies \( \epsilon_1 \) and \( \epsilon_2 \)). The total wave function can then exist in two configurations:

\[
\Psi_S = \frac{1}{\sqrt{2}}[\psi_1(r_1)\psi_2(r_2) + \psi_1^*(r_2)\psi_2(r_1)] \otimes \chi_S
\]

\[
\Psi_T = \frac{1}{\sqrt{2}}[\psi_1(r_1)\psi_2(r_2) - \psi_1^*(r_2)\psi_2(r_1)] \otimes \chi_T
\]  

(2.8)

The general antisymmetric case for \( n \) electrons is defined by a determinant of the possible states, known as Slater’s Determinant. The combined Hamiltonian for the two electrons is

\[
\mathcal{H} = \mathcal{H}_0(r_1) + \mathcal{H}_0(r_2) + V(r_1, r_2)
\]  

(2.9)

It consists of their individual single-electron Hamiltonian \( \mathcal{H}_0 \) as well as the Coulomb repulsion between them, treated here as a small perturbation

\[
V(r_1, r_2) = \frac{e^2}{4\pi \varepsilon_0 |r_1 - r_2|}
\]  

(2.10)

The Hamiltonian in Eq. (2.9) is invariant under permutation of the spatial states, and one can describe the eigenenergies as

\[
\epsilon_{S/T} = \epsilon_1 + \epsilon_2 + u \pm j
\]  

(2.11)

The last terms are calculated as

\[
u = \int d^3r_1 d^3r_2 |\psi_1(r_1)|^2 V(r_1, r_2) |\psi_2(r_2)|^2
\]

\[
j = \int d^3r_1 d^3r_2 \psi_1^*(r_1) \psi_2^*(r_2) V(r_1, r_2) \psi_1(r_2) \psi_2(r_2) = \frac{1}{2}(\epsilon_S - \epsilon_T)
\]  

(2.12)
The $u$ and $f$ terms are the Hartree and Fock terms, respectively. $j$ is also called the exchange integral or the exchange energy (the energy cost of exchanging the two electrons). This is the electrostatic energy associated with the charge distribution $e\psi_1^*(r)\psi_2(r)$. The idea from here on is to alter the Hamiltonian in such a way that the interaction between spins is taken into account, but produces the same eigenenergies. Considering a grid of spins, leads to the Heisenberg Hamiltonian, which is of a form

$$\mathcal{H}_{\text{eff}} = - \sum_{i,j} J_{ij} S_i \cdot S_j$$

in which $J_{ij}$ is the exchange integral between the two spins $S_i$ and $S_j$.

### 2.1.2.2. Superexchange

In this section we discuss a simple model of magnetic interaction that is common in many materials, including transition metal (TM) oxides such as those dealt with in this thesis. We focus only on the case of oxides, and discuss a bond between a TM ion, and O ion, and another TM ion.

From Hund’s rules we know that all unpaired $d$ electrons in the TM ions will acquire the same spin direction. In a simple chemical picture, the O ions in an oxide are at their $O^{2-}$ state, which has a full $2p$ shell. A covalent bond between the TM and the oxygen will involve the orbital along the line between the two TM ions (or closest to it). If the first TM ions has all electrons with spin $\uparrow$, Pauli’s exclusion causes the electron contributed from the O ion’s orbital to the bound state to have spin $\downarrow$. The other end of the bond (between O and the second TM ion) must then get the O ion’s $\uparrow$ electron, so the second TM ion must contribute a spin $\downarrow$. From this we can recognize that the two TM ions must have antiparallel spin arrangements in this picture. Figure 2.2 summarizes this scenario.

![Figure 2.2 – Simple picture of superexchange. A TM-O-TM bond is depicted, with the TM ions in a $d^5$ state.](image)

Other scenarios of similar nature exist, many of which are more complex. For example the bond may have an angle, or include a longer path between the two TM ions, such as one involving two or more O ions.
2.1.3 Long-range magnetic order

In general long-range order of magnetic moments can be described by a propagation vector $Q$, in units of reciprocal length. The specific case of ferromagnetism described before, is the case of $Q = 0$. In other words the moment does not evolve from ion to ion, but stays the same, is in Figure 2.3(a). Figure 2.3(b) presents a simple example of such an arrangement with $Q \neq 0$. This is an antiferromagnetic arrangement, which is defined as a magnetic order in which the macroscopic magnetic moment is 0, because in the sum over all moments they cancel each other out. Panel (c) presents a case with antiparallel spins that are not the same length, and therefore do not cancel out completely, such that the material will retain a macroscopic magnetic moment. A number of more complicated cases in which magnetic order propagates through the material is presented in Figure 2.6.

![Figure 2.3- Simple examples of magnetic order. (a) Ferromagnetism, (b) a simple case of antiferromagnetism, and (c) a simple case of ferrimagnetism.](image)

Antiferromagnetism was first proposed by Louis Néel in the 1930s. These materials were previously an anomaly, as they obeyed the Curie-Weiss law at high temperature, but unlike ferromagnets, no moment was observed below the temperature in which this behavior ceased. This temperature is the antiferromagnetic ordering temperature, known as the Néel temperature ($T_N$). Ferrimagnetism was proposed by Néel in the late 1940s [6].

2.2 Ferroelectricity

A ferroelectric material is a material with a permanent electric dipole moment. In the following a brief account is given for this effect. Ferroelectricity has many properties analogous to ferromagnetism. It appears below an ordering temperature (in this thesis it is called $T_C$), and exhibits an $E$-$P$ hysteresis curve, entirely analogous to the $H$-$M$ hysteresis. Above $T_C$ it even behaves paraelectrically, following a Curie-Weiss-like behavior. An important difference is that for electric dipolar order to appear, a loss of inversion symmetry must take place in the crystal. This can be intuitively understood as a
separation of charges to form an electric dipole within the unit cell: more positive charge on one side, more negative charge on the other.

Most conventional ferroelectrics are transition metal oxides, in which transition metal ions have empty $d$ shells. Within a unit cell, the positively charged transition metal ions shift oppositely to the neighbouring negative oxygen ions, in a covalent bonding scheme. This collective shift of cations and anions inside a periodic crystal induces bulk electric polarization [7]. This scenario is known as “proper ferroelectricity”. Figure 2.4 illustrates this for the case of the well-known ferroelectric PZT.

![Figure 2.4 - Schematic diagram of a Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ unit cell, adapted from Ref. [8]. The main graph illustrates the energy vs. atomic displacement. The cartoons of the unit cell indicate two degenerate ground states separated by an energy barrier (the ionic motion at the phase transition is exaggerated). The Pb and Ti/Zr ions are positively charged and the O ions are negatively charged.]

Physical mechanisms other than covalent bonding can also form the conditions for ferroelectricity. Most importantly, inversion symmetry must be lost. Materials with such mechanisms are known as “improper ferroelectrics”. There are discussed in Ref. [7] (mainly in the context of multiferroics).

2.3 Multiferroics

A multiferroic material is a material that exhibits multiple memory phenomena. Memory effects are also known as “ferroic” properties, in analogy to ferromagnets, in which magnetic hysteresis represents the (magnetic) memory phenomenon. The term was coined in by H. Schmid in 1994 [9]. Figure 2.5 is a sketch illustrating the ferroic properties, and how they may be controlled by external stimuli. Many such diagrams are available in literature, but this one is presented here to emphasize the aspect of coupling between the ferroic properties, which is a key feature of type-II multiferroics (described in the following), which are central to this thesis.
Figure 2.5 – Control of ferroic properties, adapted from Ref. [10]. External stimuli are shown (H,E,σ) next to the ferroic property they conventionally control (M,P,ε). Additional interactions are shown. Green arrows represent those present in magnetoelectricity.

Within the framework in the sketch, most of the interest is focused on the magnetic and electric channels: magnetoelectric multiferroics. The appeal of such materials is that one can envision new device functionalities. For example, multi-bit elements for device miniaturization, or electric/magnetic field control of magnetic/electric memory.

The magnetoelectric effect was first proposed by Pierre Curie in 1894 [11], (the term was coined by Debye in 1926 [12]) and was an active field of research until the 1970’s [13]. It can be phenomenologically described using the magnetoelectric coupling parameter $\alpha_{ij}$ in the free energy as:

$$F(E, H) = F_0 - P_i^S E_i - M_i^S H_i - \frac{1}{2} \varepsilon_{ij} E_i E_j - \frac{1}{2} \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j + \cdots$$

(2.14)

Here $M^S$ and $P^S$ represent the spontaneous magnetization and polarization of the system. From this one can extract the polarization and magnetization of a material as

$$P_i(E, H) = - \frac{\partial F}{\partial E_i} = P_i^S + \frac{1}{2} \varepsilon_{ij} E_j + \alpha_{ij} H_j + \cdots$$

$$M_i(E, H) = - \frac{\partial F}{\partial H_i} = M_i^S + \frac{1}{2} \mu_{ij} H_j + \alpha_{ij} E_j + \cdots$$

(2.15)

This demonstrates a direct link between $M (P)$ and $E (H)$. Normally $\alpha$ values are very small compared to other contributions. Recent years have seen a significant revival of the magnetoelectric effect [13]. However, magnetoelectric multiferroics are quite rare [14]. Intuitively the reason for this is simple: in most well-known ferroelectrics, the heavy displaced ion is in a $d^0$ state (empty d shell). However unpaired $d$ (or $f$) electrons are usually the requirement for magnetic order. It is for this reason that multiferroics are improper ferroelectrics, as alternative mechanisms are required to produce electric polarization.

[18]
Multiferroics are commonly divided into two groups [2]. Type-I are those materials in which the ferroic properties form independently of each other. In these cases the coupling between the ferroic properties is normally quite weak. Type-II multiferroics are those in which one order causes the other, so a strong coupling is certain. In the context of magnetoelectric materials, it is magnetic frustration that drives this strong coupling by inducing a symmetry lowering effect that allows polarization to occur. Two main sources of spin-induced electric polarization are commonly discussed. The first is antisymmetric spin exchange, in which polarization follows:

\[
P \propto \sum_{ij} \hat{e}_{ij} \times (S_i \times S_j)
\] (2.16)

Here the vector \(\hat{e}_{ij}\) points from ion \(i\) to ion \(j\). This mechanism is common in non-collinear spin arrangements, and was first described in Ref. [15]. It is commonly referred to as an inverse Dzyaloshinskii-Moriya interaction (DMI). Figure 2.6 presents a number of such cases.

The second source is due to symmetric exchange

\[
P \propto \sum_{ij} \hat{e}_{ij}(S_i \cdot S_j)
\] (2.17)
This effect allows polarization to occur also in collinear spin arrangements. It is known to occur in situations where some of the contributing spins are parallel, and some are antiparallel, such as in $RMn_2O_3$, in which loops of five Mn ions ($Mn^{3+}$ and $Mn^{4+}$) induce attractive and repulsive striction on the lattice [17].

The field of multiferroics is rapidly evolving. The aforementioned references included several relevant reviews. In addition to these, the readers are encouraged to read a recent review on control [18], and another on routes towards artificial multiferroics [19].
3 Background on Synchrotron radiation experiments

3.1 Probing matter with light

The purpose of this section is to provide adequate background for the use of X-ray radiation to study material properties, within the context of this thesis (crystal diffraction, resonant magnetic diffraction and XMCD). I begin from general concepts and rapidly progress to the present theory, without dwelling upon topics known to all graduate students (e.g. reciprocal space, second quantization of electromagnetic radiation etc.). From this we reach tools and concepts required to explain the results in this thesis.

This section is somewhat extensive, as it is intended not only to provide minimal background, but also to address questions that commonly rise in routine experimental work, which are often overlooked or taken for granted (at least in my case). Of course none of the contents are original, but I do hope that the way this chapter is constructed provides a conscious view of the underlying processes, which are often masked by simple approximations. In writing this chapter I mainly followed References [20-23].

3.1.1 Simple concepts: connecting theory and experiment

3.1.1.1. Simple observable concepts

X-ray based experiments often boil down to the relation between two measured quantities: the incoming and outgoing beam to and from the sample. These are usually quantified as intensity\(^1\), in other words photons per unit time\(^2\), although informally this is sometimes (e.g. in the case of soft X-rays) some other measured quantity per unit time such as an electric current from a photodiode. These generally relate to each other as:

\[
I = I_0 N \Delta \Omega \left( \frac{d\sigma}{d\Omega} \right) \tag{3.1}
\]

Here \(I\) and \(I_0\) are the outgoing and incoming intensities, \(N\) is the areal density of particles (or “interaction events”) in the sample along the beam direction, and \(\Delta \Omega\) is simply the solid angle covered by the detector. The last quantity is the differential cross section. This is the fundamental tool that relates these measured quantities to theory. Intuitively, this quantity is the ratio between the intensity scattered into a specific direction (defined by the solid angle \(\Delta \Omega\)), over the total incoming intensity. Formally one must write it as:

\[\frac{d\sigma}{d\Omega}\]

\(^1\) If the incoming beam is larger than the sample, it should be quantified not as intensity, but as flux, in other words intensity per unit area per unit time. The derivation that follows would slightly change, but the fundamental concepts would not.

\(^2\) Another meaningful and common definition of intensity is incident energy per unit time.
\[
\frac{d\sigma}{d\Omega} = \frac{I(\Delta\Omega)}{I_0 N \Delta\Omega}
\]  
(3.2)

In which \( I(\Delta\Omega) \) is the number of photons scattered into \( \Delta\Omega \) per unit time. However, many experiments are not interested in scattered light, but in the absorption of the incident X-rays. The cross section is also the appropriate tool for relating absorption measurements to theoretical interpretation (formally the relation between scattering and absorption is given by the optical theorem). The total number of absorption events (per unit time) from an incoming intensity \( I_0 \) can be written as:

\[
W = I_0 N \sigma_a
\]  
(3.3)

In which \( \sigma_a \) is the absorption cross section. The quantity \( W \) is related to the scattered intensity. Intuitively, the difference is that instead of integrating over the detector’s solid angle \( \Delta\Omega \), one integrates over all directions (4\( \pi \)). In the simplest absorption experiment, one measures the intensity of the beam transmitted through a thin sample. The damping of the beam as it travels in the medium (along the \( z \) direction) is described by the phenomenological Beer-Lambert law as:

\[
I(z) = I_0 e^{-\mu z}
\]  
(3.4)

The intensity \( I \) is reduced from its initial value \( I_0 \), as it travels through the medium. The exponential relation is due to the assumption that the absorption is linear with \( z \), and the linear absorption coefficient \( \mu \) essentially contains all the underlying physics. It generally relates to the cross section as its product with the density of absorbing sites. For a material with a number of different kinds of absorbers, this is expressed as:

\[
\mu = \sum_i \rho_i \sigma_i
\]  
(3.5)

The present study includes both scattering and absorption experiments, which utilize Eq. (3.2) and (3.4), respectively. The last basic observable of a material is the index of refraction, which is commonly known from Snell’s law. This can be written as a complex number as:

\[
n = \frac{c}{v} = 1 - \delta + i\beta
\]  
(3.6)

The logic behind this expression for the refractive index will become apparent immediately. We remind ourselves that it relates to the wave vector of a plane wave and the vacuum wavelength as \( k = n/\lambda \), and as such the electric field of plane wave travelling through a medium can be written as:

\[
E(z,t) = E_0 e^{i(kz-\omega t)} + c.c. = (E_0 e^{i((1-\delta)z/\lambda - \omega t)} + c.c.) e^{-\beta z/\lambda}
\]  
(3.7)

Here c.c. denotes “complex conjugate”. The second step underlines the meaning of the complex component: it relates to the absorption in Eq. (3.4) as \( \beta \propto \mu \).
Before concluding this short section it is worth noting that a few other observables exist, namely permittivity and the dielectric function. We do not discuss these further.

3.1.1.2. The electromagnetic wave

As polarized light is the main tool used in this thesis, it is reasonable to dedicate a short section to fully describe it for later use. The (complex) vector potential for an electromagnetic wave of energy $\hbar \omega$ and wave vector $k$ (with $k^2 = \omega^2 / c^2$) can be written as:

$$A(r, t) = A_0 e^{i(kr - \omega t)} \quad (3.8)$$

The electric field is then $E = -i\omega A = E_0 e^{i(kr - \omega t)}$ and the magnetic field $B = -i k \times A$. The polarization vector is defined parallel to the electric field as:

$$\hat{\epsilon} = iE_0/|E_0| \quad (3.9)$$

Of particular interest is the case of circular light, which are defined as:

$$\varepsilon_\pm = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \quad (3.10)$$

Note that in this notation $k \parallel (001)$. When the EM field is quantized into creation and annihilation operators ($a_{\varepsilon,k}^\dagger$ and $a_{\varepsilon,k}$, respectively), it can be written as:

$$A(r, t) = \sqrt{\hbar/2e_0V} \sum_{\varepsilon,k} \omega_k^{-\frac{1}{2}} \left( a_{\varepsilon,k} e^{i(kr - \omega t)} \hat{\epsilon} + a_{\varepsilon,k}^\dagger e^{-i(kr - \omega t)} \hat{\epsilon}^* \right) \quad (3.11)$$

The Hamiltonian describing this field is the standard textbook expression:

$$\mathcal{H}_R = \sum_{\varepsilon,k} \hbar \omega_k \left( a_{\varepsilon,k}^\dagger a_{\varepsilon,k} + \frac{1}{2} \right) \quad (3.12)$$

3.1.1.3. The simple microscopic model: the form factor

In this section we briefly present the simple concept behind elastic scattering of an electromagnetic wave of the electrons of an atom in order to reach a useful term used later – the form factor $f$. An incident wave of the form $E_{in} = E_0 e^{-i\omega t}$ causes an electron to acquire acceleration $a \propto E_{in}$ as the wave is absorbed. A new wave is then emitted, which can be written as

$$E_{rad}(t, R) = -\left( \frac{e}{4\pi \varepsilon_0 c^2} \right) a(t') \frac{1}{R} \sin \Psi \quad (3.13)$$

The physical intuition behind this expression for the radiation lies in the $R^{-1}$ dependence: $R$ is the distance of the observer from the emitting electron. The angle $\Psi$ is used as a factor to vary the
acceleration with the observation angle, and \( t' = t - R/c \). From this one can reach the relation between the incoming and outgoing radiation:

\[
\frac{E_{\text{out}}(R, t)}{E_{\text{in}}} = -\left( \frac{e^2}{4\pi\varepsilon_0 mc^2} \right) e^{ikR} \frac{1}{R} \sin \Psi = -r_0 \frac{e^{ikR}}{R} |\hat{\varepsilon} \cdot \hat{\varepsilon'}|.
\]

(3.14)

The logic behind this ratio is that the incoming and outgoing radiations are often measured quantities, and their ratio (squared) can be deduced. The second step in the derivation assumes that the incoming light is polarized (\( \hat{\varepsilon} \) and \( \hat{\varepsilon'} \) are the polarization vectors of the incoming and outgoing beams). The proportionality factor ensures that units are maintained, but has an important meaning of its own:

\[
r_0 = \left( \frac{e^2}{4\pi\varepsilon_0 mc^2} \right) = 2.82 \times 10^{-5} \text{Å}
\]

(3.15)

This is the Thompson scattering length, also known as the classical radius of the electron, or Lorenz radius. For our purposes it is the fundamental unit of length in such experiments. From here we can relate to an observable from section 3.1.1.1. The cross section for elastic scattering of light off of an electron (Thompson scattering) can be written as:

\[
\left( \frac{d\sigma}{d\Omega} \right) = r_0^2 |\hat{\varepsilon} \cdot \hat{\varepsilon'}|^2
\]

(3.16)

To expand this result to all electrons in an atom, one must integrate over the atom’s electron density \( \rho(r) \). To account for the difference in the phase of light at different positions in the atom \( r \), a phase factor \( \exp(iQ \cdot r) \) must be added. Here \( Q = k - k' \) (the primed term indicates the outgoing light).

We then reach the total scattering length of the atom:

\[
-r_0 f^0(Q) = -r_0 \int \rho(r) e^{iQ \cdot r} dr
\]

(3.17)

This is none other than a 3d Fourier transform of the electron density. The fundamental value \( f^0 \) is the atomic form factor. However, it does not take into account the fact that the electrons are bound to the atom. For this, a correction term is required, which is atom/ion dependent: \( f'(E) \). In addition, energy-dependent absorption (e.g. around absorption edges, see Section 3.1.2) must also be taken into account, which is done using \( i f''(E) \). This term is imaginary because it is essentially a dissipation term (in analogy to an oscillator). We thus arrive at the “full” form factor:

\[
f(Q, E) = f^0(Q) + f'(E) + i f''(E)
\]

(3.18)

---

3 A magnetic correction \( f^{mag} \) should in principle also be considered. This takes into account the direct interaction of the photon with the spin at energies far from electronic resonances, which is a weak process compared to all other terms. This should not be confused with the sensitivity to magnetism at resonance, which is in the \( f' \) and \( f'' \) terms.
This is often referred to as the *scattering amplitude*. Figure 3.1 presents selected examples of these quantities. From this we can now go back and relate this useful entity to the observables we established in the previous section. Because there is not much further insight, and in the interest of brevity, I do not present the considerations behind these relations.

\[
    n = 1 - \frac{2\pi N r_0}{k^2} f(Q, E)
\]
\[
    \delta = \frac{2\pi N}{k^2} r_0 f''(0) + f'(E)
\]
\[
    f'' = -\left(\frac{k}{4\pi r_0}\right) \sigma_a
\]

In subsequent sections we shall show how this relates to physically meaningful entities.

Figure 3.1 – Examples of \( f' \) and \( f'' \) (components of the form factor), shown for atomic Mn, Tm and Er as functions of photon energy. The names of the absorption edges are placed at their approximate location. See Table 3.1 for the meaning of these labels. Data taken from the Henke database at [http://henke.lbl.gov](http://henke.lbl.gov). \( f', f'' \) and \( f''' \) are unitless.

### 3.1.2 Probing electronic states with light

The (non-relativistic) Hamiltonian for a photon and an electron particle is given by

\[
    \mathcal{H} = \frac{1}{2m} (P - qA)^2 + qV + \mathcal{H}_\mu - g_\mu \frac{q}{2m} S \cdot B
\]  

(3.20)
Here $m$ and $q$ are the mass and charge of the electron. $\mathcal{H}_F$ is the Hamiltonian of the field from Eq. (3.12) and $A$ is the vector potential. $g_L$ is the Landé factor, $S$ is the spin and $B = -ik \times A$. An important term is the transition matrix $T$, which can be derived from the sum of the $S \cdot B$, the $A^2$ and the $P \cdot A$ terms in the Hamiltonian (i.e. the perturbation terms). In the following it is written to second order in powers of $(e/m)$ and under the assumption that the interaction is a small perturbation of the ground state:

$$ T \approx \frac{e}{m} (P \cdot A - iS \cdot k \times A) + \left( \frac{e^2}{m^2} \right)^2 \left[ \frac{m}{2} A \cdot A + (P \cdot A - iS \cdot k \times A)G_0 (P \cdot A - iS \cdot k \times A) \right] $$

$$ \equiv \frac{e}{m} \hat{O} + \left( \frac{e^2}{m^2} \right)^2 \left[ \frac{m}{2} A \cdot A + \hat{O}G_0 \hat{O} \right] \quad (3.21) $$

Here $G_0$ is a Green’s function. The absorption operator $\hat{O}$ is also identified here. It can be written in a slightly different form as:

$$ \hat{O} = (e \cdot P - iS \cdot k \cdot \varepsilon)e^{ikr} \quad (3.22) $$

Once the vector potential from Eq. (3.11) is inserted, terms of different nature can be identified. Considering only the first term in $T$ (first order in $(e/m)$, see Eq. (3.21)), the absorption cross-section can be derived as

$$ \sigma_a = \frac{V}{c} \sum_{f} \frac{2\pi}{\hbar} \langle \langle \phi_f | T^{(1)} | \phi_g \rangle \rangle^2 \rho_f = \frac{4\pi^2 a \hbar}{m^2 \omega} \sum_{f} \langle \langle \phi_f | \hat{O} | \phi_g \rangle \rangle^2 \rho_f \quad (3.23) $$

Here the subscripts $g$ and $f$ denote ground and final states. The sum is over all contributing final states. $\alpha$ is the fine structure constant, and the density of final states is given by $\rho_f$. The switch from $\phi$ to $\varphi$ signifies that this term is expressed as eigenstates of the Hamiltonian, and the energy is $E_f = E_g + \hbar \omega$. The second order term in $T$ signifies two-photon processes which allow reaching a general form for the scattering amplitude (the form factor):

$$ f = \frac{V \hbar \omega}{(2\pi \hbar c)^{3/2} r_0} \langle \phi_f | T^{(2)} | \phi_g \rangle \quad (3.24) $$

We consider only elastic scattering. Taking the $A \cdot A$ term in Eq. (3.21), we recover the Thompson scattering term:

$$ f_0 = \frac{V \hbar \omega}{(2\pi \hbar c)^{3/2} r_0} \frac{e^2}{2m} \langle \phi_f | A \cdot A | \phi_g \rangle = \varepsilon_f \cdot \varepsilon_i \int |\varphi(r)|^2 e^{-iQ \cdot r} d^3 r \quad (3.25) $$

The second part of the scattering term in Eq. (3.21) represents energy-dependent scattering. This can be divided into the resonant scattering term (for energies close to an atomic resonance) and a term far from resonance (which we will not discuss further; it is both small and irrelevant for our purposes). The resonant term takes the form:
$f = \frac{\omega_s}{\omega_i} \lim_{m \eta \to 0} \sum_n \frac{\langle \varphi_f | \hat{O}_s | \varphi_n \rangle \langle \varphi_n | \hat{O}_i | \varphi_g \rangle}{E_g - E_n + \hbar \omega_i + i\eta}$ \hspace{1cm} (3.26)

Here the sum is over intermediate excited states, and indeed the equation resembles a collection of (resonating) oscillator terms with damping $\eta$. The “$i$” and “$s$” subscripts now indicate the incident and scattered photon (which are absorbed and emitted by $\hat{O}_i$ and $\hat{O}_s$ respectively).

The $\hat{O}$ operator can be subdivided into electric and magnetic terms (first and second term in Eq. (3.22)). After expanding the exponent in powers of $\varepsilon \tilde{r}$, one can single out different terms:

$$\hat{O}_e = \varepsilon \cdot \mathbf{P} e^{ikr} = \varepsilon \cdot \mathbf{P} [1 + ik \cdot r - \frac{1}{2}(k \cdot r)^2 + \ldots ]$$

$$\hat{O}_m = -iS \cdot \mathbf{k} \times \varepsilon e^{ikr} = -iS \cdot \mathbf{k} \times \varepsilon [1 + ik \cdot r - \frac{1}{2}(k \cdot r)^2 + \ldots ]$$ \hspace{1cm} (3.27)

This is an important distinction to make, because it is commonly understood that the contribution of each term to the $\hat{O}$ excitation is different. We own conform to the naming convention commonly used: E1, E2 etc… are the names given to excitation events from different orders of $\hat{O}_e$. Similarly, the magnetic events are labeled M1, M2, etc. These are also named according to the rank of the transition event (and of the tensor they are represent by): electric/magnetic dipole, quadrupole, etc.

Next one should calculate terms of the form $\langle \varphi_f | \hat{O} | \varphi_g \rangle$, which requires summing through all the initial and final states, expressed as spherical harmonics and radial integrals. This is quite tedious and beyond the necessity of this thesis. However, I will briefly present the final result, in order to underline the logic in understanding the possible transitions from $\hat{O}$:

$$\langle \varphi_f | \hat{O} | \varphi_g \rangle = \sum_{l_o, m_o} \left( \frac{i k}{2} \right)^{l_o - 1} c_{l_o m_o} \sum_{l_m} \left( \Gamma^{l_g,m_g+\frac{1}{2}-\sigma,l_o,m_o}_{l,m+\frac{1}{2}-\sigma} \sum_s \mathcal{R}^{l_o\sigma}_{l_m+s} a_{l,m,s}^{f}(E) \right)$$ \hspace{1cm} (3.28)

Here the calculation is for a specific spin state $\sigma$. I do not discuss spin flip transitions in the context of this thesis. The $\mathcal{R}$ term is a radial integral (from 0 to the atom radius), $\Gamma$ is the angular integral, and $a_{l,m,s}^{f}$ is the amplitude term. The $c_{l,m}$ term is a coefficient from the expansion of $\hat{O}$ in spherical harmonics. The mixing between $\sigma$ and $m$ indicates that spin-orbit coupling is accounted for. The $s$ index is the index of the spin in the final state. The $l$ and $m$ indexes denote different components: those with no subscript denote the final states, those with a “$g$” subscript denote the ground state, and those with “$o$” denote terms in the expansion of the $\hat{O}$ operator.

After all this, it is the angular integral $\Gamma$ which is important for our discussion. It is zero unless:

- $l$ must be of the same parity as $l_g + l_o$
- $|l_g - l_o| \leq l \leq |l_g + l_o|$
- $m = m_o + m_g$
For the present study we only consider the “standard” cases of E1 and E2 transitions, which correspond to $l_0 = 1$ and 2, respectively. This restricts transitions to all states except those with a difference of $\Delta l = \pm 1$ or $0, \pm 2$, respectively. With this in mind, we can now gain a clear picture of the states probed upon different excitations.

The standard notation for absorption edges in the X-ray community reflects the core hole state from which the electron is excited\(^4\): (1) the principle quantum number of the shell $n = 1,2,3,4,5$ is expressed as a letter: K, L, M, N, O. (2) the possible combinations orbital momentum $l$ and total momentum $j = |l + s|$ (with $s = \pm \frac{1}{2}$) are represented by numbers $1,2,3\ldots$. This notation is explained by many literature sources, although always in an abridged form. Table 3.1 presents an exhaustive table of the characteristics of each edge (up to M$_5$). This was a main motivation for including this section in this thesis, as such a table is surprisingly hard to find in literature.

<table>
<thead>
<tr>
<th>Table 3.1 – Classification of absorption edges. The core state for each edge is given in terms of the quantum numbers $n, l, s, j$, and its spectroscopic notation. The allowed angular momentum of the probed states for E1 and E2 events is also shown</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Edge</strong></td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>L$_1$</td>
</tr>
<tr>
<td>L$_2$</td>
</tr>
<tr>
<td>L$_3$</td>
</tr>
<tr>
<td>M$_1$</td>
</tr>
<tr>
<td>M$_2$</td>
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<tr>
<td>M$_3$</td>
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<tr>
<td>M$_4$</td>
</tr>
<tr>
<td>M$_5$</td>
</tr>
</tbody>
</table>

As an example of using this table, we consider the Mn$^{3+}$ ions, which are central to this thesis. The electronic configuration of these is [Ar]3d$^4$, or explicitly: 1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 3d$^4$. An E1 event at the L$_2$ and L$_3$ edges promotes a 2p electron to a 3d state, so this configuration is excited to 1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 3d$^5$. Similarly, a Ho$^{3+}$ ion is in an electronic state of [Xe] 4f$^{10}$, which is explicitly: 1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^10$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 4f$^{10}$. An E1 event at the M$_5$ edge represents a 3d $\rightarrow$ 4f transition, excites this configuration to 1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$ 4s$^2$ 3d$^9$ 4p$^6$ 5s$^2$ 4d$^{10}$ 5p$^6$ 4f$^{11}$.

The unoccupied valence states have a higher probability of capturing an excited electron if its spin is parallel to that of the state. This is how an electric excitations (i.e. E1) can be sensitive to the magnetic (spin) state of the system. It is also worth mentioning that non resonant scattering can also

\[^4\] Specifically, the “core hole state” describes the core shell in the absence of the excited electron.
be sensitive to magnetic order. However it is a very weak effect in which \( f \propto \hbar \omega / mc^2 \). One can exploit the linear relation with energy to enhance this magnetic signal by working at high photon energies.

### 3.1.3 Crystal diffraction and resonant (magnetic) diffraction

After considering a single atom, the next obvious step is to consider scattering from an ensemble of atoms. Assuming that the first atom is at the origin \( r_i = 0 \) the scattering off of an ensemble with momentum transfer \( Q \) can be written as

\[
F(Q) = f_1 + f_2 e^{iQ \cdot r} + \cdots = \sum_i f_i e^{iQ \cdot r} = \sum_j e^{iQ \cdot R_j} \sum_i f_i e^{iQ \cdot d_i}
\]

Polarization factors have been omitted here for clarity (equivalent to the \( \sigma - \sigma' \) channel). The phase factor \( e^{iQ \cdot r} \) takes into account that phase of the light between the different positions of the ions. The last step signifies that we are considering a crystal, with the position decomposed as \( r_i = R_i + d_i \), i.e. into the position of the unit cell \( R \) and the position within the unit cell \( d \). This equation is sufficient to describe basic crystal diffraction (in combination with fulfilling the Bragg condition). In the following we consider cases in which the incoming energy is near an atomic resonance.

The operator \( \hat{O} \) in Eq. (3.22) is directly proportional to the polarization vector \( \hat{e} \). From the scattering amplitude at resonance in Eq. (3.26), it is clear that the in an E1-E1 transition, we can expect a dependence of the form \( f_{E1E1} \propto (\nu \cdot \hat{e})(\nu \cdot \hat{e}')^* \) (\( \nu \) is an example vector). This was adapted by Hannon et al [20] in 1988 to the form:

\[
\begin{align*}
f_{E1E1} & \propto \left\{ (\hat{e}'^* \cdot \hat{e}) F^{(0)} - i\hat{m} \cdot (\hat{e}'^* \times \hat{e}) F^{(1)} + (\hat{e} \cdot \hat{m}) (\hat{e}'^* \cdot \hat{m}) F^{(2)} \right\}
\end{align*}
\]

In this form, the authors assumed scattering off of classical vectors (representing the magnetic moments of the atoms). The direction of the local magnetic moment is represented by \( \hat{m} \). The terms \( F^{(n)} \) represent combinations of prefactors from the expansion in Eq. (3.28). The importance of this equation is that it underlines the polarization dependence of the three different contributions to scattering in an E1-E1 event. The first term contributes only to charge scattering (it is non-magnetic), the second is linear to the local magnetic moment, and the third is quadratic to it (quadrupolar). For magnetic scattering, the second term is of primary importance. One can already identify that rotation of polarization must occur for this term, otherwise \( (\hat{e}'^* \times \hat{e}) = 0 \).

From a practical point of view, it is convenient to write the form factor in terms of the polarization channels. This is done in the following format (first presented by Blume and Gibbs in Ref. [21]):

\[
\begin{pmatrix}
    f_{\sigma\to\sigma'} & f_{\pi\to\sigma'} \\
    f_{\sigma\to\pi'} & f_{\pi\to\pi'}
\end{pmatrix}
\]

\[
\]

[29]
The form factor of Hannon et al. was reformulated by Hill and McMorrow [22] to this format. It takes the form (the last term is not shown because it is tedious and is not used in this thesis):

$$f_{E1E1} = \begin{pmatrix} 1 & 0 \\ 0 & \hat{k} \cdot \hat{k}' \end{pmatrix} F^{(0)} - i \hat{m} \cdot \begin{pmatrix} 0 \\ \hat{k}' \times \hat{k} \end{pmatrix} F^{(1)} + \ldots$$  \hspace{1cm} (3.32)

Clearly the most obvious signature of the magnetic term is the absence of a $\sigma \rightarrow \sigma'$ term. In practical terms, when one is clearly observing only magnetic E1-E1 scattering, the structure factor can be calculated directly in a simplified form as:

$$F(Q) = (\hat{\varepsilon}'' \times \hat{\varepsilon}) \cdot \sum_i m \exp(iQ \cdot d_i)$$  \hspace{1cm} (3.33)

In this case the magnetic moment is inserted, assuming that all sites are equivalent in magnitude, and that scattering is proportional to the magnetic order parameter. This equation is used numerous times in this thesis for calculating the expected intensity $I \propto F \cdot F^*$, especially upon azimuthal rotation. One should note that this is based on the cylindrical symmetry of model of Ref. [20], in which errors can be introduced when the moments are not along principle axes.

Before concluding, it is worth mentioning that a full calculation of the scattering amplitude without assuming that the scatterers are classical vectors is also commonly conducted. The scattering amplitude is instead described in terms of its expansion into multipolar orders. The structure factor then takes the form:

$$f_{E1E1} \propto \sum_{kQ} (-1)^Q X^k Q K \Psi^K_Q$$  \hspace{1cm} (3.34)

The exact proportionality can be explicitly written using Eq. (64) (70) and (71) of Ref. [23]. This formalism is especially useful for cases in which long range order of exotic multipoles is followed. For this thesis it is not essential. Nevertheless, for completeness a full account of the signals observed in this work is given in terms of multipolar terms in Appendix 7.3 (page 144).

3.1.4 X-ray magnetic circular dichroism (XMCD)

In this section we use the tools previously derived in order to show that one may follow the magnetization of materials using an absorption signal. We start by reminding of the relation $\mu \propto \sigma_A \propto f''$ ($\mu$ is the absorption coefficient from Eq. (3.4)), and so we can set $\hat{\varepsilon} = \hat{\varepsilon}'$ in Eq. (3.30) and reach

$$\mu \propto \left\{ F''^{(0)} - i \hat{m} \cdot (\hat{\varepsilon}' \times \hat{\varepsilon}) \right\} F''^{(1)} + (\hat{\varepsilon} \cdot \hat{m}) \left[ (\hat{\varepsilon} \cdot \hat{m}) F''^{(2)} \right]$$  \hspace{1cm} (3.35)

in which the double-prime indicates only the components of $F^{(n)}$ which arise from $f''$ (imaginary). Clearly if linear polarization is used, the signal would only be sensitive to magnetism through $\hat{m}^2$ in the third component. This is known as magnetic linear dichroism. However, if one uses circular light, as in Eq. (3.10) we find that $(\hat{\varepsilon}' \times \hat{\varepsilon}) = \pm i \hat{k}$, so the absorption reduces to
Here it is clear that the absorption signal at resonance is linearly proportional to the magnetic moment.

To demonstrate the circular dichroism effect, we take the difference:

\[ \mu^- - \mu^+ = 2 F''(1) \left( \mathbf{m} \cdot \mathbf{k} \right) \quad \text{(3.37)} \]

This means that the difference between two absorption signals measured with opposite circular polarization is directly proportional to the moment component parallel to the beam direction!

This dichroic effect can be further exploited to determine the spin and angular moments of the resonating ion. For this analysis, one assumes only E1 events. We specifically discuss the case of spin-orbit split pair of edges (e.g. L\(_2\) and L\(_3\) or M\(_4\) and M\(_5\)), denoted by \(j_{\pm}\). Indeed these are often localized and can be reliably integrated over.

The basic idea is that when the absorption cross section \(\sigma_A\) is measured (in the presence of a core hole), it is sensitive to the unoccupied electronic states, because these are the states the electrons are promoted to. For example, when the absorption signal is integrated over the L\(_2\) and L\(_3\) edges of transition metals, the total number of accessible unoccupied \(d\) states is counted (all \(2p \to nd\) transitions). One must remove the contribution from \(d\) states in the continuum in order to remain with a value corresponding only to the unoccupied 3\(d\) states. This is done by removing the 2-step atomic ionization spectrum from the measured spectrum (before integration), as shown in Panel (d) of Figure 3.2. This leads to an expression for the ground state expectation value of the orbital angular momentum. This was shown by Carra [24] and Thole [25] to take the form

\[ \langle L_2 \rangle = \frac{2}{l(l+1)(4l+2-n)} \left[ \frac{1}{l(l+1)+2} \int_{j_{+},j_{-}} dE(\mu^+ - \mu^-) \right] = \frac{4}{3} \left( 10 - n \right) \frac{\int_{L_2+L_3} dE(\mu^+ + \mu^-)}{\int_{L_2+L_3} dE(\mu^+ + \mu^-)} \quad \text{(3.38)} \]

Here the first step is the general expression in the limit of only E1 transitions of angular momentum \(c \to l\), and the integration is over a spin-orbit split pair of edges (e.g. L\(_2\) and L\(_3\) or M\(_4\) and M\(_5\)), denoted by \(j_{\pm}\). \(\mu^0\) is absorption coefficient for unpolarized light, and most importantly \(n\) is the number of probed holes in the valence shell, which needs to be estimated. The second step in Eq. (3.38) is for the specific case of the L\(_2\) and L\(_3\) edges of a 3\(d\) transition metal [26] such as Co, Fe etc. the value \(n\) corresponds to the number of electrons already occupying 3\(d\) states. The resulting value, also labelled \(m_{\text{orbit}}\), is in units of \(\mu_B\) per atom. The normalization integral is over the absorption spectrum from unpolarized light (XAS integral).

The second sum rule allows one to reach a good estimate of the spin moment. It follows the same logic, and is therefore only shown for the 3\(d\) transition metal case. It is important to note that a second integral is needed, over only one of the edges (here we chose L\(_3\)
Here \( \langle S_Z \rangle = \frac{1}{2} m_{\text{spin}} \) and \( T = \sum_i (s_i - 3 \mathbf{r}_i \cdot \mathbf{s}_i/r_i^2) \) is the spin dipole operator. This quantity reflects the spatial distribution of spin moment at the ionic site, to first order. The value of \( \langle T_Z \rangle \) can be estimated (for example using a first-principles calculation), but is generally considered small compared to \( \langle S_Z \rangle \) for the 3d transition metals. The ratio between the prefactors of the two integrals in the nominator reflects the branching ratio between the two edges.

The sum rules procedure was nicely expressed in graphical terms in Ref. [26]. From that work, we show the case of Co metal in Figure 3.2. In simple terms: from the raw transmission data in Panel (a), one can calculate the absorption spectrum in Panel (b) using Eq. (3.4). Often absorption is measured through a quantity directly proportional to it, for example using total electron yield, in which the drain current back to the sample is measured. XMCD is calculated \( (\mu^+ - \mu^-) \) from absorption spectra, reaching a curve as in Panel (c). \( q \) and \( p \) represent the places in which the integrals in Eq. (3.38) and (3.39) are evaluated. Panel (d) shows the absorption spectrum from unpolarized light. The two-step continuum contribution is subtracted before the integral over this spectrum, \( r \), is calculated.

![Graphical representation of XMCD analysis](image-url)
3.2 Experimental methods

3.2.1 Synchrotron radiation

The central tools in this thesis are synchrotron radiation sources. These are light sources utilizing radiation produced using charged particles, as they move through magnetic fields. Such sources possess inherent advantages over other light sources, namely their high brightness and the ability to tune the photon energy and polarization. However such devices are extremely demanding and costly.

In this thesis synchrotron light is used for two purposes, both of which require these specific advantages of synchrotron sources. The first requirement is access to specific energies which correspond to transition metal L edges (450-1000 eV) and Lanthanide M edges (900-1500 eV). Through E1 transitions, these provide direct access to the unpaired $3d$ states of transition metals and $4f$ states in the Lanthanides (See section 3.1.2); this requires well-defined incident photon energies in the experiment. The second requirement is to observe weak variations in the crystal structure, for which extremely high flux is needed in the hard X-ray regime (above ~5000 eV).

Synchrotrons nowadays are typically storage rings, i.e. circular particle accelerators dedicated to maintaining a constant current of (usually) electrons at relativistic speeds. Along the electrons’ path are a series of “insertion devices” that force the electrons through magnetic fields. This causes them to emit light, which is then used in dedicated experimental stations known as beamlines. In the following a brief account of insertion devices will be given. However, we first discuss the matter of size.

3.2.1.1 Synchrotrons are large (light sources)

The first major issue with synchrotron radiation relates to the actual size of the light source. To give a feeling for this, I reproduce a simple calculation. A charged particle moving in a magnetic field experiences the Lorenz force, described as:

$$F = -e v \times B$$

(with $e$ as the charge, $v$ as the initial velocity, and $B$ the field inductance). From the right hand rule we see that the particle will be accelerated in the direction perpendicular to $v$ and to $B$. Assuming all values remain constant in magnitude, this scenario would cause the particle to move in a circle in a plane perpendicular to $B$, as is the basic idea in a synchrotron storage ring. Plugging this into the classical formula of centripetal force ($F = m v^2 / r$), one reaches a relation between the radius of the circle $r$, the field induction $B$ and the velocity:

$$r = -\frac{m v}{e B} \approx -\frac{m y c}{e B}$$

The last step is an extension for the case of relativistic particles with $v \approx c$, in which $\gamma$ is the Lorenz factor. From this one can show that for the specific case of synchrotron radiation from electrons of energy $E_e$, one finds [27]:

\[\text{[33]}\]
\[ r[m] = 3.3 \frac{E_e [GeV]}{B [T]} \]

Plugging in a typical value of \( E_e = 5 \, GeV \) used in synchrotron sources, along with high field values reasonably obtainable from permanent magnets \( B = 1.5T \), one reaches a radius of 11 m. Keeping in mind that refocusing and diagnostic equipment must be installed within the storage ring, this value is an over-idealized lower limit. An actual storage ring will therefore consist of multiple emitting circuits with this curvature radius, connected by straight sections. Its effective radius must therefore be much larger. Clearly a realistic synchrotron light source is large. Indeed modern storage rings typically have radii of tens to hundreds of meters. Figure 3.3 presents a schematic of a synchrotron.

![Schematic of a synchrotron](image)

**Figure 3.3 – Schematic of a synchrotron.** Straight sections are connected by bending magnets. An example of an undulator is shown on one of the straight sections, as well as two beamlines.

### 3.2.1.2. Insertion devices

Three insertion devices are commonly employed. The first is the bending magnet, which also serves to deflect electrons between straight sections of the ring. A bending magnet emits a broad spectrum of light, so a monochromator is used to single out the required energy (in practice a monochromator is usually used with other insertion devices as well). The intensity of the emitted light peaks around the characteristic energy of the bending magnetic, which can be expressed as [27]:

\[ E_{BM} [keV] = 0.665 \, E_e^2 [GeV] \, B [T] \]  

(3.40)

(note that the number 0.665 has units that permit this relation)

Using the same parameters as in the previous section, we find that the highest intensity is for photons with \( \sim 25 \, KeV \), or a wavelength of \( \sim \frac{1}{2} \, \AA \). For 2.4 GeV, such as in the Swiss Light Source, this amounts to \( \sim 5.7 \, KeV \).
Wigglers and Undulators are straight devices which consist of arrays of magnets around the main trajectory of the electrons. The main difference between these two devices is that the radiation from a wiggler adds incoherently, while that from an undulator adds up coherently. We shall only discuss the latter. Modern undulators allow the user to control the emitted radiation energy by varying the gap between the magnets (through which electrons travel). We shall now briefly demonstrate this concept.

An undulator is usually characterized by the period of the magnet array, $\lambda_u$. Assuming the electrons travel along $\hat{z}$, the magnetic field they experience can be written as $\mathbf{B} = \hat{y}B_0 \cos(k_u z)$, with $k_u = 2\pi/\lambda_u$. From the Lorenz force, their transverse relativistic velocity ($\beta = v/c$) can be written as

$$\beta_x = \frac{eB_0}{y c m k_u} \sin(k_u z) \equiv \frac{K}{y} \sin(k_u z)$$

(3.41)

The undulator parameter $K$ can be described simply as

$$K = 0.93 B_0 \ [T] \ \lambda_u \ [cm]$$

(3.42)

The forward velocity can be written as

$$\beta_z \approx 1 - \frac{1}{2} y^{-2} - \frac{1}{2} \beta_x^2$$

(3.43)

We are interested in the radiation emitted in the forward direction (see Figure 3.4). The wavelength of emitted radiation can be written as a function of the angle to the forward direction $\theta$ (assuming the angle is small) as

$$\lambda \approx R - \lambda_u (1 - \theta^2/2)$$

(3.44)

Using $R = \lambda_u / \beta_z$, and taking $\theta = 0$, we reach the undulator equation.

$$\lambda \approx \frac{\lambda_u}{2y^2} \left( 1 + \frac{K^2}{2} \right)$$

(3.45)

From this equation we can appreciate that the wavelength can be tuned through $K$, which is proportional to the magnitude of magnetic field. Harmonics of this wavelength are also emitted, and are of course also tuned by $K$.

![Figure 3.4 - Schematic of radiation from an undulator. The sinusoidal path is the electron path.](image)
3.2.2 Experimental setups

3.2.2.1. Resonant soft X-ray scattering

Most of the experiments presented in this thesis were conducted at beamline X11MA (“SIM”) [28] of the Swiss Light Source. The SIM beamline produces light in the range 90eV-2000eV using two APPLE II elliptical undulators ($\Delta E/E > 5000$), which provide fully polarized linear or circular light.

Experiments were conducted using the RESOXS II end station [29], an upgraded version of the one described by Jaouen et al. in Ref. [30]. It is essentially a high-vacuum 4-circle diffractometer (with some angular limitations). It consists of two main parts. The first is a Janis ST-400 flow cryostat, at the end of which lies the sample. It can be manipulated along three Cartesian axes, and rotated around a $\theta$ axis and around a $\chi$ axis, which is limited in range to $\pm 10^\circ$. The sample can also be manually rotated around a $\phi$ axis, allowing so-called azimuthal scans to be conducted, with an accuracy of $\sim 3^\circ$.

The second part of the diffractometer is a $2\theta$ stage that rotates around the sample (concentric to the $\theta$ rotation within $50\mu m$), and carries a series of detectors (resolution is better than $0.005^\circ$). Although a 2D detector, a channeltron and a polarization analyzer for soft X-rays are all available, in this thesis I only discuss results from measurements in which data was collected using photodiodes. These are $\sim 32$ cm from the center of rotation, and are read out by a commercial Keithley 6517A Electrometer. A slit before the diodes defines their angular acceptance.

![Figure 3.5 – Picture of the bottom half of RESOXS II. The top flange, with the flow cryostat, is not shown.](image-url)
3.2.2.2. **Hard X-ray scattering**

Diffraction experiments using hard X-rays were conducted at beamline X04SA (“Materials Science”) [31], at the surface diffraction end station. This is a Newport 2+3 circle “surface diffractometer”, which provides two sample rotations and three detector rotations. The geometry of this device is described in detail in Ref. [32]. Experiments at low temperature were conducted using an in-house designed vacuum chamber with a Janis ST-400 flow cryostat. Intensity was collected using a Pilatus 100K 2D detector mounted on the detector arm.

The geometry of this end station is not ideal for magnetic diffraction experiments, most specifically because of the limited ability to conduct azimuthal scans. However, the software at this end-station, and specifically the greatly-enhanced SPEC version is far-superior to other diffraction facilities I have worked at. Of specific advantage is the ability to gain reasonably high-accuracy lattice constants through an orientation matrix created by a least-squares fit to many reflection positions. This relatively modest feature has been of great advantage in this study, as it can provide relatively accurate lattice constant values from our thin films. This is instrumental in reliably quantifying our strain values.

![Figure 3.6 – Schematic of the surface diffraction end station. Adapted from Ref. [32]](image)

One diffraction experiment in the hard X-ray regime was conducted at the XMaS beamline (BM28) at the ESRF. This is relevant only for section 4.5 on page 80, and is therefore described therein.
3.2.2.3. Soft X-ray transmission measurements under high magnetic fields

Beamline X07MA (“XTreme”) of the SLS is dedicated to XMCD measurements under high magnetic fields [33]. This beamline uses one undulator of the same kind as the SIM beamline, and is equipped with a permanent end-station for absorption spectroscopy, primarily for magnetic materials. The end station is equipped with a superconducting vector magnet capable of applying 7T along the beam direction, and up to 2T perpendicular to it.

Routine experiments mainly use total electron yield and fluorescence measurements to follow absorption. For the present experiment, a sample holder equipped with a photodiode behind the sample is used. The diode allows collecting light transmitted through the sample or emitted by it.

![Figure 3.7 – The XTreme end-station. Figure from https://www.psi.ch/sls/xtreme](https://www.psi.ch/sls/xtreme)
4 Diffraction study of perovskite manganite films

This chapter details a study of single-crystalline films of rare-earth manganese oxides, described by the chemical formula $o$-$R\text{MnO}_3$. The “$o$-” prefix indicates that we deal with an orthorhombic species of this material, as an hexagonal species (“h-“) exists as well. The $R$ ion has traditionally been the main “knob” in the study of manganites. Literally decades of work have been dedicated to the study of manganites with a mix of manganese valance states (e.g. $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$), which are produced by doping the $R$ site (e.g. replacing La ions with Ca or Sr). The present study will focus on the single-valance case in which the $R$ sites are occupied by a rare-earth Lanthanide.

The basic motivation for this study is that with the heavier half of the lanthanide series, $o$-$R\text{MnO}_3$ materials are type-II multiferroics (see orientation sketch in Figure 4.1). In fact, the first type-II multiferroic discovered was $\text{TbMnO}_3$. Extensive studies have been carried out on $\text{TbMnO}_3$ since the discovery of its multiferroicity in 2003 [34]. Studies on the heavier $R$ cases in this family demonstrated higher transition temperatures and $\sim$10 times stronger polarization values, which were explained as a result of different mechanisms that drive the magnetoelectric coupling [35]. Unfortunately, for these heavy $R$ ions, no single crystals are readily available, so studies were limited to powder and polycrystalline samples. Recent success in growing high quality crystalline films of the heavy-$R$ materials has paved the way for single-crystal-like studies and manipulation of their ferroic properties through epitaxial strain. Strain is important also from a fundamental standpoint, as subtle changes in crystal geometry are a key ingredient in manipulating multiferroicity. This was the main motivation for this study.

$$o-R\text{MnO}_3$$

![Figure 4.1 - General orientation sketch for the o-$R\text{MnO}_3$ series.](image)

The $R$ ions are typically lanthanides or Y, because $Y^{3+}$ ions have a closed 4f shell and an ionic radius very close to that of Ho$^{3+}$. [39]
4.1 Background on perovskite manganites

This section is an overview of the existing theoretical understanding of the perovskite manganites. It is not intended to be exhaustive, but it is thorough in that it touches all aspects that are important as background. Topics are presented briefly if they are extremely well-established (e.g. JT distortion), or to the extent that confidence is maintained (in cases which are still debatable).

4.1.1 The distorted perovskite crystal structure

The perovskite structure takes its name from the mineral CaTiO$_3$. The ideal perovskite structure is cubic, and can be generally described by the chemical formula ABO$_3$. The B ion is surrounded by six O ions which form an octahedron. The space between the octahedra is occupied by the A ion. Figure 4.2 presents an idealized sketch of this structure. A commonly employed tool to describe the stability of this structure is the tolerance factor $t$, as function of the ionic radii of the constituent ions,

$$t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}$$

(4.1)

The structure is considered stable between $t$ values of 0.75 and 1. As such, a wide variety of elements can accommodate this structure, and indeed this structure is common in a wide range of fields and material functionalities, ranging from solar cells, through catalysts, to magnetic media. Most commonly the A site is occupied by an alkaline metal or a rare earth lanthanide, and the B site is occupied by a transition metal.

In the present case we deal with Mn$^{3+}$ ions and lanthanide ions, which we label “$R$”, in their $R^{3+}$ state. The O ions are in their expected O$^{2-}$ state. Two major distortions are known to occur in the crystal: the Jahn-Teller distortion, and the GdFeO$_3$-type distortion, both described below. They result in an extended primitive cell which contains four formula units. The primitive unit cell we deal with is not

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Figure 4.2 - The ideal perovskite structure. Solid lines indicate the cubic directions. Dashed lines indicate the BO$_6$ octahedra.
cubic, but orthorhombic, and is described by space group 62. An approximate relation exists to the
standard cubic lattice constant $a_c$: $a = b = \sqrt{2}a_c$ and $c = 2a_c$ ($a$, $b$, and $c$ are in Pbnm, explained
below). This relation is approximate, and in fact works well only when lighter ions in the A site. It
works poorly on the materials in this work, because $b$ is nearly 10% larger than $a$. The standard
setting of space group 62 in the international tables of crystallography is Pnma, but to conform with
literature, the setting Pbnm is used here instead. There is no substantial difference between the two,
only that in Pbnm the long axis is the c axis (the transformation between the Pnma and Pbnm settings
is a simple permutation of axes).

4.1.1.1. The Jahn-Teller distortion

The Jahn-Teller theorem states that for (nearly) any set of degenerate electronic states associated with
a molecular configuration, some form of symmetry-breaking will occur in the molecule that will lift
the distortion [36]. The theorem was presented Hermann Jahn and Edward Teller in 1936, but is said
to have been influenced by a meeting two years prior between Teller and Lev Landau at the Nils Bohr
institute [37].

Within the context of this thesis The Jahn-Teller (JT) distortion represents a displacement of O ions
towards or away from their nearby Mn ions, and can be understood as a stretching of the MnO$_6$
octahedra along a primary axis (a tetragonal distortion). This is illustrated in Figure 4.3. Before the
distortion, the Mn$^{3+}$ ion ($d^6$) is placed in an octahedral ligand field. Only one electron occupies the
high-energy doubly degenerate $\varepsilon_g$ states. Therefore a tetragonal elongation of the cage lifts the
degeneracy of the energy states, allowing the occupied $\varepsilon_g$ orbital to lower in energy at the energetic
cost of a lattice distortion.

Figure 4.3 – The Jahn-Teller distortion around a Mn$^{3+}$ ion, adapted from Stöhr and Siegmann [38]. The
octahedral symmetry is lowered by an elongation of the MnO$_6$ cage. This is favorable energetically because the listed
degeneracy allows the occupied $\varepsilon_g$ orbital, which points along the elongation direction, to lower in energy.
4.1.1.2. The GdFeO$_3$-type distortion

The GdFeO$_3$-type (GFO) distortion is a displacement of multiple ions away from their ideal position. It can be viewed as a collective tilt of the MnO$_6$ octahedra, as shown in Figure 4.4. This implies that the local coordination of the Mn ion tilts with the oxygen cage. For this to work, adjacent octahedra must alternate in their tilt direction. This causes a long range alternation of the Mn orbitals. A scenario like this is indicated in Panel (b) by two colors of octahedra. A full analysis of the possible octahedral tilts in ABO$_3$ perovskites was conducted by Woodward in Ref. [39] and Ref. [40]. It should be noted that two rotations take place, although only one is shown here for simplicity.

Figure 4.4 – The GFO type distortion. (a) The undistorted structure. (b) The distorted structure. Dark circles are the Mn ions, lighter ions are the R ions. O ions are at the vertices of the octahedra (not shown). The figures present a 2D cut-through to illustrate the concept, and the general effect occurs in all three dimensions. The structure is kept cubic in this example. It should be noted that two rotations take place, although only one is shown here for simplicity.
4.1.1.3. Known variation of crystal structure

It is worth dwelling on details of the unit cell and the crystal structure a while longer, as some terms will be referred to later on. The structure can be understood as planes of Mn ions (at the 4b positions) parallel to the \( ab \) plane, at \( c = 0 \) and \( c = \frac{1}{2} \) (in fractional coordinates, “f.c.”). Two types of Mn-Mn bonds exist:

- “Out of plane” bonds exist along the \( c \) axis. The corresponding Mn-O-Mn bond involves an Oxygen at a 4c position (\( c = \frac{1}{4} \) or \( \frac{3}{4} \)), and is parametrized with an angle, Mn-O\(_{I}\)-Mn, and a bond length Mn-O\(_{I}\).
- “In-plane” bonds exist in the \( ab \) plane. The corresponding Mn-O-Mn bond is different in that it involves an Oxygen ion at a general position (8d), which is not equidistant to the two Mn ions. Therefore the bond is parametrized by one angle, Mn-O\(_{II}\)-Mn and two bond lengths Mn-O\(_{II}^A\) and Mn-O\(_{II}^B\).

When the \( R \) ions are substituted for smaller ones, the volume in between the MnO\(_6\) octahedra is no longer fully occupied. The GFO tilting then occurs to compensate for this. Many parameters, including the bond lengths and angles above are found to vary systematically as the \( R \) ions are substituted for one another. This is shown in Figure 4.5(a). An example of an \( ab \)-plane is shown in panel (b), indicating the in-plane bond angles and lengths.

![Figure 4.5 - Distorted perovskite structure](image)

**Figure 4.5 – Distorted perovskite structure.** (a) Bond angles, bond lengths and lattice constants of \( o-RMnO_3 \) as functions of the \( R \) ions’ ionic radius (Lu smallest, La largest) from Ref. [41]. (b) An example of an \( ab \) plane in the Pbnm structure. The Mn ions are shown with an ideal E-type spin configuration. O ions between them are indicated by smaller circles, and are actually slightly above or below the plane. Pseudo-cubic \( xy \) directions are also indicated. Figure from Ref. [42]
4.1.2 Experimental background and phase diagram

In this section I aim to give a coherent picture of the magnetic and multiferroic behavior of $\alpha$-RMnO$_3$. This is important because different authors study different aspects of these materials, and as these materials exhibit multiple observable phenomena, properties such as phase boundaries (e.g. between magnetic phases) are often labelled according to the studied observables (e.g. electric polarization used to label magnetic phases). For this reason, the terminology in literature is sometimes misleading.

The main controlled parameter in many characterization studies of this family is the $R$ ion, because varying it controls the crystal distortion, and as a consequence of this, also magnetic properties. Therefore it is customary to plot the phase diagram as a function of the $R$ ions’ radius, $r_R$. Examples of such phase diagrams from different authors are shown in Figure 4.6. These roughly agree with each other, especially regarding the incommensurate (IC) sinusoidal phase.

This choice of $r_R$ as the controlled parameter reflects the understanding that the $R$ ion serves no purpose other than to distort the crystal’s perovskite structure. This implies that unpaired 4f electrons play no part in the (relevant) magnetic behavior. Indeed the phase diagram is well reproduced when solid solutions of Y, Eu and Lu are used to reach effective $r_R$ values instead of a pure $R$ ion [43], as shown in panel (a) of Figure 4.5 (these $R^{3+}$ ions have no unpaired 4f electrons). Furthermore, Y is much lighter than the lanthanides, but YMnO$_3$ fits well in the phase diagram [46,47], because the ionic radius of Y is nearly identical to that of Ho.

Figure 4.6 – Phase diagrams from literature (Top: Ref. [43], Bottom left: Ref. [41]. Bottom right: Ref. [44]). Note that the horizontal axes don’t fully match between the two references.
4.1.2.1. Magnetic phases

Here I discuss the known magnetic structures for the o-RMnO$_3$ series. Cartoons of these are presented in Figure 4.7. When considering the entire lanthanide series, there are two well-studied Mn magnetic structures (here we do not discuss the $R$ ions’ 4f order, which can occur at very low temperatures):

- The first exists for the lighter $R$ ions from La to Sm (and mostly Eu). This is the collinear A-type antiferromagnetic structure, which consists of ferromagnetically ordered $ab$ planes which are antiferromagnetically coupled to each other. The structure follows an ordering wave vector of (0 0 1). This structure was first reported for LaMnO$_3$ in 1955 by Wollan and Koehler [45]. So-called F-type canting of the Mn spins towards the $c$ axis is allowed by symmetry, and has been reported as a weak FM moment [46].

- The second well-studied structure is in the case of TbMnO$_3$, originally described in 1977 [47]. Here the Mn moments form an elliptical cycloid in the $bc$ plane (a “$bc$-cycloid”), as shown by Kenzelmann et al. using neutron diffraction [48]. A more precise image of TbMnO$_3$ was shown by Fabrizi [49] and Walker [50] using non-resonant magnetic X-ray diffraction. This order follows a wave vector of $(0 q 1)$ with $q \approx 0.27$. Reflections of the form $(0 q 0)$ appear as well, as satellites of the $(0 0 0)$ of the $c$-axis FM canting. This is a consequence of the DM interaction in the Mn-O$_{1}$-Mn bond along the $c$ axis. Variants of this structure exist for $R=$Gd-Dy.

The cycloidal phase is not limited to TbMnO$_3$, and the actual phase boundaries are not well defined (discussed later). Although the cycloidal phase was systematically studied mostly for TbMnO$_3$, DyMnO$_3$ is known to acquire a nearly identical order. Furthermore by producing mixtures of different $R$ ions a narrow range was found between Gd and Tb, an $ab$-cycloidal phase is also present [51].

Figure 4.7 – Mn magnetic orders associated with the o-RMnO$_3$ family. (a) A-type with weak c-axis FM canting (b) sinusoidal phase (c) $bc$ cycloid (d) $ab$ cycloid (e) E-type. Panels (a)-(d) taken from Ref. [52]. Panel (e) taken from Ref. [53].
When considering the values of the Neel temperature (see Figure 4.6), it is clear that as the $R$ ion becomes smaller, the A-type structure weakens, until the magnetic ground state structure is replaced by the cycloidal phases. Furthermore, for $R$ ions equal to or heavier than Eu, two magnetic transitions occur upon cooling instead of one. The first is the formation of an incommensurate sinusoidally modulated magnetic state, in which the Mn moments are modulated mainly along the $b$ direction. The absence of a third harmonic of the ordering wave vector for nearly all $R$ cases indicates that this modulation is nearly an unperturbed sinusoid. The second transition is the formation of the full magnetic order (A-type, cycloids…).

The remainder of the lanthanide series consists of $R$=Ho to Lu. This group is described in this thesis as the “heavy-$R$” group, and is the main topic of this chapter. The magnetic structure for these is widely referred to as antiferromagnetic E-type. The E-type model involves collinear spins parallel to $b$, which form $\uparrow\uparrow\downarrow\downarrow$-type chains along the $ab$ direction, and adjacent $ab$ planes oriented antiferromagnetically to each other. The E-type structure is described by a wave vector of $(0\ 1/2\ 1)$. Unlike the cycloids which are incommensurate (IC), this order has a commensurate doubling of the (magnetic) unit cell along the $b$ direction. This structure was first suggested in 2001 for HoMnO$_3$ in Ref. [54].

4.1.2.2. Ferroelectric phases

The main interest in the o-\(R\)MnO$_3$ family stems from its multiferroic behavior. This was originally discovered for $R$=Tb, in its cycloidal phase [34]. Three years later the E-type magnetic structure was predicted to induce a polarization two orders of magnitude larger than in TbMnO$_3$ [55]. Indeed the heavy-$R$ materials did exhibit a much larger value, as reported shortly after in Ref. [56] and later on for the entire series in Ref. [43]. The polarization exhibited in the magnetic phase was indeed found to rise by an order of magnitude for the heavy-$R$ group compared to the cycloids, although not to the predicted extent (see Figure 4.8). Nevertheless due to the different mechanism driving the induced $P$, considerable interest remains in these systems. It is notable that the $P(T)$ curve in many samples exhibits a step-like feature, the origin of which, to my knowledge, has not been addressed to date (see e.g. panel (c)). This is visible also for YMnO$_3$ [57], and can therefore not arise due to the $R$ ions’ 4f order (a jump in P due to 4f order is known to occur for $R$=Ho).
**Figure 4.8 – Ferroelectric polarization.** (a) and (b) temperature dependence of $P$ from powder samples of solid solutions and pure $\alpha$-RMnO$_3$, respectively. [43] (c) Temperature dependence of $P$ from a single crystal of $\alpha$-YMnO$_3$ (note the different units on vertical scale). [57] (d) Maximal $P$ as function of $R$ ionic radius. Values are multiplied by 6 to extrapolate crystal values from measured powder values. [43]

4.1.2.3. Controversial and overlooked details in experimental literature

In the following I discuss observations reported on bulk (or powder) samples. I address topics which I believe have been somewhat overlooked, and I address some specifics about the low-temperature phases, which I believe are controversial. In this I specifically refer to the assignment of low temperature phases and the boundaries between them. The cases I present are partially related to the fact that for $R$ ions heavier than Dy, special growth conditions are required to produce perovskite $R$MnO$_3$, because in ambient conditions $R$=Ho-Lu grow as hexagonal structures. As we shall see, minute changes in crystal structure have large effects on observed quantities. This means that variations in reports may be related to variations in growth conditions or crystallinity. Interesting examples of this are Ref. [58] and [59], which reported clear orthorhombic structures, with effects that appear at temperatures that correspond to the Neel temperatures of the hexagonal species (though not mentioned in these works).

The cycloidal states are somewhat ambiguous because they are meta-stable in nature: they are a result of frustration between near-equal magnetic interactions (see section 4.1.3). As such, only modest perturbations are required to flop the cycloid between the $bc$ and $ab$ planes [16,64] (an $ac$ cycloid is
not energetically favorable in any case [60]). The boundary between the cycloidal and E-type phase is also a matter of some controversy. For YMnO$_3$, three different structures have been reported: a $bc$-cycloid [61], a commensurate E-type [61,67] and an incommensurate E-type [62]. Also for HoMnO$_3$, commensurate [54] and incommensurate [68,69] structures were reported.

To put this into perspective, I present here properties which are systematic in the antiferromagnetic behavior, and which I believe have been somewhat overlooked. An exhaustive survey of the existing literature suggests three clear trends exist in the AF behavior. The first relates to the magnitude of the modulation vector ($0 \ q \ 0$). The value of $q$ changes systematically with the $R$ ion radius: from a commensurate integer value (A-type), through incommensurate phases, to the commensurate $\frac{1}{2}$ value (E-type). In other words $q$ varies from 0 to $\frac{1}{2}$. This is summarized in Figure 4.1 from existing bulk studies. The value of $q$ is, of course, normalized to the size of the $b$ lattice constant. This could potentially distort the trend. However, the variations in $q$ are too large with respect to the changes in lattice constants [43,46], so the qualitative trend would not be realistically affected.

![Figure 4.9 – bulk values of the (0 q 0) magnetic modulation vector size as function of the R ion radius.](image)

From Figure 4.9 it is apparent that only Tm, Yb and Lu exhibit a commensurate structure, as expected from an E-type, and for all other ions the magnetic order is incommensurate (although not necessarily cycloidal). However, even these commensurate structures are more complicated than expected. The magnetic structures of TmMnO$_3$ and LuMnO$_3$ were studied using neutron diffraction, and were reported as a collinear E-type in Ref. [65] and [63], respectively. However, when such samples were
investigated with soft X-ray powder diffraction, a (0 $\frac{1}{2}$ 0) reflection was also observed [70] (this study used the same sample as in the neutron study of Ref. [65]), which should be absent for a purely collinear E-type because the reflection is only sensitive to $c$-axis spin components (see Eq. (7.21)). A similar arrangement was predicted by Mochizuki et al. using Monte-Carlo simulations. Their commensurate E-type model also reproduced the expected polarization values [35]. However, they also predicted that the E-type structure is distorted such that the spins are canted towards the $c$ axis by $9^\circ$, and are canted away from the $b$ axis in the $ab$ plane by $\sim 25^\circ$. The same study found that the system can stabilize at nearly-commensurate modulation values ($q$), which still behave similarly to an E-type in the orientation of spins and in polarization values. These models are shown in Figure 4.10. This prediction is important because it potentially reconciles contradicting views on the cases of Y, Ho, and Er. On the one hand, o-$RMnO_3$ with these $R$ ions do no behave magnetically as an E-type in bulk (they are not commensurate to the lattice, see Figure 4.9), but they do exhibit the high electric polarization associated with the E-type phase (see Figure 4.6 and Figure 4.8).

![Figure 4.10](image)

**Figure 4.10** – *Predicted models for the E-type phase, from Ref. [35].* All graphs present the evolution of spin direction along the $ab$ direction (the pseudo-cubic $x$ axis). (a) Commensurate model. Circles present the spin directions in the first four positions within the $ab$ plane. (b) Incommensurate model. Note that despite the disordered interference regime, the phase appears to be maintained between the spin directions.

A second reported phenomenon is the temperature dependence of the modulation parameter $q$. For the commensurate structures a clear picture is observed: upon cooling the transition into the sinusoidal phase is observed at $T_N$, under which $q$ varies rapidly with temperature. At $T_C$ $q$ locks at $q = \frac{1}{2}$, and remains constant from there on. This is shown in Figure 4.11(a). However, for incommensurate structures $q$ appears to lock in, if at all, at temperatures lower than $T_C$. This observation is clear for the cycloidal phases, but less so for Y, Ho, Er due to the lack of high quality data in literature. An example is shown in Figure 4.11(b).
Another overlooked aspect relates to the magnitude of the magnetic moment reported on the Mn sites. This information is available only from Neutron scattering, and as such is quite limited and model-dependent. This is presented in Figure 4.12, and also exhibits a systematic dependence on the \( R \) ion radius. If one can trust such data, it could be a consequence of the variation in spin distribution along the Mn-O-Mn bonds (note that this cannot be due to the 4f ions’ moment because the nonmagnetic, \( Y^{3+} \) and \( Lu^{3+} \) are situated at the middle and end of this diagram; which is not shown, \( Eu^{3+} \) would be at the beginning).

Figure 4.11 – Temperature dependence of magnetic modulation. (a) Measured for o-TmMnO\(_3\) (adapted from Ref. [65]) and (b) for GdMnO\(_3\), TbMnO\(_3\), Tb\(_1-x\)Dy\(_x\)MnO\(_3\) and DyMnO\(_3\) (adapted from Ref. [71]).

Figure 4.12 - Mn moments in bulk RMnO\(_3\) as function of R ion radius, as reported in neutron diffraction studies. Data for Lu, Yb, Tm, Ho, Y, Dy and Tb are taken from Refs [63], [64], [65], [67], [62], [72]and [48], respectively.
**4.1.3  Theoretical framework**

In this section I present the necessary background and terminology about magnetic behavior of o-$RMnO_3$. The groundwork for understanding the magnetic behavior of these materials was originally laid out by Kohler and Wollan, who described the possible magnetic structures of mixed valance $La_xCa_{1-x}MnO_3$ in 1955 [45]. Rules regarding the type of magnetic coupling along a Mn-O-Mn bond were laid out in the same year by Goodenough [73]. Further work was conducted in the following decades on similar compounds, for example in [74] and [75], partially because some of these materials exhibited weak ferromagnetism, which is allowed by symmetry along the $c$ direction. At the base of the present-day theory is the work of Solovyev from 1996 [76], who showed that the JT distortion is responsible for the A-type AFM order observed in $LaMnO_3$. Lastly, in 2003 Kimura et al. showed that the variation of the magnetic order within the lower part of the o-$RMnO_3$ series was closely related to the distortion of the crystal structure.

**4.1.3.1. Magnetic interactions and phases**

The following description is based mainly on the work by Mochizuki, Furukawa and Nagaosa in Refs. [35] and [60]. Their description of the system is based on a classical Heisenberg Hamiltonian with spins $S$ treated as classical vectors. Each term plays a role in the overall behavior of the system. I will briefly describe the significance of each term.

$$\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_{sia} + \mathcal{H}_{DM} + \mathcal{H}_{K}$$  \hspace{1cm} (4.2)

The exchange term $\mathcal{H}_{ex}$ consists of symmetric spin exchange interactions between Mn ions (double and super exchange).

$$\mathcal{H}_{ex} = \sum_{\langle i,j \rangle} J_{ij} S_i \cdot S_j$$  \hspace{1cm} (4.3)

These are mediated by O $p$ orbitals to which the Mn $d$ orbitals are partially aligned. Four principal couplings $J$ are followed, and are indicated in Figure 4.13. Nearest neighbor couplings along the $c$ axis ($J_c$) which are AFM, and along the $ab$ direction ($J_{ab}$) which are ferromagnetic. Next nearest neighbor interactions exist in the $ab$ planes ($J_a$ and $J_b$), and involve a path of the form Mn-O-O-Mn. These couplings parameters do not change substantially with the substitution of R ions (and therefore the GFO tilts), except for $J_b$ [60]. $J_b$ is the coupling of two Mn $e_g$ orbitals neighboring along the $b$, and is expected to be weak as it involves a path which includes two O $p$ orbitals which have near zero overlap (see Figure 4.13(c)). However, as the GFO tilt increases, so does the overlap of the two O $p$ orbitals. This leads to a drastic change in the magnitude of $J_b$, until the point where it is in direct competition with $J_{ab}$, the nearest-neighbor interaction. This is directly translatable to the decrease in $T_N$ observed for increasing $R$ ($T_N \approx 140K$ for La and $\approx 40K$ for Eu, see Figure 4.6), which signifies a weakening of the A-type AFM order (discussed later).
Scrolling along the lanthanide series from $R=$La, the overtake occurs around $R=$Gd, Tb, above which $J_b$ is consistently larger than $J_{ab}$. Indeed it is in GdMnO$_3$ and TbMnO$_3$ that the sinusoidal phase first appears, and it is in TbMnO$_3$ that the A-type order no longer exists at all. It is notable, though, that all three in-plane couplings ($J_{ab}, J_b$ and $J_a$) are required to stabilize the E-type phase [35].

![Figure 4.13 – Magnetic exchange interactions in o-RMnO$_3$.](image) (a) Three dimensional picture of the crystal indicating all exchange terms considered, with $R$ ions omitted. Tilted (local) coordinates of the $i$th MnO$_6$ octahedron are indicated ($\zeta, \eta, \xi$), as well as global orthorhombic coordinates ($abc$) and global pseudo-cubic coordinates ($xyz$). (b) and (c) present a local image indicating the next-nearest neighbor interactions $J_a$ and $J_b$, respectively. Images are adapted from [35] and [60].

The single-ion anisotropy term $\mathcal{H}_{sia}$ describes effect of the local environment of the Mn ion within the oxygen octahedron. The principle axes for this term ($\zeta, \xi, \eta$) are those of the octahedron, and are therefore tilted with respect to the principle axes of the crystal ($abc$). It is important to note that this coordinate system alternates from one Mn to the next along with the octahedra, and are therefore not global. This local coordinate system, along with the crystal orthorhombic ($abc$) and cubic ($xyz$) axes, are all indicated in Figure 4.13(a). The single ion anisotropy term takes the form

$$\mathcal{H}_{sia} = \mathcal{H}_{sia}^{D} + \mathcal{H}_{sia}^{E} = D \sum_i S_i^2 + E \sum_i (-1)^{i_x+i_y}(S_i^x - S_i^y)$$

(4.4)

Here the first term denotes the direction closest to the $c$ direction. $D$ is a positive energy parameter, so $\zeta_i$ is a hard axis for the $i$th ion (as such $c$ is close to the hard axis on all ions). The second term indicates that the $\xi$ and $\eta$ axes alternate between easy and hard from one Mn site to the next ($i_x, i_y$, and $i_z$ represent coordinates of $i$th Mn ion with respect to the cubic $x, y$, and $z$ axes). This is because of the alternation in the occupied $e_g$ orbitals due to the JT distortion. The importance of this term stems from the fact that it acts to shift the spins away from the principle crystal axes, further weakening the commensurate order with GFO-type tilting.

The next term we discuss is the Dzyaloshinsky-Moriya interaction (DMI) term. This is an antisymmetric exchange term of two Mn spin along a Mn-O-Mn bond, given by
The vector $\mathbf{d}_{i,j}$ is the DM vector, which has units of energy, and is defined perpendicular to the triangle spanned by the 3 ions. This can be written as:

$$\mathbf{d}_{i,j} = |d_{i,j}|(\hat{r}_{ij} \times \hat{x})$$

In which $\hat{r}_{ij}$ is a vector pointing from one Mn ion to the other, and $\hat{x}$ is a vector orthogonal to $\hat{r}_{ij}$, spanned in the direction from the O ion (see Figure 4.14(a)). The magnitude of the DM vector for each Mn-O-Mn bond was originally calculated for LaMnO$_3$ in Ref. [76]. There it was shown that all DM vectors depend on only 5 parameters, as shown in Figure 4.14(b). Ref. [60] found that the magnitude of the DM vector changes very little upon variation of the $R$ ion. Therefore, simply from the nature of the cross product in Eq. (4.6) it is clear that strengthening of the GFO-type distortion also strengthens the DM interaction. Furthermore, from Eq. (4.5) it can be appreciated that only the case of non-collinear spin order (e.g. a cycloid) would experience a DM effect.

**Figure 4.14 - Dzyaloshinsky-Moriya interaction (anisotropic exchange).** (a) General geometry of a Mn-O-Mn bond, and the vectors defined in the main text (figure from Ref. [7]). (b) DMI parameters associated with different Mn-O-Mn bonds. Black and white spheres indicates Mn and O, respectively. The vectors indicated for different O ions are DM vectors for the Mn-O-Mn bond indicated. Note that all vectors depend on only 5 parameters (figure from Ref. [76]). The indicated planes are adjacent $ab$ planes.

The importance of this interaction for the magnetic order is mainly its effect on the cycloidal modulation. The staggered arrangement of the DM vectors in the Mn-O$_{II}$-Mn bonds (in-plane bonds) promotes this phase [35]. Ref. [60] predicts that in the absence of this term, a cycloid order would propagate with the same angle from one Mn to the next, while with the DMI the rotation angle itself is modulated. This is true for the relative angle between Mn spin components in the $ab$ plane and for the angle between adjacent spin components along $c$. Furthermore it effectively works against the single ion anisotropy to destabilize the ab cycloid phase, and pushes the system towards a $bc$ cycloid (the $c$ axis is close to the single-ion anisotropy’s hard axis).
It is also worth noting that this term plays a practical role in this thesis. Weak ferromagnetism along the c axis is allowed (and observed) in the A-type phase, which strictly follows \((0 \ 0 \ 0)\), i.e. no modulation. When the system goes from A-type to cycloidal, the magnetic order is no longer described by \((0 \ 0 \ 1)\), but by \((0 \ q \ 1)\). Spins in adjacent \(ab\) planes are no longer antiparallel to each other, so the DM term changes in magnitude and serves to modulate the weak ferromagnetism, changing its description from \((0 \ 0 \ 0)\) to \((0 \ q \ 0)\). The \((0 \ q \ 0)\) and \((0 \ q \ 1)\) modulations have been shown to be highly correlated to each other, both in theory [60] and in experiment [77]. This provides confidence in following the \((0 \ q \ 0)\). This is explained with a simplified model for the case of TbMnO\(_3\) in Ref. [77].

The last point to make about the Hamiltonian in Eq. (4.2) relates to the last term. In an attempt to reproduce the sinusoidal phase, the authors of Ref. [60] found that a global anisotropy term along the \(b\) axis is essential. This takes the form

\[
\mathcal{H}_K = -K \sum_{\langle ij \rangle} S_{bi} I
\]  

(4.7)

It was found that for nonzero (positive) \(K\), the system always enters a sinusoidal phase upon cooling, before entering the lower-temperature magnetic phase. With higher \(K\) values, the temperature range in which the sinusoidal modulation exists grows.

4.1.3.2. Magnetically-induced electric polarization

I now discuss the current understanding of the multiferroic behavior, as it is directly linked to the magnetic state of the system. The induced polarization in \(o-R\)MnO\(_3\) differs significantly between the three different multiferroic phases: the \(bc\) cycloid, the \(ac\) cycloid, and the (canted) E-type. Mochizuki et al. reproduced experimental results by calculating the polarization and dividing it into symmetric contributions of the form \(P_S = \sum_{\langle ij \rangle} \pi_{ij} (S_i \cdot S_j)\) and antisymmetric contributions of the form \(P_{AS} \propto \sum_{\langle ij \rangle} \hat{r}_{ij} \times (S_i \times S_j)\). \(\pi_{ij}\) represents the absence of inversion symmetry along the Mn-O\(_II\)-Mn bonds in the \(ab\) plane, and \(\hat{r}_{ij}\) is a unit vector connecting neighboring Mn ions. The calculated values are overplotted on experimental values in Figure 4.15(a).

The \(P_{AS}\) contribution is present in all phases, in line with the prediction that the magnitude of spin helicity does not change substantially between these phases, only its direction. The \(P_S\) contribution does change dramatically. This was found using a so-called Peierls-type spin-phonon coupling model, in which the exchange term in the Mn-O\(_II\)-Mn bond (in the \(ab\) plane) was modified in an alternating fashion as \(J_{ij} = J_{ab} + J_{ab}^b \delta_{ij}\). Here the \(\delta_{ij}\) is a small shift of the O ion (normalized), and \(J_{ab}^b\) was a calculated parameter. This causes an increase or decrease of the bond angle, see Figure 4.15(b). Note that from a diffraction point of view this corresponds to a doubling of the unit cell, which was not reported so far, but does in fact can agree with some literature data.  

[54]
For the (cyclically modulated) E-type predicted by the authors, the scenario is then reasonable: the O-II ions between nearly (anti)parallel Mn-spin pairs shift negatively (positively) to strengthen (weaken) the ferromagnetic exchanges by increasing (decreasing) the Mn-O-II-Mn bond angle, which results in the uniform electric polarization. As this term involves the large nearest-neighbor exchange $J_{ab}$, the striction is also large, ultimately producing the large polarization observed for this phase.

For the cycloidal phases, the $P_S$ contribution is only found for the $ab$ cycloid. This contribution arises from the combination of the DM interaction with the spin-phonon coupling. As mentioned before, the DMI modulates the spin rotation angles themselves (the angle with which the spin changes its direction from one site to the next). Therefore, the O ions between two spins with a smaller angle of $\phi - \Delta \phi$ shift negatively, strengthening the ferromagnetic exchange by increasing the Mn-O-Mn bond angle. The opposite occurs for the O ions between two spins with a larger angle of $\phi + \Delta \phi$: they shift positively, thus weakening the ferromagnetic exchange by decreasing the Mn-O-Mn bond angle. The combination of these shifts generates the ferroelectric polarization (see Figure 4.15(c)).

The DMI also modulates the spin rotation angle in the $bc$ cycloid. However, in this case the induced O shifts oppose each other between neighboring $ab$ planes, which cancels the net polarization from this effect.
4.2 Experimental observations

The purpose of this section is to detail the quantities we observe in diffraction experiments on o-RMnO$_3$ films. Discussions in subsequent sections will use this as a basis for argumentation without dwelling on experimental details, which would blur the discussion.

Throughout this project several o-RMnO$_3$ films were investigated with varying $R$ ions, thicknesses, substrate orientations, and epitaxial strain. Unless stated otherwise, all samples exhibit the same qualitative behaviors, which only vary in magnitude. I will therefore give a taste of all the observed effects without considering the differences between samples, as this will be discussed later. It should be emphasized that all results are from films with $R$ ions in the range Er-Lu. This means that Gd, Tb, and Dy are not covered. Observations from these materials differ from those presented here.

I will distinguish between diffraction experiments at the Mn $L_{2,3}$ edges, at the $R$ ions’ $M_{4,5}$ edges, and non-resonant experiments conducted using hard X-rays.

4.2.1 Resonant diffraction at the Mn $L_{2,3}$ edges

X-ray diffraction at the Mn $L_{2,3}$ absorption edges (2p→3d transitions) is directly sensitive to the unpaired 3d electrons at the Mn$^{3+}$ sites. This allows studying magnetic ordering solely of the Mn moments through magnetic reflections arising from their periodicity. However, these energies are quite low (around 650 eV), which limits the accessible reciprocal space. In fact, the only available magnetic reflection at these energies is $(0 q 0)$ with $q \approx \frac{1}{2}$. As this is the only one, I dwell on all measurable characteristics of this reflection.

Figure 4.16 – Raw data taken at the Mn $L$ edges. (a) Reciprocal space scan along $(0 k 0)$ taken 10 K from a 400 nm o-YbMnO$_3$ film at the Mn $L_3$. The solid line represents the best fit to a Voigt function. (b) Intensity of the $(0 q 0)$ reflection as function of the incident photon energy, taken at 10K from a 400 nm o-TmMnO$_3$ film. Both measurements were taken at $\Psi = 0^\circ$, so intensity from incident $\sigma$ light is zero (see Eq. (7.21)). The observed energy dependence of the $\sigma$ channel in (b) is due to spectral dependence of reflectivity. The non-zero baseline is due to specular reflectivity, as both samples are [010] oriented.
Figure 4.16 presents typical raw data from this reflection, measured from two different samples (all data are normalized by the measured incoming intensity, $I_0$). Figure 4.16(a) presents a scan along the (0 $k$ 0) direction of reciprocal space at 10 K. We note the absence of a (0 1-$q$ 0) reflection. Another example of such data is presented in Figure 7.2. Figure 4.16(b) presents the energy dependence of this reflection. The shape of this curve varies very little between samples with different $R$ ions. The absence of intensity from $\sigma$ incoming light is because of the azimuthal angle used ($\Psi = 0^\circ$), as explained below. Intensity from incident circular light is a combination of $I_\pi$ and $I_\sigma$. The appearance of circular dichroism could indicate the presence of a cycloidal structure. In the present case the circular dichroism is negligible and the difference does not reproduce well. This effect can be an experimental artifact, or due to variations in cycloidal domain populations, if these exist.

Figure 4.17 presents different features of the (0 $q$ 0) reflection as functions of temperature, namely the integrated intensity, the magnitude of the ordering wave vector $q$, and the correlation length, defined as $\zeta = 2/FWHM$. Data were collected from a [010]-oriented, 104 nm thick o-LuMnO$_3$ sample, with $\pi$ incident linear light and $\Psi = 0^\circ$. The parameters presented are from the best fit between the data and Voigt profiles (95% confidence). Intensity from this reflection appears below $T_N \approx 40$ K, in agreement with the expected appearance of magnetic order [43]. No signature of a second magnetic transition is observed in the intensity’s temperature profile, which follows a linear temperature dependence below $T_N$. This indicates that the order parameter to which the reflection is proportional has a critical exponent of $\beta = \frac{1}{2}$. The intensity does not change below $\sim 14$ K, which we label $T_L$. The magnitude of $q$ varies with temperature down to $\sim T_L$, below which it converges to a constant incommensurate value slightly below $\frac{1}{2}$, as previously reported for films of $R$=Lu and Y [62,84] (“L” in $T_L$ signifies “lock-in”). This is in stark contrast to results from bulk samples of $R$=Lu, Yb and Tm (See Figure 4.11). In the case of bulk, a fixed and commensurate $q = \frac{1}{2}$ value is reported from low temperatures up to $T_C$, and it becomes incommensurate only in the narrow temperature range $T_C < T < T_N$. A second feature observed in Figure 4.17(b) is a sharp change in the trend of $q(T)$ at a temperature a few degrees below $T_N$, which we label $T^*$. I believe this change is an indicator of $T_C$, which I justify because (a) also in bulk $q(T)$ changes its trend at $T_C$, and (b) the values of $T^*$ are in close agreement with $T_C$ values obtained from measurements of the crystal structure distortion on the same samples (see section 4.2.3). Figure 4.17(c) presents the correlation length obtained from the width of the Voigt profile. In most samples such values do not exceed a few tens of nm, however in this sample it exceeds 100 nm (therefore at the measured spot, the sample is probably thicker than the nominal value of 104 nm). Below $T_L$ the correlation length is constant. Between $T_L$ and $T_N$ it shortens with heating at a rate of $\sim 2.8$ nm/K. Above $T_N$ it disappears rapidly, as the intensity is only due to short-range correlations.
Figure 4.17– Characteristics of the (0 q 0) magnetic reflection as functions of temperature. Data are from a 104 nm thick o-LuMnO$_3$ film. (a) The integrated intensity (b) the magnetic modulation vector q and (c) the correlation length. Data were taken using $\pi$ incident light at a photon energy of 643 eV (Mn $L_3$) at $\Psi = 0^\circ$.

Figure 4.18 presents the variations in diffracted intensity as the sample is rotated about the momentum transfer vector $\mathbf{Q} = (0 \ q \ 0)$. The intensities are normalized to the intensity from unpolarized incident light ($I_p + I_s$), which compensates for misalignments errors during sample rotation (for [010] oriented films these errors are small, but the normalization allows easier comparison to data from other samples), and for any inhomogeneity in the sample, which could result in a variation of absolute intensity. We find that for $\Psi = 90^\circ$ and $270^\circ$ the intensities for $\sigma$ and for $\pi$ polarized incident light are equal, while for $\Psi = 0^\circ$ and $180^\circ$ the intensity from $\pi$ is maximal, and that from $\sigma$ is absent. A full inspection of the possible multipolar contributions to the intensity of the (0 q 0) reflection from
the resonant Mn ions in Pbnm is given in Eq. (7.21) of Appendix 0. There it is explicitly shown that any intensity contribution from dipolar order terms (K=1) can only arise from c-axis components, which are absent in the “pure” E-type structure. Indeed, the intensity calculated for an E-type configuration using Eq. (3.33) is exactly zero. Further discussion of the Mn magnetic order is given in the following sections. The solid lines in Figure 4.18 are calculations based on a model for the magnetic structure given there, and are in excellent agreement with the data.

![Figure 4.18 – Azimuthal dependence of (0 q 0).](image)

Figure 4.18 – Azimuthal dependence of (0 q 0). The measurement was conducted on a 200 nm thick o-TmMnO₃ film with incident light tuned to the Mn L₃ edge. The polarization of the light was linear $\sigma$ and $\pi$. Intensities are normalized to the sum of intensity from both linear polarizations.

### 4.2.2 Resonant diffraction at the R ions’ $M_{4,5}$ edges

The R ions’ $M_{4,5}$ absorption edges ($3d\rightarrow4f$ transitions) occur at higher photon energies than the Mn $L$ edges, granting access to additional reflections. Resonant X-ray diffraction at these edges is a measure of the R ions’ unoccupied 4f states (and 4f magnetic moments, when measuring magnetic reflections). It is noteworthy that for the case of Lu$^{3+}$ there are no unpaired 4f electrons, so this section does not apply to o-LuMnO₃. Figure 4.19 presents a scan along the (0 k 0) direction of reciprocal space at the $M_{5}$ absorption edge for o-ErMnO₃ and o-TmMnO₃ samples. A commensurate (0 1 0) reflection, which is forbidden in Pbnm symmetry, is observed due to Templeton and Templeton scattering [78], along with a (0 q 0) reflection that has the same incommensurate $q$ value as the magnetic reflection found at the Mn $L_{3}$ edge. As in the Mn $L_{3}$, the (0 1-q 0) reflection is also absent. The value of $q$ is always in excellent agreement with that of the (0 q 0) measured at the Mn $L$ edges. The ratio between the intensities of the two reflections varies significantly, owing to the different configuration of the 4f electrons in Er and Tm. Appendix 7.3.3 present all possible multipolar contributions to these reflections. Unlike before, (0 k 0) type reflections are not limited to c-axis contributions, although the induced order calculated on the R ions’ sites in Appendix 7.1.2 suggests that only c-axis components exist.
Figure 4.19 – scans along $(0 \, k \, 0)$ at the $R$ ion’s $M_\ell$ edge. (a) Measurement of a 400 nm thick $o$-ErMnO$_3$ film. The $90^\circ$ azimuthal angle causes measurements with $\sigma$ and $\pi$ incident light to produce the same intensity. (b) Measurement of a 400 nm $o$-TmMnO$_3$ film. In this case signals from incident $\sigma$ and $\pi$ light are both shown, as the azimuthal angle $0^\circ$ causes a difference. Both figures are provided to indicate the differences that can occur between different samples: the position and width of the magnetic $(0 \, q \, 0)$ reflection, and the intensity ratio between $(0 \, q \, 0)$ and $(0 \, 1 \, 0)$. Note the absence of a $(0 \, 2q \, 0)$ reflection and a $(0 \, 1-q \, 0)$ reflection. The variation of the background is due to specular reflectivity, as both samples are [010]-oriented.

Figure 4.20 – Energy dependence of $(0 \, 1 \, 0)$ and $(0 \, q \, 0)$ around the $R$ ion edges. The reflection intensities are presented for $\pi$ incoming light only, and were all measured at $\Psi = 0^\circ$. For $o$-YbMnO$_3$ no clear $(0q0)$ was observed, so $(010)$ is shown also for incoming $\sigma$ light. All samples are [010]-oriented and 400nm thick, except the $o$-HoMnO$_3$ film which was 120 nm thick. An inset shows a close up of the Er $M_5$, as in this case intensity from the $M_5$ is clear, even though it is dwarfed by the $M_4$. 
Further proof that these reflections are of different origin is given by their energy dependences, which are very different. Their spectral shape also varies completely from one $R$ ion to another. Figure 4.20 presents the energy dependence of the scattered intensity from $(0 \ q \ 0)$ and $(0 \ 1 \ 0)$ at the $M_4$ and $M_5$ edges of Ho, Er, Tm, and Yb. Only intensity from $\pi$ incident light is shown, as the spectral shape does not vary significantly with incident polarization, only the intensity does (this can also depend strongly on azimuth). The intensity ratio between the reflections also varies from one $R$ ion to another: for Ho and Tm the $(0 \ 1 \ 0)$ is 25-50% more intense than the $(0 \ q \ 0)$, while for Er the difference is an order of magnitude. For the case of Yb, the $(0 \ q \ 0)$ reflection was too weak to be clearly measured. These ratios can be directly compared because they are collected in the exact same experimental configuration.

Apart from $(0 \ q \ 0)$, other magnetic reflections are also obtainable, namely $(0 \ q \ 1)$ and $(1 \ q \ 0)$, all with the same value of $q$ (a $(0 \ 1-q \ 1)$ reflection is absent (at 10 K), and most likely also $(1 \ 1-q \ 0)$, although no extensive search was conducted for the latter). These can, in principle, provide additional information about the magnetic configuration of the $R$ ions’ 4f system (see explicit derivation in Appendix 7.3.3). The magnetic moment of the $R$ ions’ unpaired 4f electrons do not order independently, except at very low temperatures (for example Tm$^{3+}$ ions are expected to acquire independent magnetic order only below $\sim$4K [43,72]). As such all the discussed results are taken at temperatures in which the $R$ ions are paramagnetic. An exception to this is the case of Ho$^{3+}$ ions, which order independently from the Mn below 15 K and will be discussed later. A temperature dependence of the $(0 \ q \ 1)$ reflection measured at the Tm $M_5$ edge is presented in Figure 4.21. The intensity vanishes near $T_N$, indicating that the reflection is from the same origin as the Mn order shown in Figure 4.16. The good agreement in $q$ is further evidence of this. A direct comparison of $(0 \ q \ 0)$ measured at the Tm $M_5$ and the Mn $L_3$ from the same o-TmMnO$_3$ sample in the same experiment is presented in Figure 7.2 and Figure 7.3 in Appendix 7.1. The 4f electrons are not independently ordered, so the observed order must be induced by the mean magnetic field from the Mn moments in the $R$ ions’ crystal environment. As such, the $R$ ions’ order is a measure of this field.

As this is not directly related to the present discussion, a complete account of the induced order is given in Appendix 7.1, including a detailed account of the azimuthal dependence of $(0 \ q \ 0)$ and $(0 \ q \ 1)$.
4.2.3 Non-resonant crystal diffraction

In this section I detail observations from diffraction experiments conducted using hard X-rays, and at energies reasonably far from resonances of the constituent ions in o-RMnO$_3$. In these materials the high magnetic frustration at low temperatures is lifted by distorting the crystal lattice as the ground state magnetic order sets in, resulting in ferroelectricity (in the multiferroic phase). This disturbance is known to lower the crystal symmetry as it breaks inversion symmetry. This is evidenced by the appearance of reflections with miller indexes which are forbidden by the high temperature symmetry (Pbnm). For example, Pbnm allows intensity at positions (0 $k$ 0) and (0 $k$ $l$) only if $k$ is even. Figure 4.22 presents the intensity of (0 5 0) measured as a function of temperature from a 400 nm thick o-LuMnO$_3$ film. Indeed at high temperatures the Pbnm extinction rule is fulfilled, but at low temperatures this rule is broken. The onset temperature of this behavior agrees well with those expected for the transition at $T_C$ [45], and we conclude that this effect is indeed a result of the ferroelectric crystal distortion. This observation was first reported by Wadati et al. in Ref. [84] on a thin film of o-YMnO$_3$. However due to the absence of single crystals, information about this effect is not readily available in literature because non-centrosymmetric crystal structures cannot be refined accurately by powder diffraction. A method to quantify this effect using reflections of type (0 $k$ 0) is presented in detail in Appendix 6.2.1.

![Figure 4.21 – Temperature dependence of (0 q 1) at the Tm $M_s$. The data are from a 400 nm thick, [010]-oriented o-TmMnO$_3$ sample with $\pi$ incident light and $\Psi = 0^\circ$. To access this reflection a 60° wedge was used.](image-url)
Another type of distortion was previously reported for o-RMnO$_3$ with lighter rare earths (Gd-Dy). Refs [36,48,56,75,86,87], all report structural reflections of type (0 2$q$ 0) in which $q$ is the same as in the magnetic reflections (measured using neutrons or non-resonant X-rays). These reflections were observed already in the sinusoidal phase, which is para-electric. This reflection has been interpreted as a result of exchange striction [79], i.e. a slight deformation of the lattice due to the magnetic interaction between neighboring sites. For the case of o-RMnO$_3$ with heavy rare earths, $q$ is $\frac{1}{2}$, which means that (0 2$q$ 0) will coincide with (0 $k$ 0) with $k$ being an odd integer, in other words the same position as the effect presented in Figure 4.22. Indeed no such reflections have been reported for heavy rare earths. In our case it is clear that the (0 $k$ 0) reflections observed (as in Figure 4.22) are not of this origin, as their modulation vector does not vary with temperature, while the magnetic modulation ($q$) does vary, as in Figure 4.17. Nevertheless, if exchange striction is the cause for reflections of type (0 $k \pm 2q$ 0), they should exist in the present study as well. However, as we know $q$ is close to $\frac{1}{2}$, in the presence of the symmetry lowering effect such reflections can be overshadowed by the tail of (0 $k$ 0) reflections with $k$ odd. Figure 4.23 presents two scans along the $k$ direction, from an o-TmMnO$_3$ film and an o-YbMnO$_3$ film (both are [010] oriented and 400nm thick). In these cases a 3-peak feature appears around the (0 5 0), in apparent agreement with this scenario (in some cases the same was observed around (0 3 0)). The side features can then be labelled (0 $4+2q$ 0) and (0 $6-2q$ 0), and it is noteworthy that they appear to vary their position with temperature. Interestingly the (0 2$q$ 0) reflection is absent in Figure 4.19(b), which was recorded at the Tm $M_5$ edge from the same sample. It is important to note that the value of $q$ in these cases is higher than in the RSXD data. This may indicate that $q$ varies within the sample, and the XRD data here is an average of the entire film, while the RSXD data only reflect the top of the samples (due to the limited probe depth, see Appendix D on page 158).
Figure 4.23 – Non-resonant \((0 \, k \pm 2q \, 0)\) satellites. Three-peak features observed around the \((0 \, 5 \, 0)\) reflection from a (a) \(\alpha\text{-TmMnO}_3\) film and a (b) \(\alpha\text{-YbMnO}_3\) film. Both films are 400 nm thick and [010]-oriented. The experiment was conducted with \(\pi\) linearly polarized light. The intensities presented are corrected for the polarization factor.

Ref. [57] details a study of a rare single crystal of \(\alpha\text{-YMnO}_3\), and is in fact the only source of information available about the low temperature structure. The study concluded that the transition at \(T_C\) lowers the crystal symmetry from \(Pbnm\) (space group 62) to \(P2_1nm\) (space group 31). It shows that all ions move away from their positions in \(Pbnm\). Most notable is the change in the Mn positions: in \(Pbnm\) the Mn sit at special sites with high symmetry, but in \(P2_1nm\) their reported positions are entirely general, and they move nearly 0.012 Å away from their \(Pbnm\) positions. It can be shown that even though the unit cell consists of 20 atoms, only 16 parameters are required to describe all 60 (i.e. \(3 \times 20\)) possible Cartesian shifts that occur when symmetry is lowered. These parameters are explicitly given in Appendix 7.2.2. Unfortunately no magnetic diffraction data was presented in Ref. [57]. However, it is worth noting that reflections of type \((0 \, k \pm 2q \, 0)\) were reported in the publication between \(T_N\) and \(T_C\) (i.e. in the sinusoidal phase), and converged to a position equivalent to \(q = \frac{1}{2}\) below \(T_C\). For this reason it is reasonable to consider the low-T structure reported therein as that of a crystal with commensurate magnetic order.

Below and in following sections I use the reported \(P2_1nm\) structure to interpret \(Pbnm\)-forbidden reflections observed in this thesis. To do so, two assumptions must be made:

- For \(\alpha\text{-RMnO}_3\) materials with smaller \(R\) ions, the ions move away from their \(Pbnm\) positions in the same directions as in the \(\alpha\text{-YMnO}_3\) crystal (in fractional coordinates), regardless of the \(R\) ion. This assumption is reasonable because these materials are nearly isostructural [41].
- To first order, the ions’ displacement distance is linear with respect to temperature.

The intensity of \(Pbnm\)-forbidden reflections is weaker in our films than in the \(\alpha\text{-YMnO}_3\) crystal. Based on these assumptions, we can say that the crystal distortion effect is weaker in our films than in the \(\alpha\text{-YMnO}_3\) crystal, so the the displacement of the atoms away from their \(Pbnm\) position is shorter
(as a fraction of the lattice coordinates). This is supported by the theoretical prediction that compressive \(ab\) strain weakens the contribution of ionic displacements to the macroscopic polarization \(P\) [80].

One can now interpolate between the high and low temperature structures. Based on the intensity measured from different Bragg reflections, an estimate of the whole crystal structure can be made. This approach and the associated calculations are presented in detail in Appendix 7.2.2. As an example of this, we follow the positions of the Mn ions in a film of \(\alpha\)-LuMnO\(_3\). Figure 4.24 presents the integrated intensity measured from the (054) and (044) reflections upon warming. We note that these reflections differ from the (0 \(k\) 0) previously discussed, as they are sensitive to distortions along 2 directions, so motion along an individual axis cannot be disentangled. Nevertheless using the present method, the shifts of all ions can be calculated. The shifts of the Mn ions are presented in the figure as functions of the ratio between the two reflections (shift parameters of all ions are presented in Figure 7.14 in Appendix 7.2). The maximal measured ratio is \(~0.95\%\) (at 10 K), corresponding to a maximal shift of \(8.5 \times 10^{-4}\)Å along the \(b\) axis. For comparison, at 21 K the ratio in the \(\alpha\)-YMnO\(_3\) crystal of Ref. [57] reaches \(~11\%\), which corresponds to a \(1.2 \times 10^{-2}\)Å shift along \(b\). The same shift in \(\alpha\)-LuMnO\(_3\) would result in an 6% ratio due to the different form factor of the \(R\) ion.

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**Figure 4.24 – Calculation of ionic shifts.** (a) integrated intensity from the (054) and (044) charge reflections, taken at 10.8 KeV. (b) The shifts of the individual Mn ions as functions of the ratio between the two reflections. Data were taken from the same sample as in Figure 4.22, and the incident light was linearly polarized at an angle to the scattering plane. Intensities were corrected for the polarization factor.
4.3 Effects of epitaxial strain on multiferroic properties

The previous section dealt with presenting the quantities that we can observe in our experiments. In this section, we use these to explore how strain can affect the magnetic and electric behaviors observed. Most of the results presented in this section are reported in Refs. [81] and [82].

4.3.1 Epitaxial strain

Before using epitaxial strain as a parameter, a brief discussion of its behavior is necessary. As this is a research topic of its own, I only touch the key issues required for the present context. Epitaxy is a term used to describe the growth of one material on a crystal of another. This usually refers to growth of a film on a substrate. The film itself can often grow as a single crystal if its crystal structure is close to that of the substrate (more specifically - the substrate’s crystal spacing at the interface surface should be close to spacing along a crystal direction in the sample material). An exact match is rare, which means that the film crystal is usually distorted with respect to the bulk crystal. This is comparable to permanently compressing or stretching the film anisotropically (most pressure-based studies apply isotropic pressure), which can change electronic properties, such as magnetic anisotropy. Strain is a term used to quantify the deviation of the film’s crystal from the nominal bulk crystal. It is usually defined to express the compression or expansion of a lattice constant. In this work we adopt the convention:

\[ \eta_x = \left( \frac{x_{bulk} - x_{film}}{x_{bulk}} \right) \]

(4.8)

Here \( \eta_x \) represents the strain along the \( x \) axis. Positive numbers indicate compressive strain, negative numbers indicate tensile strain.

The study of perovskites makes extensive use of epitaxy, owing to the fact that completely different materials have similar crystal structures, and can thus be grown on each other. In the study of \( \text{o-RMnO}_3 \) films, epitaxy is an essential tool. This is because the absence of high-quality crystals renders this method the only way to study bulk-like samples. Nevertheless strain is still present, even in highly relaxed films. Ref. [82] details how strain propagates through \( \text{o-RMnO}_3 \) films (the same films studied in this thesis). Unlike other materials, \( \text{o-RMnO}_3 \) films grow in two layers. A thin (<30nm) layer grows at the interface with the substrate, and is highly strained because it is locked to the substrate. A discontinuity occurs above a threshold thickness of \( \sim 30 \) nm, above which the rest of the film grows as the second layer. The second layer is partially relaxed towards bulk values, and is not strongly bound to the substrate crystal. This scenario is in contrast to other materials, in which strain gradually relaxes through a gradient parallel to the film normal. Figure 4.25 is an excerpt from Ref. [82], which nicely presents the present scenario. Panel (d) presents a sketch of the cross-section of such a film, indicating the two layers. Panels (b) and (c) present the evolution of two structural reflections as functions of the film thickness. They demonstrate that up to a thickness of 32 nm the
film’s in-plane lattice directions are locked to the substrate (in this case the [010] is out of plane), and when it is thicker, it deviates towards bulk values. This behavior is summarized in panel (e). It should also be emphasized that strain is not directly controlled in this study, it is evaluated for each film individually. This is in contrast to other studies in which strain is directly manipulated, such as Ref. [83] and [84].

The two following sections are divided based on the model of Ref. [82]. Section 4.3.2 deals with results attributed to the partially relaxed top layer, while section 4.3.3 deals with effects associated with the highly strained bottom layer.

![Image](image.png)

**Figure 4.25**- Strain relaxation in o-RMnO$_3$ films, from Ref. [82]. All films here are [010]-oriented o-HoMnO$_3$ (HMO) grown on YAIO$_3$ (YAO). (a) specular ($\theta/2\theta$) scan of a 400 nm HMO film. (b) and (c) Reciprocal space maps around the (130) and (041) reflections (respectively) of HMO films of various thicknesses. A white marker indicates the position for bulk HMO. (d) Schematic side-view of the relaxed and the strained layers of the film. (e) Lattice parameters of HMO films (open symbols: strained layer, closed symbols: relaxed layer) derived from (b) and (c). Horizontal solid and dashed lines indicate the values of HMO [85] and of YAO [86] respectively. Figure courtesy of Kenta Shimamoto, PSI.

### 4.3.2 Multiferroic properties under partially relaxed strain

In this section I discuss o-LuMnO$_3$ films that are thick compared to the 30 nm threshold thickness mentioned above. Results are attributed to the top (partially relaxed) layer of the films only, because X-rays have limited penetration/probe depths. My confidence in this argument is extremely high for RXD results, as the probe depth of X-rays at the Mn (and $R$ ion) absorption edges does not exceed 20-30 nm at best (See Appendix D on page 158). For XRD data taken with hard X-rays (in the range ~8 to ~11 KeV), probe depths exceed the film thickness, so results are definitely sensitive to the lower (highly-strained) layer as well. This can affect the integrated intensities and the measured epitaxial
strain (inferred from measured lattice constants). However, as I explain below, this is likely to produce only small errors. The effect on the measured lattice constants (and hence on strain values) can be easily avoided because the same reflection from the two layers (i.e. the same Miller indexes) appears at positions that are well-separated in real space, and they are differently shaped.

The buried layer’s effect on collected intensities from the top layer is also small. This is due to its small volume with respect to the thick layer (the thinnest film discussed here is 78 nm thick), and because the X-rays are less sensitive to this volume since they exponentially decay in the thick layer before reaching it. This is relevant because most incident angles used are around 5°, so the attenuation length can be comparable to the film thickness at ~10 KeV. Furthermore, as the positions of the same reflection from the two layers are well-separated, the erroneous contributions to intensity from the buried layer will arise only from the foot of the buried layer’s reflection, not from its peak.

**Figure 4.26 – strain dependence of the lattice distortion.** (a) the average ionic displacement along the $b$ direction ($\delta_b$, calculated according to Appendix B in section 7.2.1) as function of temperature, from three differently strained films of $\alpha$-LuMnO$_3$. Samples: triangles indicate [110]-oriented films ($\eta_b$ = 0.19 and 1.18% correspond to 200 and 90 nm thick films, respectively), circles indicate a [010]-oriented 104 nm thick film. (b) Contributions to polarization from some of the films studied in this section from first-principles calculations, as functions of $b$-axis strain. The ionic contribution (“point charge model”) reduces with compressive $b$-axis strain, in agreement with the experimental data in panel (a). Calculations in Panel (b) were provided by Christof Findler, Natalya Fedorova, and Prof. Nicola Spaldin (ETH Zurich).

For each film the strain values in each direction were evaluated using Eq. (4.8). A clear correlation to thickness was not observed for any measured quantity, perhaps since both [010] and [110] oriented films were studied. Clear correlations were observed to the strain along the $b$ axis. Curiously, the $c$-axis strain remains at ~ -1% in all films, and does not appear to relax, whereas the $a$-axis strain varies but remains small.

The lattice distortion was followed in a number of films using Pbnm-forbidden charge reflections of type $(0 \ k \ 0)$. The average ionic shift in the $b$ direction $\delta_b$ (which is the axis with the largest shifts
away from Pbnm) was evaluated using the phenomenological model described in Appendix 6.2.1. Figure 4.26(a) presents $\delta_b$ as function of temperature from differently strained films. The lowest temperature reached in this experiment was $\sim$20 K. The value of $\delta_b$ (at 20 K) grows significantly as $\eta_b$ is reduced. Indeed it has been recently predicted that reducing compressive $ab$-strain increases the contribution to $P$ arising from ionic displacements [38]. Using the measured strain values of the same films, a first-principles calculation was conducted by our colleagues at the Materials Theory group (in ETH Zurich) to estimate the contributions to polarization. This is presented in Figure 4.26(b). Indeed the ionic contribution to $P$ lowers with compressive $b$-axis strain, which correlates to the smaller distortion shown in Panel (a). Interestingly though, the total polarization increases due to the electronic contribution.

The magnetic order, followed by the $(0 \ q \ 0)$ magnetic reflection, is also affected by $b$-axis strain. A systematic variation is observed in the deviation of $q$ from its locked-in value near $\frac{1}{2}$. To demonstrate this, we align the temperature dependences of $q$ from different films with each other by calculating the deviation as $\Delta q = q(T) - q(T_L)$. This is necessary as the locked in value of $q$ below $T_L$ is not the same for different films, and in fact does not reproduce well in subsequent cooling cycles. This is consistent with the Monte Carlo simulations in Ref. [35] that predict deep minima on the energy landscape of the ordering wave vector near $(0 \ 0 \ 0)$. $\Delta q$ is presented in Figure 4.27(a) for differently strained films.

**Figure 4.27 – The effect of strain on Mn magnetic order** (a) temperature dependence of $\Delta q$, the deviation of $q$ from the locked in value below $T_L$, measured from differently strained films (labelled by their $\eta_b$ value at low temperature). $T^*$ values are marked by ticks. Inset: the value of $\Delta q$ at $T^*$ as a function of $\eta_b$. (b) Intensity of $(0 \ q \ 0)$ (in logarithmic scale) as a function of $\Delta q$, from the same datasets as in panel (a), from the temperature range $T_L < T < T^*$. Inset: $\alpha$ and $\beta$ parameters as functions of $\eta_b$. Lines are guides for the eye. Samples: triangles indicate [110]-oriented films ($\eta_b =0.19$ and $1.18\%$ correspond to 200 and 90 nm thick films, respectively), circles indicate [010]-oriented films ($\eta_b=0.32$, $0.55$ and $0.88\%$ correspond to 78, 104 and 26 nm thick films, respectively). The 26nm film does not fill the thickness criterion (see main text), but as it behaves like a partially-relaxed film, it is included here.
A second observation was made in the temperature range $T_L < T < T^*$: a phenomenological relation exists between the integrated intensity $I(T)$ and the change magnetic modulation $\Delta q(T)$. The relation follows $I(T) = \exp(\alpha \Delta q(T) + \beta)$, and is satisfied in all tested films, as shown in Figure 4.27(b). Since intensity of the $(0 \ q \ 0)$ reflection is sensitive only to $c$-axis magnetic moments (see Eq. (7.21)), the parameter $\beta$ is a measure of the magnitude of Mn spins’ canting towards the $c$-axis. As it is believed that the magnetic order is an E-type, $\beta$ relates to a canting angle of the Mn moments away from the main moment direction, which is along the $b$ axis. However, as no other magnetic reflection can be accessed at the Mn $L$ edges, the angle cannot be quantified from the data. $\alpha$ is a parameter that relates the $c$-axis moment to the incommensurability of the magnetic modulation, and is a positive number.

A definite interpretation of this effect is not available. However, a simple approach could involve interference between different parts of the sample. If interference effects are not considered, the temperature dependence of $(0 \ q \ 0)$ should simply follow that of an order parameter (squared). The observed relation with $q$ means that as order strengthens/weakens, the modulation of this order shrinks or expands. The $\alpha$ and $\beta$ parameters are also found to depend on $b$-axis strain. This is shown in the inset of Figure 4.27(b). The $c$-axis moment is expected to grow with $\beta$, which grows as $\eta_b$ is reduced. However, $\alpha$ (the ICM contribution) is enhanced by larger values of $\eta_b$, indicating that the proposed canted E-type structure is destabilized by compressive $b$-axis strain. This is supported by the trend in the size of $\Delta q(T^*)$ which increases approximately linearly with $\eta_b$ (inset of Figure 4.27(a)).

4.3.3 The effect of high strain

This section deals with films of o-$R$MnO$_3$ which are thinner or comparable in thickness to the threshold thickness of 30nm. As such, these results are attributed to the highly-strained thin layer which is fixed to the substrate. We will deal here with a number of specific cases that underline each observed effect.

The first case is that of TbMnO$_3$. While it is nearly isostructural to our heavy-$R$ materials [85], o-TbMnO$_3$ bulk crystals are not rare, but commonly grown. It is known to acquire a $bc$-cycloid order of the Mn moments [48], which does not necessarily behave according to the descriptions in section 04.1.2. Most notably the azimuthal angle dependence of $(0 \ q \ 0)$ differs from that presented in Figure 4.18 (see Ref. [87]), and a ~15 K gap exists between $T_N$ and $T_C$ (see Figure 4.6). Figure 4.28 presents scans along the $(0 \ k \ 0)$ direction taken at 10 K with photon energies at the Mn $L$ edges. Data are taken from a 10 nm thick [010]-oriented film and from a single crystal. In both cases an azimuth of $\Psi = 0^\circ$ was used ($a$ axis in the scattering plane). Integrated intensity and $q$ are both presented as functions of temperature in panels (b) and (c). Clearly a significant difference is observed between the wave vector of the film ($q \approx 0.45$) and bulk ($q \approx 0.28$). Furthermore, intensity from $\sigma$ incoming light is completely suppressed, as in our heavy-$R$ films, while in bulk it is only partially suppressed, as
expected at this azimuth. We thus conclude that the high strain has pushed TbMnO$_3$ from the well-known cycloidal structure, towards the heavy-$R$ structure.

The integrated intensity in bulk TbMnO$_3$ (using π-polarized incoming light) exhibits a two-jump profile, expected from the appearance of one order parameter at $T_N \approx 40K$ and another at $T_C \approx 25K$. Interestingly, the integrated intensity from the film appears at $T_N$ and it does not exhibit the second jump, but instead it exhibits a maximum near the $T_C$ value of bulk.

Unlike the partially-relaxed films, in which $b$ was compressed, this film experienced tensile strain of $\eta_b = -0.385\%$ along $b$. The in-plane lattice constants were not resolved in the experiment, but as it is only 10 nm thick, adopting the substrate’s in-plane lattice constants for this film is reasonable. Indeed we find that, in combination with the measured tensile out-of-plane strain, the unit cell volume reduces by $\sim 3.1\%$ from bulk TbMnO$_3$. The strain values we calculate are $\eta = (2.137\%, -0.385\%,$
The largest effect is compressive strain along the $a$ axis, in agreement with the observations of Ref. [82] (see also Figure 4.25).

The second case I present is that of o-ErMnO$_3$. According to the phase diagrams of Figure 4.6, this material is expected to acquire the E-type magnetic phase. This is because it exhibits equally high electric polarization values, and because Er is a heavier lanthanide than Ho (o-HoMnO$_3$ has been often considered an E-type material). However, bulk o-ErMnO$_3$ does not, in fact, acquire a commensurate magnetic structure, but a value of $q \approx 0.43$.

Figure 4.29(a) presents scans along the (0 $k$ 0) direction taken at 10 K with photon energies at the Mn $L_3$ edge and $\pi$ incoming polarization. Data are taken from two [010]-oriented films: a 400 nm thick film and a 38 nm thick film (corresponding to the relaxed layer, and the highly-strained layer, respectively). In both cases an azimuth of $\Psi = 0^\circ$ was used. The magnetic (0 $q$ 0) reflection was observed for both films, and panels (b) and (c) present its integrated intensity and $q$ value as functions of temperature. The relaxed film exhibited the expected bulk value of $q \approx 0.43$. As in the previous case, the wave vector of the highly strained film is shifted away from the bulk value, but this time it is shifted to the commensurate value of $q = \frac{1}{2}$. The films also differ in the temperature dependence of $q$. For the relaxed film $q$ varies with temperature, as observed in other films. However, the strained film exhibits a fixed $q = \frac{1}{2}$ value up to $T^*$. This behavior matches that of bulk commensurate structures, as shown in Figure 4.11, in which $q$ remains locked at $\frac{1}{2}$ up to $T_c$, above which it unlocks.

Non-resonant XRD experiments were conducted on these two films using photon energies of 9 keV, as described in section 4.2.3. The strain values were calculated for the thick film as $\eta_{thick} = (0.08\%, 0.40\%, -0.32\%)$ and for the thin film as $\eta_{thin} = (1.26\%, -0.09\% - 0.33\%)$. As in the previous case, the dominant strain term in the thin film is the $a$ axis. For each film, charge reflections of the form (0 $k$ 0) were followed with temperature. As an example of this, Figure 4.29(d) presents the (0 5 0) reflection collected from the highly-strained film. Using even and odd $k$ values, the crystal distortions of the two films were calculated using the method described in Appendix 6.2.2, the crystal distortion was calculated (i.e. the ionic shifts of all ions from their Pbnm positions). As an example, the shifts of the Mn ions along the $b$ axis are presented in Panel (e). Clearly the symmetry lowering effect is larger in the thinner film, as is expected from o-RMnO$_3$ with a commensurate magnetic structure. We conclude that the high $a$-axis strain exhibited by the thin film causes the ferroic behaviors to favor the heavy-$R$ behavior (commensurate magnetic order and high crystal distortion).
Figure 4.29 – Magnetic order and crystal distortion in strained and relaxed o-ErMnO$_3$. (a) Reciprocal space scans along (0 k 0) taken using π polarized incoming light at the Mn L$_3$ edge. Data were taken from 38 nm and a 400 nm thick film (both [010]-oriented) at Ψ = 0°. (b) and (c) the magnitude of $q$ and integrated intensity of the (0 q 0) reflection, respectively, as functions of temperature. (d) Scans along (0 k 0) using 9 KeV photon energy, measured at different temperatures from the 38nm film. (e) Calculated displacement of Mn ions along the b axis from both films. Calculations were done using collected intensities from (0 5 0) and from a Pbnm-allowed reflection (For the thin film (0 4 0), for the thick film (0 2 0)). The inset is a sketch of the displacement.

The last case in this section deals with films of o-HoMnO$_3$. The behavior of this material is discussed in greater detail in Section 4.4. Most important to remind here is that it acquires a relatively weak polarization below $T_C$. However, at ~15 K it undergoes a second transition due to magnetic ordering of the Ho$^{3+}$ ions. The electric polarization is significantly enhanced below 15K, which is then comparable to the polarization of commensurate o-RMnO$_3$ materials.

The following results were reported on in greater detail by Shimamoto et al. in Ref. [82]. As in the previous two cases, we deal here with a thin and thick films of o-HoMnO$_3$, and as in the previous two cases, scans along (0 k 0) were conducted at the Mn L$_3$ edge, with the two films under the same conditions. $q$ values as functions of temperature are presented in Figure 4.30(a) for 32 nm and 120 nm
thick films, both [010]-oriented. The $q$ value of the highly strained film is shifted from the bulk value of $\sim 0.41$ to the nearly commensurate value of $\sim 0.49$.

A second experiment was conducted by Shimamoto et al. to measure the electric polarization of thick and thin films. Figure 4.30(b) presents the electric polarization of these films as functions of temperature. The thick 200 nm film exhibits weak polarization down to $\sim 20$ K, under which it rises to high values, in reasonable agreement with bulk. The 20 nm film however, exhibits the same high values of polarization directly below $T_C$, as expected from the commensurate o-RMnO$_3$ materials (the kink at $\sim 20$ K is due to experimental limits).

It is thus concluded that the high strain experienced by the film does not only enhance the ordering wave vector, but changes the behavior of the ferroelectric ordering.

Figure 4.30 – Magnetic order and ferroelectric polarization of o-HoMnO$_3$ in strained and relaxed films, from Shimamoto et al. in Ref. [82] (a) the temperature dependence of the magnetic ordering wave vector, acquired from measurements of the (0 $q$ 0) reflection at the Mn $L_3$ edge, with $\pi$ polarized incoming light and $\Psi = 0^\circ$. Insets present examples of scans along (0 $k$ 0) for each film at $\sim 10$ K. (b) Temperature dependence of effective polarization $P_{\text{eff}}$ of a 20 nm and a 200 nm thick film (both are [010]-oriented). Data were derived from FE hysteresis curves using a field of $E = 47$ kV cm$^{-1}$. A part of the FE hysteresis curve is shown in the insets.
4.4 The specific case of o-HoMnO$_3$

In this section I focus on the case of o-HoMnO$_3$, which is not strongly related to the main theme of the rest of this chapter. This material sits at the boundary of the heavy-$R$ group (see Figure 4.6 and Figure 4.9), and its magnetic ordering wave vector acquires the value $q \approx 0.41$ [67] (not far from o-DyMnO$_3$, which acquires a cycloidal magnetic order with $q \approx 0.36$ [89]). Furthermore, the $P$ values it acquires below $T_C$ are comparable to those from DyMnO$_3$ and TbMnO$_3$, which are $\approx$10 times weaker than the heavy-$R$ materials. Most notably, this material differs from the other heavy-$R$ materials because it undergoes a second magnetic transition within its multiferroic phase, in which the Ho$^{3+}$ ions order independently. Ref. [67] and [90] claimed that this ordering occurs at 11K and 15K, respectively. Ref. [54] observed Ho$^{3+}$ order already below $\approx$22K, and claimed a significant growth in intensity below 9 K. It is notable that the latter study does not agree with the former two (nor with our study), as it claimed that the Mn order locks in at a commensurate $q = \frac{1}{2}$ value (instead of $\approx$0.41).

The most notable feature of the Ho transition was reported in Ref. [90]: at $\approx$14.5K the electric polarization of the material grows by an order of magnitude, to values typical of the E-type phase (this is not accompanied by a lock-in of $q$ at the typical E-type value of $\frac{1}{2}$). That study differed from previous studies because it studied a single crystal of the material, and not a polycrystalline/powder sample. The effect of $R$ ion order on macroscopic polarization was also shown for the case of Dy [91], although in that case the result was not a clear increase of $P$. Here I detail the study of thick films of this material grown in [010]-oriented NdGaO$_3$ substrates. These are expected to behave like crystalline bulk, as they are only weakly strained and exhibit comparable magnetic order (as shown in the following).

![Figure 4.31 - Crystal distortion in a film of o-HoMnO$_3$. The films is 240nm thick and [010]-oriented. (a) rocking curves of the (033) reflection taken at various temperatures. (b) Integrated intensities of the (022) and (033) reflections, as functions of temperature. Intensity values are comparable.](image)

We begin with a structural distortion. This was followed in a 240 nm thick [010]-oriented sample. Rocking curves around the (033) reflection are presented in Figure 4.31(a) for different temperatures. Integrated intensity from the (033) and the (022) reflections are presented in panel (b). The distortion due to the Mn ordering is clearly apparent, as the (033) intensity increases and the (022) intensity...
decreases below ~39 K. However, the Pbmn-forbidden (033) reflection is already present above the Mn ordering. This is mostly likely due to a small monoclinic distortion, and is indeed on the same order as the magnetically-induced distortion, which is known to be very small. For this reason I do not attempt to calculate the ionic shift. Nevertheless, the monoclinic distortion does not appear to interfere with the ferroelectric distortion, whose temperature dependence remains linear. We note the absence of a clear signature from an additional transition within the probed temperature range, which may indicate that the rise in polarization is purely electronic, and not due to an enlarged ionic displacement.

Next we focus on the (0 q 0) magnetic reflection, measured at the Mn L3 and the Ho M5 edges. As discussed in detail in Section 4.2 and Appendix 0, the Mn (0 q 0) reflection is sensitive only to the c-axis component of Mn moments, while the Ho signal can be sensitive to all components of the Ho moment (see Appendix 7.3.3). However, the Ho order is initially expected to only be an induced order. This induced order was shown to acquire magnetic moments only along the c axis (see Appendix 7.1.2). Panels (a,b,c) of Figure 4.32 present the integrated intensity, q value and correlation length as functions of temperature. The integrated intensities do not exhibit clear evidence of Ho ordering: the Mn signal appears as a saturated order parameter, and the Ho signal exhibits a near-linear profile, typical of the induced order from the Mn (see Appendix 7.1). A kink in the Mn signal is seen around 23K (discussed below). The q value and the correlation length, however, show a clear change in trend around ~15 K. The temperature at which this is observed is 1K-1.5K higher at the Ho edge than at the Mn edge. This was concluded by a best fit of the data around the transitions in panels (b) and (c) to 2nd degree polynomials5. To better illustrate the effect of this transition on the Mn, panel (d) shows a color plot of the raw (0 q 0) data taken at the Mn edge as a function of temperature. One clearly observes the widening and weakening of the reflection, as well as the change in position.

The clearest indication of the transition is apparent in reciprocal space scans along (0 k 0). These are presented in panel (e) at the Ho and Mn edges, and were taken at 8 K: a (0 1-q 0) reflection appears at the Ho edge (due to missing data at the Mn resonance it is not clear if this reflection exists there too). This indicates a difference in symmetry between the two orders, because the Mn order produces satellites of (0 k 0) reflections with even k only (as does the induced order on the R site, as shown in Figure 4.19). The temperature dependences derived from this reflection are shown alongside those from the (0 q 0) in panels (a,b,c).

5 To eliminate experimental artifacts between the Ho and Mn (0 q 0) signals, the two signals were measured in the same temperature sweep and in the same spectral geometry. The sample was glued directly onto the cryostat with silver paint, so beam-heating effects are not expected.
Figure 4.32 – Magnetic (0 q 0) and (0 1-q 0) reflections measured at the Ho and Mn edges. Data are taken on a 120 nm thick [010]-oriented film grown on NdGaO₃. Panels (a), (b) and (c) present the integrated intensities, correlation lengths and q values as functions of temperature. Measurements were conducted at the Mn L₃ (642.5 eV) and the Ho M₅ (1349.75 eV) with incident π polarized light and Ψ = 0° as function of temperature. Intensities from the Ho resonance are directly comparable in panel (a). Vertical lines indicate the appearance of the (0 q 0) reflection at the Mn edge and the (0 1-q 0) at the Ho edge. The solid lines near 15K in panel (c) are best fits to 2nd degree polynomials. (d) Original data from the (0 q 0) reflection at the Mn edge, shown to highlight the transition. The color scheme represents X-ray intensity, and the axes denote temperature and 2θ values (k). (e) Reciprocal space scans along (0 k 0) taken with π polarized light with photon energies at the Ho and Mn resonances, at 8K and Ψ = 0°. (f) Azimuthal scan around (0 1-q 0) at 10 K. Signals for incoming π and σ light are presented, and are normalized by the sum of the two signals.

It is noteworthy that the (0 q 0) signal at the Ho edge does not appear affected from this transition (see Panel (a)). This could indicate that the additional order parameter is a weak contribution to the reflection, compared to the preexisting induced order (at least at this azimuth). An azimuthal scan taken at 18K around (0 q 0) is presented in Figure 4.33, alongside a calculation of the expected azimuthal dependence of the induced order (solid lines). It is nearly identical to the scans shown in Figure 7.5 and in Figure 7.15. In this case small deviations from the calculation (solid lines) are clearly visible, albeit small (note that this scan was taken at T > 15K). The structure factor for this
type of reflection is calculated in Eq. (7.25). It shows that the reflection is, in principle, sensitive to all dipole components (K=1). Inspection of the prefactors indicates a preference for the $\langle T^{2}_1 \rangle$ terms over the $\langle T^{2}_2 \rangle$ (i.e. c moment components are dominant over a and b moment components). This is specifically because Ho 4c sites are defined by the crystallographic parameters $x$, which is small ($x \approx 0.08$). An azimuthal scan around (0 1-q 0) is presented in Panel (f) of Figure 4.32. Direct comparison to the azimuthal scans around (0 q 0) indicates that a different components is probed.

For further inspection of the Ho order, off-specular reflections were also investigated at the Ho $M_{5}$. Figure 4.34 presents data taken from the (0 q 1) and (0 1-q 1) reflections. Panels (a) and (b) present reciprocal space scans taken at 10K and an azimuth of $\Psi = 0^\circ$ (a axis in the scattering plane). The scans were taken with $\sigma$ and with $\pi$ polarized incoming light, and different dichroism was observed for the two reflections. Panel (c) presents the temperature dependence of the two reflections, taken with $\pi$ polarized light. Unlike the specular reflections, here two transitions are observed within the multiferroic phase. The (0 q 1) appears with the Mn order at $T_N \approx 38K$, and is initially only due to the induced order. At $\sim 23$ K the slope of the (0 q 1) intensity rises significantly, and the (0 1-q 1) appears (the kink in the Mn and Ho (0 q 0) reflection was also at 23 K). At 16 K both reflections increase sharply, concomitant with the appearance of (0 1-q 0) at this temperature.
Figure 4.34 – the (0 q 1) and (0 1-q 1) reflections measured at the Ho edge. (a) and (b) present reciprocal space scans along the ordering wave vector of the (0 q 1) and (0 1-q 1) reflections, respectively. The data were taken at 1348 eV (Ho M₅) with σ and π polarized light at 10K, with the sample oriented such that the a axis is in the scattering plane (Ψ = 0°). The intensities are comparable, as mismatch between the two reciprocal space vectors is only ~8.5°. (c) temperature dependence of the two reflections in the same configuration, measured with π incident polarization.

These data shed new light on the Ho order. Unlike for the case of Tb order in TbMnO₃, here the relation 3q₁ - q₂ₐₙ = 1 is not obeyed, as indeed predicted by Ref. [92]. Clearly both the reported transitions occur, although different reflections are sensitive to them.

- At 38 K the Mn ions order, inducing an order on the Ho ions.
- At ~23 K a transition occurs, which involves satellites of (0 1 1). As the effect of this order on the Mn appears negligible, it is reasonable to assume that it is not along the c direction, since it is along this axis that the Mn-Ho dipolar interaction induces the Ho order already at higher temperatures. This Ho component could explain the deviations observed at 18K in Figure 4.33 (deviations of the Ho (0 q 0) azimuthal dependence order calculation).
- At 15K the appearance of satellites around (0 1 0) indicates that another contribution to the Ho order occurs. This time a strong effect is observed on the Mn, and is therefore most likely due to a second contribution to Ho moments along the c direction. Indeed the (0 1-q 0) reflection strongly prefers components along the c direction (due to the same prefactor as in (0 q 0)), and is too weak to measure above ~15K, even if non-c axis components do contribute to it.

It is worth reminding that the (0 q 0) reflection measured at the Ho edge is sensitive to the main (0 q 1) order on the Mn, and not just the DMI-induced (0 q 0) Mn spin canting. This direct link is most likely a driving force for an increase of exchange striction in the Mn-Mn ab planes, and thus a larger contribution to $P_3$ (see section 4.1.3.2).

[79]
4.5 Monitoring the ferroelectric state

In this section I describe an experiment conducted to follow the ferroelectric state of our film. This is not strongly related to the main theme of the rest of this chapter.

The appearance of a (non-resonant) structural reflection that is forbidden by Pbnm, as in section 4.2.3, is a clear indicator of the multiferroic phase (specifically: it indicates the lowering of crystal symmetry), but it is not an indicator for the state of ferroelectric (FE) polarization. For this, the reflection in question must be sensitive to the distortion along the direction of the polarization. Contrast to the FE state of the system can be accessed through Friedel pairs. In the context of this thesis, a Friedel pair is a pair of reflections of type $Q$ and $-Q$ (i.e. with $(hkl)$ and $(\bar{h}k\bar{l})$ Miller indices). When inversion symmetry is lost, the intensity of one does not necessarily equal that of the other. This is a consequence of the imaginary part of the X-ray form factor $\Im(f)$, which interferes with the phase factor, such that $\left|\sum_i f e^{2\pi i Q \cdot r_i}\right| \neq \left|\sum_i f e^{-2\pi i Q \cdot r_i}\right|$ can occur. This effect is often quite small, as the Friedel pairs are usually close to each other in intensity, and $\Im(f)$ is usually small compared to $\Re(f)$.

The samples in this study are films (grown on substrate crystals), so observing both reflections in a Friedel pair is not feasible because one will always be blocked by the substrate. However, as the intensity difference between them reflects the ferroelectric distortion, upon ferroelectric switching the intensity of one of the pair should switch to that of the other. In other words, if the intensity of $I(Q)$ is monitored, and polarization is reversed, the observed intensity should change to that of $I(-Q)$. In the following I describe a measurement utilizing this effect. Similar experiments were reported in Ref. [93] and Ref. [94].

The first step is to identify reflections in which the intensity contrast of the Friedel pair is large. We define a contrast parameter $\delta$ to quantify the magnitude of the effect:

$$\delta = \frac{|I(Q) - I(-Q)|}{\max(I(Q),I(-Q))}$$

Here $I(Q)$ is the expected intensity from a reflection $Q$, neglecting polarization and Lorenz factors (i.e. just the form factor squared). As the effect relates to $\Im(f)$, the contrast is strongly energy dependent. Figure 4.35 presents a calculation of the energy dependence of two reflections: (050) and (160) from ErMnO$_3$. Lattice parameters used are those of the 38 nm ErMnO$_3$ film presented in section 4.3.3 (Figure 4.29 on page 73). The calculation is done for the high and low temperature structures reported in Ref. [57] (Pbnm and P2$_1$nm, respectively). A complete account of the structural distortion and the use of P2$_1$nm, is given in Appendix 7.2.

The (160) reflection, and its Friedel counterpart, are presented in Panels (a) and (b) as function of photon energy. The contrast $\delta$ is shown for each case. While this reflection is not forbidden by the
Pbnm extinction rules, it shows very strong contrast: in Pbnm we calculate $\delta = 0$, but in P2$_1$nm the contrast reaches tens of percent. The (050) reflection is forbidden by the Pbnm extinction rules, and is allowed in P2$_1$nm. However as it possesses a component only along $b$, it is not sensitive to the FE state (which is perpendicular to $b$). Therefore (050) is only sensitive to the lowering of crystal symmetry, but not to the FE state.

![Figure 4.35 – Simulated Friedel pair contrast](image)

Top panels present intensity from a pair (Q and $-Q$), lower panels present the contrast parameter $\delta$, both as functions of incident Photon energy. (a) Pair of (160) in P21nm symmetry. (b) Pair of (160) in Pbnm symmetry, exhibiting no contrast. (c) Pair of (050) in P21nm (no contrast).

These two separate indicators provide an ideal setting for an experiment, provided that these reflections are accessible. To ensure this, we conduct the following experiment on the thin (38nm) ErMnO$_3$ sample in Figure 4.29, in which the intensity ratio between (050) and (040) is large at low temperatures. From Figure 4.35 we expect the (160) reflection to be weaker than (050) (at ~10K).

![Figure 4.36 – Experimental setup for Friedel pair experiment](image)

The schematic represents the experiment, depicting a thin film with poled contacts applying an E-field (along the $\hat{a}$ axis), and an X-ray beam probing a spot between them. The picture is of the sample during the experiment at BM28. Here multiple contacts are seen on the surface.
We now aim to control the Friedel pair contrast by means of an electric field. To follow this effect, the variation in intensity of these reflections must be followed in a uniformly poled region of the sample. For this, a pair of 400nm gold contacts was deposited on the sample surface, separated in the [100] direction by a gap of 500 $\mu$m, as shown in Figure 4.36. This configuration allows us to apply an electric field along the $a$ direction of the crystal.

Unlike the other experiments presented in this thesis, this experiment was not conducted at the SLS, but at beamline BM28 at the ESRF, because of their ability to apply strong electric fields (up to 10 KV) during a hard X-ray diffraction experiment (at low T). 10KeV light was used, which is just above the Er $L_1$ edge, to ensure good Friedel pair contrast. The X-ray beam was cut down to 50$\mu$m width, which is small compared to the 500$\mu$m gap between the contacts. For every reflection, a scan along the surface was conducted in diffraction geometry to ensure that the beam does not overlap with the contacts.

The sample was cooled from 60K to 10K under electric fields of $E = \pm 20KV/cm$. Three successive field-cooling cycles were conducted to ensure reproducibility: $+E$, $-E$, $+E$. Figure 4.37 presents integrated intensities from (050) and (160) from these three cycles.

![Figure 4.37 – Temperature dependence of intensity upon 3 subsequent field cooling cycles. Fields of $+E$, $-E$ and $+E$ (again) were used ($E=20KV/cm$). Panels (a) and (b) present reflections (050) and (160), respectively. Lines are guides for the eyes.](image)

The largest contrast observed is $\delta \approx 35\%$, which is lower than the expected contrast. Furthermore, the intensity of (160) rises upon cooling for both poled states, even though the weaker member of the pair is expected to exhibit a reduction in intensity (see panels (a) and (b) in Figure 4.35). We therefore believe that the sample is not fully-poled. Nevertheless, errors due to the structure used for the calculation in Figure 4.35 can also play a role, as the P2$_1$nm structure of YMnO$_3$ in Ref. [57] may not fully account for the distortion undergone by ErMnO$_3$. 

[82]
4.6 Discussion of the multiferroic phases of the heavy-$R$ group

Clearly a wealth of information can be obtained about the o-$RMnO_3$ system using diffraction techniques. However, because the macroscopic effects observed vary widely in response to small perturbations, a clear picture of the multiferroic orders in this system is hard to produce.

Figure 4.38(a) presents the temperature dependence of $q$ for a set of (very) thick films, each with a different $R$ ion in the heavy-$R$ group. These correspond to the relaxed layer, which is expected to behave like a bulk crystal. Figure 4.38(b) presents the low-temperature values of $q$ for bulk (from literature), from our relaxed films, and from our highly strained films. As shown before, bulk values vary smoothly, and at a certain point a jump to the value $q = \frac{1}{2}$ occurs. Relaxed films appear to agree well with bulk, except the jump to $\frac{1}{2}$ does not occur: a disagreement exists for $R = \text{Tm, Yb and Lu}$ (the materials that are commensurate in bulk). For highly strained films, the situation is more complicated, but there is a clear tendency towards this jump, even for much lighter $R$ values.

![Figure 4.38](image)

**Figure 4.38 – Comparison between $q$ in different o-$RMnO_3$ samples.** (a) Temperature dependence of $q$ for very thick films of o-$RMnO_3$, corresponding to the relaxed film layer. All samples are 400nm thick, except the o-$\text{HoMnO}_3$, which is 240nm. (b) Modulation at low temperature, as function of the $R$ ions’ radius. Data are shown for bulk, thick films (relaxed layer), and thin films (<40nm) which correspond to the highly strained layer.

Clearly the horizontal axis in Figure 4.38(b) is only sufficient for the case of bulk. Indeed theoretical studies have used $J_{\perp}$ as the controlled parameter, because this was understood as the only interaction that varies strongly between o-$RMnO_3$ with different $R$ ions. However, this variation is actually due to the lattice distortion that occurs as a side effect of changing $R$ ions (mainly of GFO type), which
increases the overlap of the two O\textit{p} orbitals involved in the exchange path of $J_b$ (see Figure 4.13(c)). It is therefore clear that it is a geometric (or structural) parameter governing the variation in $J_b$ (and therefore $q$). The same “knob” is tuned when strain is applied, and is most likely the reason why other cycloidal o-RMnO$_3$ can be “pushed” to behave like an E-type by strain or under pressure [96,101]. It has been clearly demonstrated here that $b$-axis strain plays a systematic role in controlling the relaxed layer [81], while $a$-axis strain controls the strained layer [82]. The dependence of $q$ on these lattice parameters is shown in Figure 4.39. One can make out a possible relation for the $a$ parameter, but not $b$. It is highly likely that this is because it is an \textit{internal} parameter (i.e. bond angle or length) of the structure which is most important. Indeed the Mn-O\textit{II}-Mn angle was used in [79] as a controlled parameter in producing the phase diagram, as it is reasonable that the nearest-neighbor interaction in the \textit{ab} plane ($J_{ab}$) plays a crucial role in determining the Mn magnetic order.

To simulate the internal structure of o-RMnO$_3$ films, our colleagues at the ETH materials theory group (Natalya Fedorova and Prof. Nicola Spaldin) conducted first-principles calculations in which the energy of the system was minimized while the lattice constants were kept fixed to experimental values [95]. These calculations are performed using projector-augmented plane wave (PAW) method of DFT as implemented in Vienna \textit{ab initio} Simulation Package (VASP). Further details will be available in future publication. A control calculation was conducted using bulk values to ensure the validity of this process, which was indeed systematic with respect to reported values from experiments on bulk samples. The idea in doing so is to check whether a correlation exists between structural parameters such as bond angles (\textit{calculated from} experimental data) and measured $q$ values. To account for possible correlations in all parameters a cross product along the Mn-O-Mn was calculated for each sample (for in-plane and out-of-plane bonds). This is shown in Figure 4.40.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig4_39.png}
\caption{\textbf{Figure 4.39 – Measured lattice constants and magnetic modulation.} The correlation between experimental values for magnetic modulation and the \textit{a} or \textit{b} lattice constants, for bulk (from literature [43,46]) and for films from our experiments. The solid line is a guide for the eye.}
\end{figure}
Figure 4.40 – Correlation between crystal structure and magnetic modulation. Calculated values for the cross product within the in-plane and out of plane Mn-O-Mn bonds (II and I respectively) are based on measured lattice constants at low temperature. The magnetic modulation $q$ is measured at or below $T_L$. Colors highlight the main features observed.

While a relation clearly exists, the step-like jump to $q = \frac{1}{2}$ is still present (indicated). A relation of similar nature was suggested in Ref. [60]. The exchange terms in the $ab$ plane (which are directly proportional to the path taken by the electrons) were suggested to control the magnetic modulation as:

$$q = \frac{1}{\pi} \cos^{-1} \left[ \frac{f_{ab}}{2(f_b + f_3)} \right]$$  \hspace{1cm} (4.10)

Here $f_3$ is the third-nearest neighbor in a Mn-O-Mn-O-Mn bond along one pseudo-cubic axis in the $ab$ plane. From these results we conclude that the incommensurate modulation is indeed of structural origin. However, the nature of this order is still not clear. From the soft X-ray data at the Mn $L$ edges one can only follow the $(0 q 0)$ reflection. The azimuthal dependence of this reflection only serves to rule out the presence of a $bc$ cycloid, but cannot distinguish an E-type from an ab-cycloid (commensurate or not). The order induced by the Mn ions on the paramagnetic $4f$ electrons at the $R$ sites was also considered as a tool to learn about the Mn order in the ICM state, as discussed in Appendix 7.1. Unfortunately it cannot be used to distinguish different Mn domains from one another.

We now take another look at the results by Mochizuki et al in Ref. [35]. The commensurate E-type model produced by the authors is shown in Figure 4.10(a). One can fully describe this model using $q_{ab} = 2\pi(0 \frac{1}{2} 1)$ and $q_c = 2\pi(0 \frac{1}{2} 0)$ as:

$$S = S_{ab} + S_c$$  \hspace{1cm} (4.11)

With the $ab$ component written as
\[ S_{ab} = \sqrt{2} (S_a \cos(q_{ab} \cdot r + \frac{\pi}{4}) \hat{a} + S_b \cos(q_{ab} \cdot r - \frac{\pi}{4}) \hat{b}) \]
\[ = \sqrt{2} e^{i\pi/4} \left(\frac{1}{2} (S_a \hat{a} - iS_b \hat{b}) e^{i q_{ab} r} - i\frac{1}{2} (S_a \hat{a} + iS_b \hat{b}) e^{-i q_{ab} r}\right) \]
\[ = \frac{1}{2} (1 + i) (e^{i q_{ab} r} M - i e^{-i q_{ab} r} M) \]

(4.12)

in which the last step was done by defining \( M = S_a \hat{a} + iS_b \hat{b} \). The \( c \) component is described by

\[ S_c = \sqrt{2} S_c \cos(q_c \cdot r - \frac{\pi}{4}) \hat{c} \]

(4.13)

This is none other than a commensurate \( ab \) cycloid with an additional modulated \( c \)-axis canting. Taking \( S_a \to 0 \) and \( S_c \to 0 \) would yield the “pure” E-type AFM structure in which an ↑↑↓↓ chain is realized along the pseudo-cubic \( ab \) direction. This is schematically depicted in Figure 4.41. One can then postulate that the ICM structure is described in the same manner, but with \( q \) values other than \( \frac{1}{2} \) in Equations (4.11) - (4.13). However, the \( ab \) cycloid was previously described as a meta-stable state of TbMnO\(_3\), which is only stable in bulk o-RMnO\(_3\) within a narrow range between the A-type and \( bc \)-cycloid phases (See Figure 4.6). This was because the DMI overcomes the single ion anisotropy, making a flop to the \( bc \) plane energetically favorable.

![Figure 4.41 - Sketch of the E-type along the ab direction. A sine wave is overplotted with a \( \pi/4 \) phase with respect to the first Mn ion, to demonstrate that the E-type is, in fact, a collection of commensurate sinusoids.](image)

To reconcile these two theories, another look at the proposed E-type state is required. Mochizuki et al [35] followed the DMI and the single ion anisotropy (SIA) upon cooling into the E-type phase (see Figure 4.42). This was originally done to explain the cycloidal contribution to the predicted E-type. The transition they predict is an abrupt jump from an incommensurate sinusoidal phase to the commensurate E-type phase. In reality, though, this transition is not a jump, but a smooth variation in \( q \) upon cooling (as in Figure 4.11). Their model showed that at the transition, the SIA increases by \(~100\%\) (negatively), while the DMI weakens and nearly cancels out.

This means that the preference for spins in the \( bc \) plane due to the DMI does not persist. Since the value of \( q \) does not suddenly jump to \( \frac{1}{2} \) with temperature, but gradually shifts to it, it is also reasonable to assume that the SIA gradually regains prominence over the DMI. We therefore conclude that the variation of \( q \) can be explained as a recovery of the \( ab \) cycloid and the trend of Eq. (4.10), in which the nearest neighbor interaction \( J_{ab} \) grows with respect to the next-nearest neighbor interactions. It is now worth reminding that the symmetric contribution to electric polarization, \( P_S \) is
also directly proportional to \( J_{ab} \) (see section 4.1.3), and is present in the \( ab \) cycloidal phase (though not the \( bc \) cycloid). We therefore predict that the actual polarization of the system changes smoothly to the large values of the E-type, just as the \( q \) values do. Indeed the calculated and measured polarizations in Figure 4.15 suggest that a constant rise would exists in \( P_S \) from the \( ab \) cycloid to the E-type phase, if not for the interruption from the \( bc \) cycloid phase.

Figure 4.42 – Simulation of the sinusoidal-to-E-type transition upon cooling, from Ref. [35]. Values shown are the expectation values of the components of \( \mathcal{H}_{DMI} \) and \( \mathcal{H}_{SIA} \) in the \( ab \) plane, for \( J_b = 1.4 \) meV, which corresponds to the E-type phase. At the transition to the E-type phase upon cooling the value for SIA abruptly decreases with a large jump, while that for DMI slightly increases. Note that the transition also marks a jump in \( q \) from incommensurate to \( \frac{1}{2} \).

Two observations still need to be addressed. The first is that the system eventually locks in to the commensurate value \( q = \frac{1}{2} \). The mechanism behind this does not presently have an explanation. The second is the system’s behavior in the temperature range \( T_L < T < T^* \) (see Figure 4.17). The variation of \( q(T) \) and its relation with \( I_{(0q0)}(T) \) (see section 4.3.2) simply do not exist for the commensurate state with \( q = \frac{1}{2} \). To explain this, we remind ourselves that intensity of \((0 \ q \ 0)\) is a direct result of the DMI. The variation of \( q \) with temperature may be due to a gradual quenching of the DMI and strengthening of the SIA. This would imply that a relation would exist between \( q \) and \( I_{(0q0)} \) as temperature is lowered, because the \((0 \ q \ 0)\) reflection is a result of the DMI (see section 4.1.3.1). This relation would indeed be absent in the commensurate state, because \( q \) does not vary after locking into \( \frac{1}{2} \).

In conclusion, our study indicates that the ICM states are most likely an \( ab \) cycloid, as is the commensurate E-type. The gradual increase in \( q \) is accompanied by an increase in \( P_S \), and thus most likely in total \( \mathbf{P} \). The variation in \( q \) and \( I_{(0q0)} \) upon cooling is a gradual change in the balance between the SIA and the DMI, which can explain the relation seen between \( q \) and \( I_{(0q0)} \).
5 Soft X-ray study of strained CoCr$_2$O$_4$

This chapter details the study of films of CoCr$_2$O$_4$ (CCO), a type-II multiferroic material. The magnetoelectric properties of CCO are rare within the type-II classification, as it retains a macroscopic magnetic moment $M$ alongside its electric polarization $P$. Nevertheless it is not a simple ferromagnet, but a ferrimagnet in which the Co and Cr sublattices do not cancel out. It belongs to a family of materials of type $AB_2X_4$, which were originally studied many decades ago, especially the Chromites of type $ACr_2O_4$. Renewed interest in this family stems from recent discovery of multiferroic behavior in these materials [103-106].

5.1 General background

In the following, background related to the current understanding of this material is presented.

5.1.1 Ferroic phases

In this section the main experimentally observable behaviors of CCO are presented. We start with the magnetic (B-T) phase diagram of CCO, which has been revisited in recent years. Phase diagrams from literature are presented in Figure 5.1. The interest in this material has traditionally been due to its magnetic behavior. Therefore, it is best classified according to magnetic observables. Two well-established magnetic phases are known:

- **Collinear ferrimagnet.** Below $T_C \approx 92K$, CCO acquires a net magnetic moment [96], which is attributed to moments from non-compensating sublattices aligned antiparallel to each other along [001].

- **Conical (multiferroic) phase.** Below $T_S \approx 27K$ a spirally modulated component is added to the magnetic structure [96], resulting in a conically modulated magnetic order (see Figure 5.5). Furthermore, a macroscopic electric polarization appears. Strong magnetoelectric coupling is evidenced by the switching of both $M$ and $P$ with a magnetic field [97]. The spiral is modulated by an incommensurate ($q,q,0$) modulation vector. The parameter $q$ varies upon cooling, from $\sim 0.6$ at $T_S$ up to a commensurate 2/3 value at $T_L \approx 14K$, below which it remains locked in [97], though the lock-in feature remains controversial (see following). $T_L$ is magnetic field dependent, indicating that the magnetic order can be externally manipulated.
Additional features have also been reported. Figure 5.2 presents macroscopic observables as functions of temperature from bulk CCO. All of the transitions can be observed through the magnetization of the material. The dominant feature is that the magnetization peaks at ~75K, which is just below $T_C$, and then becomes weaker upon cooling. The shape of the curve suggests that the different magnetic sublattices in the material have different temperature dependences. This is common in ferrimagnetic materials, but unlike many others, CCO does not exhibit a compensation temperature. Instead, a series of small variations in $M(T)$ occur:

- Around 50K several authors have reported an anomaly in their data [105,109-111]. This feature is often referred to as $T_{kink}$, and it has been suggested as this feature relates to the independent ordering of Cr ions (See Figure 5.12), or to the appearance of a short range ordered spiral.
- The spiral transition at $T_S$ causes a small jump in magnetization. This is most likely due to a change in the balance between the magnetic sublattices that form the ferromagnetic moment, because the spiral ordered moments come at their expense.
- At $T_L$ another small jump in $M$ appears, most likely because of an additional change in magnetic modulation (see following), at the expense of the [001] spin component.
Figure 5.2 – Macroscopic observables in bulk CoCr$_2$O$_4$ as functions of temperature, taken from Ref. [97]. (a) The magnetization and specific heat divided by temperature. (b) The dielectric constant measured at 110 kHz and the electric polarization, both along the [1\bar{1}0] axis. Polarization was measured after cooling in simultaneous magnetic and electric fields of 0.01 T along [001] and 400 kV/m along [1\bar{1}0], respectively.

Several changes occur at the lock-in transition at $T_L$, which is a first-order transition [100], which exhibits a hysteresis of ~1K. Figure 5.3 presents the effects of this transition on M and on P. Upon cooling in a magnetic field, the transition causes a rise of ~40% in $M$, and causes $P$ to flip its sign, and grow in magnitude. This is shown in Panel (a). Panels (b) and (c) present magnetic field dependence curves of $M$ and $P$, above and below the transition. Clearly the $M(H)$ curve retains its sign, while the sign of $P(H)$ is reversed.

Figure 5.3 – Magnetization and Polarization in the multiferroic phase, taken from Ref. [101]. (a) Temperature dependence of M and P, along [001] and [1\bar{1}0], respectively. (b) and (c) present the magnetic field dependence of M and P above and below the lock-in transition.
The $T_L$ transition also affects the spiral spin component. The intensity from the magnetic ($\frac{3}{2} \frac{3}{2} 0$) reflection weakens significantly, and two new weak reflections appear: ($\frac{3}{2} - \delta \frac{3}{2} 0$) and ($\frac{3}{2} \frac{3}{2} - \delta 0$), with $\delta \approx 0.06$ r.l.u. The nature of this splitting, and indeed of this commensurate low-temperature phase is a subject of debate, but it has been observed by two independent studies, one using neutron diffraction [100], and one using RXD [101].

A new low-temperature and high-field phase was also reported (see Figure 5.1(a)), but is not important for this work.

5.1.2 Crystal and magnetic structure

CCO has a spinel crystal structure, with a cubic crystal symmetry described by space group #227 ($Fd\bar{3}m$), and a lattice constant of $a = 8.33\text{Å}$ [96]. The $\text{Co}^{2+}$ ions sit on the 8a sites (diamond sites, two fcc sublattices) and are tetrahedrally coordinated, and the $\text{Cr}^{3+}$ ions sit at 16d sites (pyroclore sites, four fcc sublattices), and are octahedrally coordinated. Nominally both ions have 3 unpaired 3d electrons in their $t_{2g}$ states. This is presented in Figure 5.4.

![Crystal structure and energy levels of bulk CoCr$_2$O$_4$, taken from Ref. [102].](image)

Figure 5.4 – Crystal structure and energy levels of bulk CoCr$_2$O$_4$, taken from Ref. [102].

It is commonly accepted that the magnetization $M$, the polarization $P$ and the ordering wave vector of the spiral component $Q$ are all perpendicular to each other ($M \perp P \perp Q$), as shown in Figure 5.5. Although the system is cubic, directions are commonly described as $M \parallel [001]$, $P \parallel [1\bar{1}0]$ and $Q \parallel [110]$. 

[91]
5.1.3 Strained CoCr$_2$O$_4$

While crystals of CCO have been studied for many decades, epitaxial films have not been the subject of interest. The discovery of strong magnetoelectric coupling in CCO has also sparked interest in thin films, because of the possibility to manipulate the ferroic orders using strain. This has been recently demonstrated by Heuver et al. [103], who studied high-quality [001]-oriented films. They identified significant variations in magnetic ordering between tensile and compressive strain. Most notably, tensile strain was shown to reduce or enhance the net moment and to alter the easy axis of magnetization. This is summarized in Figure 5.6.

![Diagram showing important crystal directions in CoCr$_2$O$_4$.](image)

Figure 5.5 – Important crystal directions in CoCr$_2$O$_4$. Figure is from Ref. [100]

![Graphs showing the effect of strain on CoCr$_2$O$_4$ films.](image)

Figure 5.6 – The effect of strain on [001]-oriented CoCr$_2$O$_4$ films, from Ref. [103]. (a) Magnetization data as function of temperature from a compressively strained film (grown on MgAl$_2$O$_4$). (b) Data from a tensile strained film (grown on MgO). Measurements were conducted in a field of 0.01 T after cooling in 1 T. The magnetic response of a bare MgO substrate is added as a solid line. (c) and (d) are magnetization data taken at 20K from the same films, along the surface and the normal.

The authors followed the anisotropic part of the Hamiltonian to model variation in anisotropy with strain. The calculated energy was evaluated as

$$E(\theta) = \alpha \cos^2 \theta + \beta [\cos^4 \theta + \sin^4 \theta] + \gamma$$  \hspace{1cm} (5.1)
and was found to be in good agreement with the experimental observations. Here $\theta$ is the angle between the moments and the [100] direction. The resulting behavior is shown in Figure 5.7. The $\alpha$ and $\beta$ parameters represent second and fourth order anisotropy terms. In the cubic (unstrained) case, $\alpha$ vanishes. $\gamma$ is a constant offset. The strain was shown to introduce magnetic anisotropy.

Figure 5.7 – Calculated anisotropy of CCO from Ref. [103]. (left) The calculated angular dependence of the anisotropy energy for $-3.12\%$ (compressive) and $1.08\%$ (tensile) strain. $\theta = 0^\circ$ corresponds to the magnetic moment along the [100] axis while $\theta = 90^\circ$ corresponds to the magnetic moment along [001]. (right) Calculated strain dependence of the constants $\alpha$ and $\beta$ from Eq. (5.1).

5.1.4 Present theoretical understanding

A theory aimed at describing the magnetic behavior of CoCr$_2$O$_4$, and more generally the family of such spinel oxides, was first introduced in the 1960’s, shortly after the first major experiments were performed. It was based on the work on Neel in the 1940s, which suggested the ferrimagnetic model in which nearest-neighbor Heisenberg interactions were assumed to be dominant. This model consisted of sublattices of spins all pointing along one axis, but in opposite directions, producing an uncompensated moment. This is known as the Neel state, and is associated with the aforementioned ferromagnetic state below $T_C$ (see Figure 5.1). Experiments in the 1950’s could not be explained by this theory alone. Therefore Yafet and Kittel proposed a solution based on the notion that other interactions besides $A$-$B$ may be significant, specifically the A-A and B-B sites (notation based on the formula $AB_2O_4$). Neglecting the A-A interaction (in our case Co-Co), the theory suggested that above a threshold value of the ratio $j_{BB}/j_{AB}$ a non-collinear state is preferred over the Neel state. This simple model was adapted to the case of cubic spinels by introducing a stability parameter:

$$u \equiv \frac{4j_{BB}S_B}{3j_{AB}S_A} \quad (5.2)$$

The system was said to prefer the Neel state when $u \leq 8/9$. In analyzing the $k$ dependence of spin waves, only the [110] direction (and its cubic equivalents) were found to destabilize the Neel state. Indeed the addition of an incommensurate spiral component to the ferromagnetic order was already suggested at this time, and did not require additional anisotropy considerations (unlike spirals in some
Lanthanide metals). The full theory from 1962 [104] is now known as LKDM, named after Lyons, Kaplan, Dwight and Menyuk. Due to many inconsistencies in the decades that followed, two of the original authors have recently (2007) published a revised account of this theory [105]. I do not go further into detail here, but state only information critical to understanding our case. The theory suggested the conical ordered phase for $B/9 < u < 1.298$. The conical order refers to a ferrimagnetic order with a transverse spiral component (i.e. in the plane perpendicular to the ferromagnetic axis). In this model, the spin on each sublattice $\nu$ (two $A$ fcc sublattices, four $B$ fcc sublattices) was defined as:

$$S_{\nu} = \sin \phi [\hat{x} \cos (k \cdot r_{\nu} + y_{\nu}) + \hat{y} \sin (k \cdot r_{\nu} + y_{\nu})] + \hat{z} \cos \phi$$

(5.3)

In which $k$ is the ordering wave vector, $y_{\nu}$ is a phase and $\phi$ is half the opening angle of the cone (i.e. the canting angle that the spiral causes away from the $\hat{z}$ axis). For the experimental results on CCO, they estimated that $u = 2$. This theory, while correctly estimating a close approximation of the ground state, is incomplete. Its most notable shortcoming is that it only takes into account sufficient exchange interactions, most notably $A$-$A$. Figure 5.8 presents the paths of these interactions.

The recent developments (namely the discovery of multiferroicity) have motivated new computational studies which were not available five decades ago. The magnetic behavior of the material was reexamined using LSDA+U first principles calculations in Ref. [107]. Furthermore, Monte Carlo simulations were conducted to follow the appearance of polarization [106], and First-principles calculations aimed at studying the introduction of Fe ions into CCO were also conducted [108]. The magnetic interactions, as well as the magnetic ordering wave vector, were found to be directly connected to the magnitude of polarization. This is shown in Figure 5.9. Most important was the finding that the effect of changing the magnitude of the $B$-$B$ and $A$-$A$ interactions is not negligible.
Figure 5.9 – Calculated polarization in CCO, from Ref. [106]. The figure is meant to underline the relation between many magnetic terms and the polarization, which is shown as function of (a) ordering wave vector (units: 0.29 corresponds to ~-(0.6 0.6 0) in our coordinate system) (a) B-B (Cr-Cr) interaction, and (c) A-A (Co-Co) interaction. See Ref. [106] for specifics.

Figure 5.10 – Crossover transition observed in Ref. [100] between incommensurate (higher temperatures) and commensurate (lower temperatures) phases. (a) and (b) present scans along \((q q 0)\) of a satellite and a fundamental reflection, respectively. (c) The integrated intensities of phase one at \((1.37, 1.37, 0)\) at different temperatures.
The nature of the low-temperature ground state remains somewhat unclear. Many of the experimental data do not agree well with each other. For example, a short range spiral was suggested to exist already below 80K [96], while most authors agree a spiral exists only below $T_S$. The magnetic diffraction experiments conducted in the multiferroic phase are also controversial. Some authors follow a $(q_x q_y 0)$ reflection with $q = 0.63$ [96], others with 0.67 [109]. It is not clear which of these locks in at $T_L$. Furthermore, the $T_L$ transition significantly weakens some reflections, and strengthens others. This was explicitly shown in Ref [100] (reproduced in Figure 5.10).

It is important to note that the recent neutron diffraction studies were conducted on single crystals, not powders as in the 60’s. In these studies the correlation length of the spiral was limited to $\sim$3.1 nm, compared to the 10’s of nm for the ferromagnetic component [110]. It was thus concluded that the low-temperature spiral is a short-range order only. Before moving on, it is worth highlighting a relevant finding from Ref. [108]. Although not the main target of the first principles study therein, the authors presented the spin-spin correlation function they calculated for CCO. This is shown in Figure 5.11. Interestingly, both $q \approx 0.63$ and $q \approx 0.67$ features appear simultaneously.

Lastly, we now turn to a simpler case. Study of Ref. [111] attempted to reconstruct the size of the ferrimagnetic moments of the Cr and the Co (effective) sublattices as function of temperature from measured magnetization data. They used a simple model which included the Co$^{2+}$ sublattice, assumed to order at $T_C = 94K \equiv \Theta_1$ and a Cr$^{3+}$ sublattice, which orders at an unknown (field-independent) temperature $\Theta_2$. The total moment was defined as a sum of the mean field from both sublattices: $M(T) = M_1 + M_2$. The $M_i$ terms were defined as a Brillouin function $M_i = B_{ij}(x_i)$ (see also Appendix A on page 126), with a modified $x_i$ field:
Here the mean field is modified to include the influence of the other sublattice \((i \neq j)\), through a coupling constant \(\lambda\) (in units of temperature), which should be negative. \(M_0^i\) is the magnetization at base temperature for the \(i\)th sublattice. Their least-squares fit of this model to magnetization is presented in Figure 5.12. Good agreement is found, and the best fit to the ordering temperature of Cr is found to be \(\Theta_2 = 49K\), in excellent agreement with \(T_{kink}\). However, quantitative data on the Co and Cr sublattices’ magnetization as functions of temperature would be ideal to test this approach.

\[
x_i = \frac{\mu_B}{k_B T} \left[ \frac{3S_0}{S_i} + \frac{k_B \lambda M_j}{\mu_B M_0^i} + H M_i \right]
\]

(5.4)

Figure 5.12 – Model representing the magnetization of the Co and Cr sublattices, from Ref. [111]. Contributions of the Co and Cr sublattices are shown with opposite signs. The contribution of the Cr sublattice diminishes at \(T_C\), rather than at 49 K, because of the coupling between the sublattices. Note that a \(T_{kink}\) feature is not observed in these data.
5.2 Experimental study

In this chapter we study a [110]-oriented strained film of CCO. This orientation sets both macroscopic quantities ($P$ and $M$) in the film plane (perpendicular to each other), and $Q$ out of plane (see Figure 5.5).

In this orientation, only the [001] direction is in plane; the other two principle axes are both out of plane. As the important directions are not principle axes, it is worthwhile to address the effect on the crystal lattice. Figure 5.13 presents a schematic of the unit cell in bulk and under strain in the present orientation. The most notable feature is that the $\gamma$ angle is no longer 90 degrees. Nevertheless the system can be represented by an orthorhombic symmetry, but with the diagonals of the cube as the new orthonormal axis system.

Figure 5.13 – geometry of strained [110]-oriented CoCr$_2$O$_4$. (a) A 3D view of the unit cell. The dark shaded (blue) area represents the films surface. The lightly shaded (pink) area represents the square enclosed by diagonals. (b) and (c) represent the a 2D projection of the original unit cell onto the $ab$ plane, in the unstrained and the strained cases, respectively. The lightly shaded (pink) area from (a) is also shown here to emphasize that the diagonals remain orthonormal. The film surface is also shown as a thick (blue) line.

This study focusses on one high-quality [110]-oriented film grown on an MgO crystal substrate, and unless specifically mentioned, only results from this sample are shown. The structural parameters of this sample were resolved at the SD station of beamline X04SA [31] of the Swiss Light Source, and are listed in Table 5.1. A precise estimate of the thickness was calculated using reflectivity (which allows calculating the sample’s volume, and thus present magnetization data in $\mu_B$ per formula unit.
Table 5.1 – Structural parameters of the film in this study. Values are in Angstroms, and strain values indicated compressive strain (when positive).

<table>
<thead>
<tr>
<th></th>
<th>[100]</th>
<th>[010]</th>
<th>[001]</th>
<th>[110]</th>
<th>[110]</th>
<th>γ (°)</th>
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<tr>
<td>Bulk</td>
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<td>8.332</td>
<td>8.332</td>
<td>11.783</td>
<td>11.783</td>
<td>90</td>
</tr>
<tr>
<td>Film</td>
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<td>8.294</td>
<td>8.383</td>
<td>11.676</td>
<td>11.780</td>
<td>90.5</td>
</tr>
<tr>
<td>Strain (%)</td>
<td>0.48</td>
<td>0.45</td>
<td>-0.61</td>
<td>0.91</td>
<td>0.024</td>
<td>/</td>
</tr>
</tbody>
</table>

Our study focuses on employing soft X-ray techniques. Two studies have studied CCO using soft X-rays. Choi et al. [101] employed RSXD to study single crystals, and focused mainly on the spiral handedness, which was probed with circularly polarized light. Liu et al. [112] employed photoemission and magnetic reflectivity around the Co and Cr L edges to characterize epitaxial films. A complete account of the separate magnetic behavior of Co and of Cr was not reported.

5.2.1 Study of the ferrimagnetic moment

Based on the notion that the $u$ parameter controls the ground state, one can intuitively realize that since $u$ depends linearly on exchange terms, strain will alter it by varying the bond lengths (and thus changing exchange paths). To follow the sample’s magnetic moment, magnetization measurements were conducted using a commercial SQUID device. Figure 5.14(a) presents a magnetic hysteresis curve at 23K. Direct comparison with Figure 5.3(b) reveals that the coercive field is two orders of magnitude larger than in bulk. Furthermore, a jump around $\mu_0 H = 0T$ is observed. The magnetic moment is presented in Figure 5.14(b) as a function of temperature. The magnetization is roughly a factor of 2 higher than in bulk (compared to Figure 5.3(a)), an effect similar to that observed in Ref. [103] for tensile strained films (see Figure 5.6). One can also identify a kink at ~18 K indicating that the spiral phase may still persist, but the low-temperature paramagnetic contribution from the substrate’s impurities to the measurement prevents clearly observing small features in that range.

![Figure 5.14 - Magnetization of the CCO sample](image)

Figure 5.14 – Magnetization of the CCO sample. (a) Magnetization as function of temperature, measured upon warming in a field along [001] of 10 mT after field cooling in 2T. The noise at ~45K is most likely an experimental artifact. The inset is a close-up of the box in the main figure. (b) Magnetization as function of magnetic field along [001], measured at 23K. Linear contributions were removed above 6T, which is approximately the saturation field of the hysteresis loop.
5.2.1.1. Reflectivity experiments

We now attempt to separately follow the Co and Cr moments. As it is reasonable to assume that they have opposing magnetization (as in bulk), the shape of the temperature dependence in Figure 5.14 is likely due to their different temperature dependences. To follow each sublattice separately, we tune the X-rays to the corresponding absorption edges. We aim to employ XMCD, but unfortunately the sample is a good insulator so standard electron yield measurements cannot be carried out. Conventional transmission measurements are not possible either, because the film is grown on a crystal substrate. Fluorescence yield is not reliable because it mixes with the intense optical luminescence from the substrate due to the x-rays transmitted into it through the sample. For this reason we attempt to measure magnetic circular dichroism in reflection. Inspecting Eq. (3.10) and (3.30) it is clear that the resonant cross section will indeed be sensitive to the local moment with incoming circular light, but a contribution from the non-magnetic component will also remain.

Writing the incoming and outgoing polarizations as \( \vec{\varepsilon} = (\varepsilon_1, \varepsilon_2, 0) \) and \( \vec{\varepsilon}' = (\varepsilon_1', \varepsilon_2', 0) \) in their local coordinate system, one can show that the three polarization terms in (3.30) become

\[
\begin{align*}
(\varepsilon' \cdot \varepsilon) F^{(0)} &= \left[ \varepsilon_1' \varepsilon_1 + \varepsilon_2' \varepsilon_2 \cos 2\theta \right] F^{(0)} \\
(\varepsilon' \times \varepsilon) F^{(1)} &= \left( \begin{array}{c}
\frac{1}{2} \sin 2\theta \varepsilon_2' \varepsilon_2 \\
- \sin \theta \left[ \varepsilon_2' \varepsilon_1 + \varepsilon_1' \varepsilon_2 \right] \\
\cos \theta \left[ \varepsilon_1' \varepsilon_2 - \varepsilon_2' \varepsilon_1 \right]
\end{array} \right) F^{(1)}
\end{align*}
\]

(5.5)

Here \( \theta \) is the incident angle. The \( F^{(2)} \) term is dealt with in the following. Clearly the \( F^{(0)} \) is not generally zero (note that \( F^{(0)} \) is a resonant term from Eq. (3.30), not to be confused with the \( f^0 \) scattering term; also note that non-resonant charge scattering will also contribute). The \( F^{(1)} \) term is shown for a coordinate system useful for this experiment: the \( \vec{y} \) axis is the sample’s surface normal while \( \vec{x} \) and \( \vec{z} \) are in the scattering plane. The sample is oriented such that its [001] crystal direction corresponds to the \( \vec{z} \) axis. For the present experiment we are interested in magnetization along the [001] direction, so we can write \( \vec{m} = m\vec{z} \). From inspection of Eq. (5.5) it is clear that the \( \vec{z} \) component depends on the incident angle as \( \cos \theta \), so to maximize this term a shallow angle must be chosen. In simple terms we want the x-rays to be as close as possible to being parallel to the magnetic axis. This is equivalent to the idea in an XMCD absorption experiment, which is only sensitive to the moment direction parallel to the incoming beam. The last term from Eq. (3.30) is then:

\[
(\varepsilon \cdot \varepsilon)(\varepsilon' \cdot \varepsilon' \cdot m) F^{(2)} = \left( \sin \theta \varepsilon_2 \cdot m \right) \left( - \sin \theta \varepsilon_2' \cdot m \right) F^{(2)} = - (m \sin \theta)^2 \left( \varepsilon_2 \varepsilon_2' \right) F^{(2)}
\]

(5.6)

This term depends on \( \sin^2 \theta \), so with grazing angles it will become very small, which allows us to neglect the \( F^{(2)} \) term. The scattering intensity \( |f_{k \varepsilon 1,1}|^2 \) will then contain four terms:

- The “pure” magnetic term, proportional to \( (m \cos \theta)^2 |F^{(1)}|^2 \).
The non-magnetic term, proportional to $|F^{(0)}|^2$.

Two mixing terms, proportional to $m \cos \theta F^{(1)*} F^{(0)}$ and $m \cos \theta F^{(1)} F^{(0)*}$.

The measured signal can be assumed to be purely magnetic only if $\cos \theta |F^{(1)}| \gg |F^{(0)}|$. But this is not clearly the case, and to maintain the sign of magnetization, the mixing terms are required. To present the results, we refer to the intensity measured from scattering circularly polarized incident light as $I_\pm$, where $\pm$ indicates the chirality (handedness) of the incoming light. Figure 5.15 presents reflectivity data taken around the Co and Cr L edges. Clearly the resonant non-magnetic term is dominant both over the non resonant reflectivity at the Co and Cr L edges (see Panels (a) and (b)). It is also the largest contribution to the resonant signal, although the mixing terms (terms linear in $m$) are not small compared to it.

![Figure 5.15](image-url)

**Figure 5.15 – Raw reflectivity data taken from CCO using circular light of both chiralities.** (a) and (b) are reflectivity signals as functions of incoming photon energy around the Co and Cr L$_{2,3}$ edges, respectively. Data were taken at 10K. Solid lines indicate the energies used for the lower panels (577.9 and 779.15 eV). (c) and (d) present these data at the L$_3$ edges as functions of temperature. The line indicates the apparent $T_F$ value. All data are taken after field cooling in $\pm 400 \, mT$. 

[101]
For easily following the circular dichroism, we define asymmetry as \( (I_+ - I_-)/(I_+ + I_-) \). Figure 5.16 presents asymmetry measured at the Co and Cr L\(_3\) edges (779.15 eV and 577.9 eV) upon warming, using \( \theta = 4.1^\circ \) and 7.3\(^\circ\), respectively. These angles were chosen because they exhibited the highest asymmetry contrast. The experiment was conducted twice, after field cooling in \( B_{[001]} = 400 \text{ mT} \) and after field cooling in \(-400 \text{ mT}\).

The results clearly show that the asymmetry reverses with opposite field cooling, indicating that it is indeed proportional to the magnetic moments linearly, and that the mixing terms (which are proportional to \( m \), not \( m^2 \)), are the dominant terms. Furthermore the moment directions of Co and Cr are clearly opposite to each other.

![Graph showing asymmetry as a function of temperature measured at the Co and Cr L\(_3\) edges](image)

**Figure 5.16 – Magnetic asymmetry as a function of temperature measured at the Co and Cr L\(_3\) edges (779.15 eV and 577.9 eV).** The solid line indicates a constant offset from zero, which may be an experimental artifact. The left and right panels present the same procedure after cooling in magnetic fields of opposite signs: -400 mT and 400 mT. (along [001])

The most important result from this experiment is that the temperature dependence of the magnetization from the two sublattices is qualitatively different. Figure 5.17 presents all four asymmetry curves from Figure 5.16, normalized to their value at 20K (this is denoted as \( M(T)/M_0 \) for simplicity). The main observation is that the Co and Cr differ most around \(~70K\). This is in agreement with the magnetization measurements, which show that the total moment is highest in this region. A second point is that the difference quantitatively differs between the two opposite field coolings: the gap between the two sublattices appears to vary (Cr is weaker, Co is stronger, or vice versa), which can agree with an exchange bias. Lastly, below 20K a split occurs: for \(-H\) the Cr magnetization grows further upon cooling, while for \(+H\) the Co magnetization does (see inset of Figure 5.17). This feature occurs where the low-temperature magnetization feature occurs in Figure 5.14.

It is worth noting that the field was applied manually with a permanent magnet. As such, the effective applied field may not be the exact same magnitude in when it was reversed. One could assume that
the variation in the Cr-Co gap around 70K is due to this experimental artifact. However, this would not explain the low-temperature behavior in the inset of Figure 5.17, which switches between the sublattices when opposite field cooling is conducted. This effect can be explained as the result of an exchange bias, possibly coming from the interface to the substrate.

![Figure 5.17](image)

**Figure 5.17** – **Normalized asymmetry as a function of temperature.** All curves from Figure 5.16 are normalized to their value around ~20K for direct comparison. The lines are guides for the eyes. The inset is a close-up of the low temperature region.

### 5.2.1.2. X-Ray exited optical luminescence (XEOL) XMCD study

The main setback in the reflectivity experiment is that it is difficult to obtain quantitative information. Furthermore, small variations in spectral shape may occur in the different magnetic phases, which would appear as changes in the observed moment. To overcome this, we now aim to employ XMCD and apply sum rules analysis (see section 3.1.4). Unfortunately, measuring electron yield, fluorescence yield, and standard transmission are all not possible, as mentioned in the previous section.

As an alternative to these methods, we now aim to use the sample’s substrate as a scintillator. For this we employ the intense X-ray excited optical luminescence (XEOL) of the substrate, which is a measure of the intensity of the beam transmitted through the thin film. XEOL is not a common tool, but it has been successfully employed in the past [113], both as an XMCD probe [114] and for sum rules analysis [115]. This section goes into detail about the application of sum rules. While this is a rather standard procedure nowadays, part of the motivation for doing so stems from the rarity of sum
rules using XEOL. This will provide the reader with an impression of the data quality available using XEOL.

The efficiency of XEOL varies with energy. To account for this, the transmission relation in Eq. (3.4) must be altered as:

\[ I(z) = I_0 \Lambda(E) e^{-\mu z} \]  \hspace{1cm} (5.7)

The term \( \Lambda(E) \) is a measured efficiency function of the XEOL.

---

**Figure 5.18 – schematic of the XEOL experiment (within the XTreme chamber).** The sample is mounted on a cold copper piece with a hole through which it can luminesce to the photodiode, which is in a closed environment with no external light.

To conduct this experiment a sample mount for the XTreme station (section 3.2.2.3) was altered to accommodate a photodiode behind the sample. This is schematically shown in Figure 5.18. The substrate is mounted on a cold copper plate with a small hole, through which light from the substrate can reach a photodiode. The photodiode region is closed so no other signals can enter. The substrate is ~1 mm thick, which is enough to absorb the entire transmitted X-ray beam (the attenuation length of MgO is between 0.3 and 0.7 \( \mu m \)). It is therefore reasonable to assume that the entire measured signal is XEOL.

To demonstrate this, Figure 5.19 presents raw XEOL spectra around the Co L edges, taken from our CCO sample. A spectrum is also shown from a bare MgO substrate with no film on top. This is used as our \( \Lambda(E) \) function. Most importantly, Figure 5.19 also presents data collected using circularly polarized incoming light of both chiralities, and clear circular dichroism is observed. In the remainder of this section the application of sum rules analysis is described for Co and Cr. The analysis generally follows that shown in section 3.1.4 and specifically in Figure 3.2.
We begin with measurements around the Co edges. Sum rules analysis is commonly employed on the Co L\textsubscript{2} and L\textsubscript{3} edges in other contemporary studies. Figure 5.20 presents data taken at 15.5K. Panel (a) presents the XAS spectrum (\(\mu_+ + \mu_\text{-}\)) and two nearly identical two-step functions (described in the following). Also shown are two integral curves (right axis). Each one represents an integral over the XAS spectrum, after a two-step function is subtracted from it. The integral value is taken at the point labelled “\(r\)”, which is at an energy that represents the approximate end of the L\textsubscript{3} edge (estimated also using the XMCD spectrum). The XAS data are binned in 0.25 eV steps, a step which is well above the monochrometer resolution, but does not appreciably affect our results.

The two-step function represents the continuum contribution to the \(2p \rightarrow nd\) E1 transitions (see section 3.1.4 for more details). As we are only interested in probing the unoccupied 3\textit{d} valence states, the two-step contribution must be removed before integration. The two steps together complete the jump between the XAS below the L\textsubscript{3} edge and at the “\(r\)” energy above the edges. The ratio between their heights represents the branching ratio, i.e. the ratio between the probability of excitation at the L\textsubscript{3} and at the L\textsubscript{2}. This is nominally \(1/2\) because of the higher degeneracy of the core state with \(j = 3/2\) (L\textsubscript{3}) with respect to that with \(j = 1/2\) (L\textsubscript{2}). However, the nominal \(1/2\) branching ratio causes the calculated step function to exceed the XAS signal between the edges (See Panel (a)). This is often ignored as the error introduced is assumed to be small. One reason for this may be the interference of the EXAFS spectrum above the edges, which raises the total L\textsubscript{2} XAS signal and/or decreases the signal between the edges, which could reflect the change in the valence states in the presence of a core hole. A possible solution for this would be to change the branching ratio such that the L\textsubscript{3} step matches the XAS spectrum between the two edges. In our case we find that this weakens the L\textsubscript{2}/L\textsubscript{3} branching.

Figure 5.19 –XEOL data from CCO and from a bare substrate. CCO data are taken with the sample at 15.5K, and using two opposite chiralities of circularly polarized incoming light. XEOL data from a bare MgO substrate are also shown. All spectra are normalized to their value at 760 eV.
from ½ to 1/1.2. This corresponds to a significant reduction in the ratio between excitation probabilities from the j=3/2 and j=½ states, which should not occur for Co. Nevertheless in the following we shall use both the ½ and the 1/1.2 branching ratios to demonstrate the effect of this uncertainty.

![Figure 5.20](image)

**Figure 5.20** – XAS and XMCD spectra from CCO, taken around the Co L\_2,3 edges. (a) XAS data (μ\_+ + μ\_-) and calculated two-step functions (see main text). The right axis is for the integral over the XAS, after the two-step function is subtracted. (b) Derivative of the XAS spectrum with respect to energy. The maximums at each edge are indicated. (c) XMCD spectrum (μ\_+ − μ\_-) and the integral over it (right hand axis). The “r” and “q” notation is in line with that in Figure 3.2.

The two-step function is calculated as

\[
\Theta \propto \left[ 1 - x \left( 1 + \exp \left( \frac{E - E_{L_3}}{\delta} \right) \right)^{-1} \right] - \left[ 1 - x \left( 1 + \exp \left( \frac{E - E_{L_2}}{\delta} \right) \right)^{-1} \right]^{-1}
\]  

(5.8)

Here the nominal branching ratio of ½ is given by a value of \( x = 2/3 \), and is altered when the 1/1.2 ratio is calculated. The \( E_{L_3} \) and \( E_{L_2} \) energies are maxima of the derivative of the XAS spectrum (indicated in Panel (b) Figure 5.20). The steps are assumed to be narrow, and therefore their width \( \delta \)
is set to the size of an energy bin (0.25 eV). This is slightly narrower than the core-hole lifetime of the Co L₃, which is tabulated at 0.43 eV (±25%) [116], but we assume this error to be negligible.

Panel (c) presents the XMCD spectrum ($\mu_+ - \mu_-$). Also shown is the integral over the edge, which is evaluated at the point labelled “q” (at the same energy as “r”). To complete the sum rules analysis we must also choose a point on the XMCD integral curve that corresponds to a sum over the L₃ only. To emphasize the importance of this choice, Figure 5.21 presents the calculated Co spin moment as function of the L₃ cutoff energy. Two curves are shown, one for calculation with the nominal $\frac{1}{2}$ ratio, and one for the 1/1.2 ratio. The offset between the two curves is roughly $\sim 0.02 \, \mu_B$, which is generally small but not negligible with respect to the absolute spin moment (roughly 5%). We choose to evaluate the spin moment at the nominal $\frac{1}{2}$ ratio. Results of the sum rules analysis are summarized in Figure 5.24 for all measured temperatures.

![Figure 5.21 – Calculated Co spin moment as function of the chosen cutoff energy between the L₂ and L₃ edges. Two curve are shown: one for calculations with the nominal $\frac{1}{2}$ branching ratio, and one for the 1/1.2 ratio. The vertical line indicates the energy at which the derivative of the XMCD spectrum is zero.](image)

A similar procedure is conducted for the Cr L edges. Figure 5.22 presents the XAS, XAS derivative and the XMCD spectra for this case, in the same format as Figure 5.20 presented it for Co. Here the $\frac{1}{2}$ ratio does not cause the calculated L₃ step to exceed the measured XAS between the edges, so only the nominal two-step function is calculated.

[107]
Figure 5.22 - XAS and XMCD spectra from CCO, taken around the Cr L\(_{2,3}\) edges. (a) XAS data (\(\mu_+ + \mu_-\)) and calculated two-step function. The right axis is for the integral over the XAS, after the two-step function is subtracted. (b) Derivative of the XAS spectrum with respect to energy. The maximums at each edge are indicated. (c) XMCD spectrum (\(\mu_+ - \mu_-\)) and the integral over it (right hand axis). The “\(r\)” and “\(q\)” notation is in line with that in Figure 3.2.

However, another problem occurs here: the overlap of the L\(_2\) and the L\(_3\). This is a general limitation in applying sum rules analysis to the lighter 3\(d\) ions. Significant uncertainty can occur when determining the spin moment, because one cannot easily separate the XMCD integral over the L\(_3\) from that over the L\(_2\). Figure 5.23 presents a close up of the XMCD (and its integral) between the two Cr L edges. The source of the uncertainty lies in the highlighted region. The XMCD integral over the L\(_3\) edge is very small because the L\(_3\) XMCD has both positive and negative contributions. Therefore, even though only a small overlap occurs between the two edges, its contribution to the integral is of the same order as the total L\(_3\) integral. This can easily cause errors in excess of 50\% in the spin moment of Cr[117].
Figure 5.23 - Close up of the XMCD (and its integral) between the two Cr $L_{2,3}$ edges. The highlighted region indicates the cause of high uncertainty in the Cr spin moment: the XMCD integral over the $L_3$ edge is very small because the $L_3$ XMCD has positive and negative contributions which nearly cancel out, and the integral is of the same magnitude as the $L_2$-$L_3$ overlap.

XMCD spectra were taken at many temperatures below $T_C$, under a magnetic field of 0 T and 6.8 T. It is important to note that the data were taken with an incidence angle of 30°, so a correction factor is required because XMCD probes only the moment’s component in the beam direction (the actual in-plane moment is larger). The results of the sum rules analysis are shown in Figure 5.24 and Figure 5.25, in which the correction was already taken into account. For the Cr ions only the orbital moment is presented. We note that the magnetic field is applied along the direction of the X-rays. As such the applied field in the [001] direction is reduced by a factor of $2/\sqrt{3}$.

Figure 5.24 – Spin and orbital moments of Co as functions of temperature. Data are shown at zero field and 6.8 T. A correction factor of $2/\sqrt{3}$ was used to account for the 30° incidence of the beam. The field component in the [001] direction (corresponding to the applied 6.8 T field) is 5.19 T.
Figure 5.25 – Orbital moments of Cr as functions of temperature. Data are shown at zero field and 6.8 T. A correction factor of $2/\sqrt{3}$ was used to account for the $30^\circ$ incidence of the beam. The field in the [001] direction corresponding to the applied 6.8 T field is then 5.19 T. Lines are guides for the eye.

For completeness, we also discuss the effective spin moment of the Cr ions. This was calculated in two methods. The first method is the sum rules analysis, which was just shown to be problematic due to the overlap of the $L_2$ and $L_3$ edges. The second method involved subtracting the other calculated moments (i.e. Co $M_L$, Co $M_{S,eff}$ and Cr $M_L$) from the measured temperature dependence of the sample (Figure 5.14(a)). Co and Cr contributions were weighted (two Cr to one Co). The results of both methods are presented as functions of temperature in Figure 5.26. These results are in disagreement. The indirect values acquire larger error bars because each of the value contributing to the calculation also has an error estimate. Furthermore the magnetization data also have a small contribution from the substrate. This contribution is large for the lowest temperatures, which is why the 2K data point is not calculated.

Figure 5.26 – Effective spin moments of Cr as functions of temperature. Two data sets are shown: a direct sum rules calculation, and an indirect calculation, deduced by subtracting Co moments and Cr orbital moment (all from sum rules analysis) from the magnetization data.
We now turn to the magnetic field dependence of the ferromagnetic moment. A main difference between the film and the bulk was that the film exhibits a coercive field which is two orders of magnitude higher than in bulk (at ~20K). To follow this behavior, magnetic-field dependent magnetization curves were acquired using a SQUID magnetometer. Results are presented in Panel (b) of Figure 5.27. A linear term has been removed from all presented data. The linear term is both from the substrate and from any possible non-hysteretic contributions to magnetization from the sample itself. The shape of the curves strongly suggests the existence of two contributions to magnetization. At 5K and 15K the setup was unable to saturate the sample. Data were also taken out of plane, along [110] (not shown), and no clear hysteresis or saturation were observed, as expected from a hard axis.

To investigate this further, we followed the XMCD signal using XEOL at the Co and Cr L₃ edges as functions of magnetic field. Results are shown in Panel (a) of Figure 5.27. At every field a data point was taken on and off resonance, and therefore the data could be corrected using Eq. (5.7). However the data from the two experiments cannot be directly compared, because the XMCD experiment was not (and cannot be) conducted exactly parallel to the sample surface. It was therefore conducted at a 30° angle from the [001] direction (in the plane spanned by [001] and the film normal). Therefore in the XMCD experiment the field along [001] is weaker than the applied field. Nevertheless it is clear that the two sublattices behave oppositely with respect to the magnetic field. The magnetization data in Panel (b) exhibit a jump around 0T. This cannot be reproduced by the sum of the XMCD data in Panel (a), because the Co and Cr signals exhibit the same coercive field. This discrepancy could be due to the 30° measurement angle of the XMCD signal.
Figure 5.27 – Magnetic hysteresis of CCO. (a) XMCD as function of magnetic field measured with photons energies at the Co and the Cr L\textsubscript{3} edges. Data are shown for 5 different temperatures, and have been corrected using Eq. (5.7). All data are on the same scale. (b) Magnetization as function of magnetic field, measured at a number of different temperatures. All magnetization are on the same scale, except for the 23K data, in which the scale is doubled. Note that direct comparison to XMCD is not straightforward because the magnetization was measured along [001], while XMCD was measured at an angle of 30° from the surface (i.e. from the [001] axis), so a correction factor is required.
This effect was modelled by Dr. Andrea Scaramucci (PSI), in the same manner as in Ref. [103]. The model used a crystal structure relaxed using LDA, with the lattice constants constrained to the substrate in the same manner as in our film: the strain along [001] was fixed to -0.6 % (i.e. tensile) and there is no mismatch along [1\(\bar{1}\)0]. The cell was free to relax along the out of plane direction [110], and indeed it was found to compress with respect to bulk, resulting in a strain value of 0.3% (i.e. compressive) rather than ~1% as found in our experiment. In this relaxed unit cell, the magnetic moments were uniformly rotated from the [110] (out of plane) to the [001] direction (in-plane). The energy of the spin system was calculated for different rotation angles, as presented in Figure 5.28. The same procedure was conducted between [1\(\bar{1}\)0] and [001]. From this calculation we conclude that the minimal energy was for spins oriented along [001]. Furthermore the energy different between [001] and the other two axes is nearly the same. In other words, the [1\(\bar{1}\)0] axis is the hard axis in plane, and is nearly as hard as the out of plane [110] direction.

![Figure 5.28](image)

Figure 5.28 – Calculated energy cost of spin rotation from [001] to [110] and [1\(\bar{1}\)0]. A constant value was removed for clarity.

The energy dependence fits well to the dependence of anisotropy energy in Eq. (5.1). The best fit parameters are listed in Table 5.2. Interestingly, a direct comparison with the calculated values in Figure 5.7 indicates that the present scenario corresponds to very high strain in the [001]-oriented films, because the magnitude of both \(\alpha\) and \(\beta\) is beyond the plotted axes limits. It is worth reminding that in bulk \(\alpha = 0\) and \(\beta \approx -44.5 \mu eV\) (see Figure 5.7).

Table 5.2 – Best fit parameters to Eq. (5.1), for the energy values calculated and shown in Figure 5.28

<table>
<thead>
<tr>
<th>Rotation direction</th>
<th>(\alpha) ((\mu eV))</th>
<th>(\beta) ((\mu eV))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[110] (\rightarrow) [001]</td>
<td>344.56</td>
<td>-68.80</td>
</tr>
<tr>
<td>[1(\bar{1})0] (\rightarrow) [001]</td>
<td>324.61</td>
<td>-68.45</td>
</tr>
</tbody>
</table>
5.2.2 RSXD experiments

In this section we follow the multiferroic phase using RXD. The appearance of the spiral component of the spin order below 27K is considered an indicator of the multiferroic phase. The spiral is modulated by \( (q \neq 0) \). For this component the Bragg condition can be fulfilled only for the Co L edges, as the Cr L edges are too low in energy.

Figure 5.29 presents the temperature dependence of the \((q \neq 0)\) reflection at the Co L\(_3\) edge. Panel (a) presents the raw data, and the right edge of the data is limited by the edge of accessible reciprocal space at this energy. Panel (b) presents the integrated intensity of the reflection, which grows significantly below 27K, as expected from bulk. Short range correlations are found also above this temperature. The modulation parameter \( q \) changes in the range 0.63 – 0.69 r.l.u., which includes all previously reported positions (0.63 [96], 0.67 [100] and 2/3 [101]). This may indicate that the observed reflection overshadows weaker reflection. The correlation length does not change considerably throughout the measured temperature range, and remains at around 10-12 nm (Panel (d)), suggesting that the probed order is short-ranged.

![Figure 5.29](image)

**Figure 5.29 – Temperature of the \((q \neq 0)\) reflection from a [110]-oriented CoCr\(_2\)O\(_4\) film.** (a) Raw data taken upon warming, using incoming \( \pi \) polarized linear light with an energy of 779.2 eV (Co L\(_3\)) with the sample at an azimuth of \( \Psi = 0^\circ \) (which is when the [001] axis is in the scattering plane). Note that the scans were conducted along the [110] direction, and the horizontal axis is the corresponding \( q \) value in \((q \neq 0)\). The right hand edge of the graph is at the edge of accessible reciprocal space at this energy. (b) (c) and (d) present the temperature dependence of the integrated intensity, the modulation parameter \( q \), and the correlation length, respectively. The dashed line is a guide for the eye.
The energy dependence of this reflection is presented in Figure 5.30. The simple energy profile that emerges suggests that most of the intensity is from a few transitions around the \( L_3 \), which are dominant over all others. The ratio between the intensity if the two edges is \( I_{L_2}/I_{L_3} \approx 1/30 \approx (3/16)^2 \). In the last step we emphasize that the observed spectrum is that of scattered intensity, i.e. amplitude squared. The value obtained is reasonably close to the \( \sim 4.1/16 \) amplitude ratio in the Co XMCD (see Panel (c) of Figure 5.20).

![Figure 5.30 - Energy dependence of the \( (q \ q \ 0) \) reflection](image)

**Figure 5.30 – Energy dependence of the \( (q \ q \ 0) \) reflection**, taken using incoming \( \pi \) polarized linear light with the sample at 10K and at an azimuth of \( \Psi = 0^\circ \). Data are corrected for variations in peak width. Lines are guides for the eye.

The azimuthal dependence of the reflection was also probed, and is presented in Figure 5.31. Calculations based on two models are presented as solid and dashed lines. To understand them, we remind ourselves of Eq. (5.3). It describes each of the magnetic fcc sublattices, which are numbered by \( \nu = 1 \ldots 6 \). Each sublattice is described as a spiral of the form \( \sin(\mathbf{k} \cdot \mathbf{r}_{\nu} + \gamma_{\nu}) \). Here \( \mathbf{k} \) is the ordering wave vector, \( \mathbf{r}_{\nu} \) is the position of the \( \nu \)th atom in sublattice number \( \nu \), and \( \gamma_{\nu} \) is the phase of the spiral on sublattice \( \nu \).

In the present measurement we are only concerned with the (two) Co fcc sublattices. LKDM theory [104] (See section 5.1.4 on page 93) defines that the two Co sublattices have the same \( \gamma_{\nu} \) phase in their spiral components. The azimuthal dependence of this model is presented as dashed lines. Clearly this model does not agree with the measured data.

Assuming that this model is the correct description for bulk CCO, one could argue that strained state of the system induces a change in the spiral ordering, which is indeed a result of the delicate balance of interactions that lifts the magnetic frustration. In order to remain loyal to the bulk picture, only one parameter is changed: the phase \( \gamma_{\nu} \) on the two Co sublattices is no longer the same. A constant phase
is introduced between them. The solid line in Figure 5.31 represent a calculation for a phase of π/4 between the two Co sublattices. A reasonable agreement with experimental data is achieved, and we conclude that the spiral state is not the same as in the bulk picture presented by LKDM theory.

![Figure 5.31](image)

**Figure 5.31 – Azimuthal dependence of the \((q, 0, 0)\) reflection in CCO.** Solid lines are calculations with a phase of π/4 between the Co sublattices. The dashed lines are a calculation with no phase, as in LKDM theory (see Eq. (5.3) in section 5.1.4). Calculations assumed \(q = \frac{\pi}{2}\) and used Eq. (3.33) to calculate the structure factor.

### 5.2.3 RSXD Measurements on inhomogeneous CCO films

Before moving on, we wish to focus on additional measurements that were carried out on CCO films. These measurements were originally dismissed because they were conducted on a film sample that was found to be inhomogeneous. This was concluded due to large variations in the size of \(q\) in the ordering wave vector \((q, 0, 0)\), when this reflection was measured at different spots on the film (the X-ray beam is more than an order of magnitude smaller than the sample size). However, they are shown here because they shed light on the possibilities of manipulating the magnetic state with strain. The aim of this section is therefor to underline the fact that different behaviors can be observed when epitaxial strain is tuned.

Figure 5.32 presents scans along [110] at different temperatures. The horizontal axis is normalized to the bulk ~8.29Å lattice constant. Clearly (at least) two different reflections are observed. This could be because the X-ray beam hits two different positions on the sample, which experience different strain values. However, this cannot be the same magnetic order (i.e. same \(q\) value) from two different crystallites, as it corresponds to compressive strain values in excess of ~14%. Remarkably, these two reflections are in good agreement with the calculation shown in Figure 5.11, so they may actually be
from a single bulk-like phase. From closer inspection of Figure 5.11 it appears as though the $q \approx 0.63$ peak is also narrower than the $q \approx 0.7$ peak, as in our data.

One of the reflections survives well-above the bulk value of $T_s = 27K$. Furthermore the approximate correlation lengths are 10’s of nm. We conclude that strain can strengthen the spiral phase. We note, however, that as before, we observe no lock in near $q \approx 2/3$. Nevertheless both reflections appear sensitive to $T_L \approx 15K$.

Figure 5.32 – RSXD scans along [110] exhibiting a two-peak feature. Data were taken from a ~30nm CCO film. (a) Raw data taken upon warming, using incoming π polarized linear light with an energy of 778 eV (Co L$_3$) with the sample at an azimuth of $\Psi = 0^\circ$ ([001] axis is in the scattering plane). The scans were conducted along the [1 10] direction, and the horizontal axis is the corresponding $q$ value in ($q q 0$), calculated using $\alpha = 8.29 \text{ Å}$. (b) (c) and (d) present best-fit parameters to a two-peak function, as function of temperature: peak height, the modulation parameter $q$, and the correlation length. The inset presents the integrated intensity in logarithmic scale. All lines are guides for the eye. Note that the correlation length for the small peak (in blue) is presented without error bars because best fits would not converge with reasonable confidence on the Lorenzian width. Therefore this dataset is presented for completeness only.

We now turn to a second measurement of this inhomogeneous film, shown in Figure 5.33. In this case, we observe only one reflection, but unlike before, here the reflection clearly locks in and remains locked below ~18K. The lock-in value may not be precise (i.e. not 2/3) because the lattice constants used for normalization may not be precise enough. The main reflection exhibits a transition
temperature of $T_2 \approx 27K$, as in bulk. However, a peak-like shape persists above the experimental noise level up to $\sim 40K$. This may indicate the existence of short-range order.

**Figure 5.33 - RSXD scans along [110] exhibiting lock-in feature.** Data were taken from a $\sim 30$nm CCO film. (a) Raw data taken upon warming, using incoming $\pi$ polarized linear light with an energy of 778 eV (Co $L_3$) with the sample at an azimuth of $\Psi = 0^\circ$ ([001] axis is in the scattering plane). The scans were conducted along the [110] direction, and the horizontal axis is the corresponding $q$ value in $(q q 0)$, calculated using $a = 8.29 \, \text{Å}$. (b) is a close up of the high-temperature data, emphasizing that a short-range order may persist. (c) (d) and (e) present the temperature dependence of the integrated intensity, the modulation parameter $q$, and the correlation length, respectively. The dashed line is a guide for the eye. The error bars of the integrated intensity represent a confidence band. This means that the actual error is most likely smaller, but due to the cutoff at $q = 0.715$ the error cannot be further reduced.

Lastly, a third measurement is presented in Figure 5.34. Here we present reciprocal space scans around the expected position of the reflections. Three panels are shown, corresponding to different temperatures: directly below $T_2 \approx 27K$, directly above $T_L \approx 15K$, and below $T_L$. These data are not consistent with the previously shown data, but show a remarkable agreement to the neutron diffraction data presented in Figure 5.10 from Ref. [100]. In that work, the (0.63 0.63 0) reflection was followed. It appeared to intensify upon cooling below $T_2 \approx 27K$, but suffered a significant reduction in intensity when the temperature dropped below $T_L \approx 15K$. Below $T_L$ a second reflection appears: (2/3 2/3 0). The qualitative agreement of our data with this observation is good, but the quantitative agreement in q values is not precise.
5.3 Discussion

The interest in CCO stems from the interplay between different magnetic sublattices, which produces the macroscopically observed $M$ and $P$, and the strong magnetoelectric coupling between them. Resonant X-ray measurements present a clear path to separately follow the behavior of each ion species.

The main topic of this chapter is the systematic study of a high-quality CCO film. Indeed, using resonant X-ray techniques we were able to separate the Co and Cr signals. We have explicitly shown that the two sublattices exhibit different temperature dependences, as predicted. In a further step, the orbital and magnetic moment were also followed, thanks to the successful application of XMCD sum rules using XEOL. The film was grown along [110], a direction which keeps both macroscopic observables in plane. This allows, in principle, applying strain directly along these directions. Furthermore, the [110] and its cubic counterparts are theoretically expected to be directions along which a modulation would destabilize the Neel state. In our case the direction of $P$ ([110]) remained virtually unstrained (see Table 5.1), and indeed the onset of the multiferroic phase remained at $T_S = 27K$, as in bulk (indicated by the appearance of the Co magnetic spiral). The direction of $M$, however, experienced tensile strain. The main difference between the film and bulk was indeed in its magnetization, which was larger than bulk and exhibited an enlarged coercive field, indicating a stronger anisotropy. This was observed through field-dependent magnetization measurements (hysteresis curves). Element-selective hysteresis measurements indicated that both the Co and the Cr exhibit the same widening of the hysteresis loop, suggesting that they acquire the same strong magnetic anisotropy. Indeed the calculations by our colleagues confirm that [001] remains the easy axis. The agreement between the coercive fields is in agreement with the expected strong coupling

Figure 5.34 – Reciprocal space scans around $(q, q, 0)$. Data were taken from a ~30nm CCO film. The three panels correspond to three temperatures: ~26K (right below $T_S$), ~19K (right above $T_C$) and ~10K (below $T_C$). All color scales are the same.
between the two moment species. Furthermore, the two elements exhibit oppositely polarized magnetization, in agreement with the expected antiferro-type coupling.

The exchange coupling between the Co and Cr sublattices is understood by all authors to be either the strongest, or among the strongest interactions [107]. Cr-Cr interactions were understood as the main driving force behind the frustration that destabilizes the Neel state, and indeed the $T_{kink}$ feature has been largely associated with Cr. We see no evidence of this feature, indicating that it is perhaps absent due to the strained state of our lattice. This is in contrast to the RXSD experiments, in which the Co spiral is clearly observed at the exact $T_s$ temperature known from bulk studies. The spiral evidences the existence of magnetic frustration, and it serves as an indicator for the onset of the multiferroic phase.

The peculiar shape of the temperature dependence of magnetization is due to the competition between the magnetic sublattice, as is expected in a ferrimagnet. To our knowledge the only study in which the shape of this curve was addressed quantitatively is that in Ref. [111]. The model in that study is simplistic in that it employs the well-known paramagnetic behavior in a mean field, described by a Brillouin function $Br(x)$, with $x$ representing the competition between the mean field and temperature as $x \propto H/T$. The behavior of the mean field on a sublattice was altered (see Eq. (4.13)) to include three terms: the external field, the internal magnetization of the sublattice, and the a cross-coupling term between the Co and Cr sublattices. The magnetization is then governed by three variables: the onset temperature of Co, the onset temperature of Cr, and a coupling constant between them $\lambda$. Their model reproduced the experiment surprisingly well: the onset $T$ of Co was fixed to $T_C = 94K$, but the best fit to the onset of Cr was 49K, in good agreement with $T_{kink}$. Furthermore, the best fit to the coupling $\lambda$ was -18K (-1.5 meV), in reasonable agreement with the calculated $J_{AB}$ values of $\sim -3.5$ meV to $\sim -4.4$ meV in Refs. [107] and [108]. However, the basic intuition in this picture is somewhat lacking: it requires the Co sublattice to order at $T_C$ for any macroscopic magnetization to appear. Once magnetization of the Co sublattice exists, the model works because the Co couples to Cr, which is why the model predicts a moment on the Cr sites above 49 K. But realistically one cannot assume that one sublattice orders independently, and drives the other. The Co-Co coupling $J_{AA}$ is weaker than $J_{AB}$ and $J_{BB}$, and the exchange path between two Co ions is ~3.6Å, which is why the LKDM theory neglected it in the first place. Furthermore when the pure dipolar mean field of the Co ions is evaluated at the Cr sites, it cancels out in the [001] direction, and only (mutually-canceling) $ab$-plane components remain.

The second point in this chapter was the application of strain. Already from the simplistic LKDM theory, the parameter $u$ was defined to quantify the level of distortion in the system. It was argued that by altering exchange paths, the Neel state was destabilized. Clearly the same idea can be achieved using strain. In our RSXD studies on other CCO films we have observed different phenomena
associated with bulk, for example the appearance of multiple reflections, as shown in Figure 5.11. However, the data in that figure represent a calculation over the entire spin system, including both Co and Cr. One could argue that some magnetic sublattices (there are 6 in total) acquire spiral components with slightly different magnetic modulations, which are then induced on the other sublattices. This does not imply that the all the Co ions acquire one modulation and all the Cr acquire another. In our RSXD study of the main film, only one reflection is observed at the Co L\textsubscript{3} edge, although in other films two were observed. This may be due to a change in the ordering of the Cr, that may change or weaken the $T_k$ transition, that \textit{is} observed in RSXD data from other films. Indeed we observed no $T_{kink}$ feature (which is associated with the Cr) in any of our data.

This system shows great potential, and while it is limited to relatively low temperatures, it has been predicted that doping it with Fe can increase its transition temperatures dramatically. The outlook from this work is twofold. On the one hand, the high degree of magnetic frustration can clearly be manipulated to alter the functionality of $M$. It remains to be seen whether or not $P$ can be manipulated in a similar fashion. A first step would be a successful measurement of $P$ from such a film, which has not been reported to date. Second, resonant X-ray techniques can provide quantitative information regarding the separately ordered sublattices. While it is unfortunate that the Cr L edges are too low for RXD in this system, one can perhaps conduct resonant scattering experiments at the Cr K edge to separately follow the Cr spirals. Linear dichroism in absorption also remains untapped, and may provide valuable information on the variations between differently strained states. Lastly, we have demonstrated the feasibility of utilizing XEOL. While this is not the first study to utilize this technique, it remains largely untapped. A systematic study into the feasibility of using XEOL with different substrates would be a valuable source of information for future applications of this technique.
6 Summary and outlook

Some conclusions from this work have been previously listed at the end of Chapters 0 and 5. We first dwell on specifics of the systems we have studied. This will be followed by a broader perspective.

The approach to the rare earth manganites in this thesis is clearly from a diffraction point of view. This is of great advantage, as it is now clear that many characteristics of this system are easily observed through diffraction. It also underlines a key difference between this and other studies. In this study, we guide ourselves using the magnetic modulation vector \((0 \, q \, 0)\). By gathering existing data from previous bulk studies, we have shown that \(q\) varies smoothly within the phase diagram. Furthermore, it is this parameter which serves as the clearest indicator that the magnetic order in thin films differs from that of bulk.

The first and foremost conclusion here is that the magnetic order and the ferroelectric distortion in the manganites can be manipulated through the lattice – i.e. via strain. We have shown that strain along specific directions alters these ferroic properties. In thick (partially relaxed) films, the \(b\) axis appears to be dominant, while in thin (highly strained) films, it is the \(a\) axis that assumes the controlling role (thick and thin are terms relative to the cutoff value of approximately 30nm). This is in good agreement with all previous studies, which have indicated that the interactions that determine the magnetic ground state are all in the \(ab\) plane. However, an open question remains as to what is the relationship between the \(a\) and the \(b\) axes’ control.

A second major observation is that all but the most strained films possess an incommensurate (ICM) magnetic order, irrespective of their \(R\) ion. This is in contrast to bulk, where a commensurate \(q = \frac{1}{2}\) value is expected for several \(R\) ions. This is intuitively associated with “weaker” multiferroic behavior, because the highest polarizations are known to exist in bulk for the \(R\) ions with \(q = \frac{1}{2}\). However, strong polarization is observed also for films with ICM order. An open question remains as to what exactly is this ICM order. Our evidence suggests that it is an \(ab\) cycloid (with an additional \(c\)-axis canting). Indeed we have pointed out that even the commensurate “E-type” order is, in fact, a commensurate \(ab\) cycloid (with a specific phase). In relation to the previous point, we have shown that high \(a\) axis strain can push \(q\) towards a value of \(\frac{1}{2}\).

These thin film results point to a more fundamental aspect of the o\(-\)RMnO\(_3\) family: the ferroic properties are strongly coupled to the lattice. The nature of this relation is not fully clear, because the correct structural parameter that affects them has not been identified. It is most likely related to a variation in the Mn-O-Mn bonds in the \(ab\) plane, which are believed to govern the multiferroic behavior. This sends us back to the magnetic ordering parameter \(q\), which serves as an indicator for the magnetic order. Under the assumption that \(q\) varies smoothly within the phase diagram, our films should also fit on that scale. However, they do not fit on the conventional phase diagram (Figure 4.6) because the controlled parameter there is the \(R\) ion radius. Clearly this cannot be considered the true
controlled parameter, and must be replaced by a structural parameter. The major open question is then what is the structural parameter that controls the phase diagram? Bond angles and bond lengths are the immediate culprits, but these do not correlate well with $q$.

A major anomaly in this context, is the lock-in feature of the magnetic order at $q = \frac{1}{2}$. This commensurate magnetic order is known to cause the strongest electric polarization. The symmetric exchange striction mechanism ($P \propto \mathbf{S}_i \cdot \mathbf{S}_j$) behind this is well understood (the same mechanism also applies for the $ab$ cycloid case). But it is not clear why the magnetic order locks in at $\frac{1}{2}$ in the first place. We have shown that with correct strain applied, materials which are nominally ICM can be \textit{pushed} to the lock in.

We have also followed the specific case of o-HoMnO$_3$, which is known for the strong enhancement of polarization when Ho orders. We have clarified that two Ho transitions occur, but only one is specifically responsible for the enhancement of $P$. Furthermore, we have specifically shown that this transition clearly affects the Mn order, which may indicate that the change in $P$ due to Ho order is mediated by the Mn.

Some of the questions that remain open can be solved with the use of hard x-ray or neutron diffraction. This includes the nature of the ICM order, which we claim is an $ab$ cycloid. The advantage of these techniques is that they provide access to a much larger portion of reciprocal space. Both, however, come at a cost: the cross section of neutrons with matter is small, which is why such experiments require large samples. The cross section of non resonant magnetic X-ray diffraction is also much weaker than RSXD, as is the resonant enhancement at the transition metal K edge. Diffraction experiments are also the best setting to address the main question that this study has not successfully answered: \textit{can the magnetic structure be manipulated electrically?} This information would have a major implication on the understanding of the magnetoelectric coupling, which is the main advantage of type-II multiferroics.

The results from the second system studied, CoCr$_2$O$_4$, are clearer, and do not need extensive explanation. They serve to point out that \textit{the ferroic orders in multiferroic systems with coupled magnetic sublattices can also be enhanced by strain}. This is shown in two separate examples. The first is that the magnetic coercive field can be greatly enhanced, in our case by two orders of magnitude. The theoretical model presented agrees with this case. The second is that the Co spiral, associated with the multiferroic phase, is found to survive to temperatures higher than the bulk $T_S$ (shown for a certain strain state). This suggest that strain directly affects this phase.

However, the effect of strain on this system has only been theoretically approached in the collinear phase. It has not been addressed for the multiferroic phase, and therefore whether this enhancement is relevant to the multiferroic behavior is still an open question. Hard X-ray or neutron diffraction
experiments can provide insight on this, as they allow other magnetic reflections to be measured. However, as mentioned above, these techniques are not without their own disadvantages.

Aside from the main topic of that study, it also underlined the usefulness of the XEOL technique. This has proven to be an effective tool for applying sum rules analysis for insulating thin films. No other absorption or transmission measurement can be practically applied to such samples.

From a broader perspective, the ferroic properties in such type-II multiferroics are linked to the lattice, and are a result of a delicate balance between competing interactions. One can appreciate that strain can play an important role in determining the ground state of our systems, as it can manipulate this balance. It is important to point out that we have seen that introducing strain does not a-priori destroy the multiferroic nature of the system. We have demonstrated the feasibility of this manipulation by changing magnetic modulation, ferroelectric polarization, coercive fields and even the magnetic structure itself. To systematically manipulate these properties in a given system, one must understand the source of magnetic frustration. For example, in the o-RMnO$_3$ family, it is the strengthening of $J_b$ (and $J_a$), to the point where it directly competes with $J_{ab}$.

As an outlook beyond the scope of this work, a number of central questions are to be addressed:

*In what direction(s) should strain be applied?* The answer to this question depends on the system in question, but the underlying point is that the direction (and sign of the strain) should intensify the frustration in the system. Realistically these questions would be best answered by computational studies.

*Can the frustration be altered by strengthening the magnetic interactions?* Strain can increase (or decrease) magnetic interaction strength by virtue of the variation in distance it causes. In other words, pushing ions closer to each other can strengthen the interaction between them. One can also approach this question by substituting ions with ones that have higher (or lower) spin. Such a scenario was suggested for CoCr$_2$O$_4$, in which Cr ions would be substituted for Fe ions [108].

*Can we manipulate the magnetic order with electric fields?* So far this has been a rare feat, and magnetoelectric coupling has been demonstrated the other way around: manipulating polarization with magnetic fields. This is not surprising, as the multiferroic phase is a result of magnetic frustration. Manipulating the magnetic order with voltages is an important prospect, but has so far remained quite untapped. One such manipulation was presented in Ref. [118].

*Can multiferroic domain switching occur?* An extension to the previous question – the specific case of switching between two magnetic domains using an electric field is a central goal in this field. Directly applying strong voltages has proven to be difficult, and even the polarization requires very strong voltages to be switched. Exotic alternative means have been recently explored, including a
resonant excitation of an electromagnon using a THz field [119], although this approach is at its infancy, as even regular ferroelectrics are not presently switchable with THz fields.

Lastly, it is worth noting that a major point that has (purposely) not been addressed is that of the ordering temperature. In order for multiferroics to become useful, it is imperative that they withstand temperatures well-above room temperature. At present, barely a handful of multiferroics achieve this, such as the well-known case of BiFeO$_3$. In our study we have not witnessed systematic variations in ordering temperatures on scales which differ greatly (and beneficially) from bulk. This point should be addressed in future studies

[125]
7 Appendixes

7.1 Appendix A: Utilizing induced orders

7.1.1 General concept

Magnetically ordered ions in a crystal can induce a magnetic order onto neighboring paramagnetic ions through the mean magnetic field distribution that they create around themselves. The magnitude and direction of the field propagates throughout the crystal with the same periodicity as the magnetic order, so the induced order would also acquire the periodicity on the inducing magnetic order. In this section I describe a calculation intended to predict such induced orders. In order to distinguish between measured signals that originate from the induced and the inducing orders, element selectivity is a prerequisite, so RXD is the technique of choice (unless the ions are of the same species), and will be the focus of this section. The motivation for doing so in the context of this thesis was to learn more about the inducing ions (e.g. Mn ions in the o-RMnO₃ family) through the paramagnetic “spectator” ions (e.g. the R ions). This is useful because the inherently small reciprocal space available when working at transition metal (TM) L edges limits the number of accessible Bragg reflections. The Lanthanide M edges are usually higher in energy, providing access to additional reflections. This allows us to better-determine order induced on the Lanthanide sublattice, and infer conclusions regarding the transition metal ions.

Once a magnetic reflection is identified at the lanthanide M edges, we must certify that the order observed is indeed an induced order by checking if the ions in question are indeed paramagnetic. The induced magnetic amplitude should follow the ideal paramagnetic behavior expected with respect to temperature and magnetic field. This is described as

\[ m \propto g \mu_B J \cdot B_f(x) \]  

(7.1)

with

\[ x = \frac{g \mu_B B}{k_B T} \]  

(7.2)

Here \( B_f \) is the Brillouin function, \( g \) is the Lande factor, \( \mu_B \) is the Bohr magneton, \( J \) is the quantum number representing the total angular momentum on the Tm site, and \( B \) is the magnitude of the local magnetic induction. The proportionality factor in Eq. (7.1) simply relates to the number of paramagnetic electrons contributing to the moment. In the limiting case of \( x \ll 1 \) this equation reduces to the well-known Curie-Weiss behavior.

In the following description I assume that the RXD intensity measured from a magnetic order is proportional to the magnetic moment amplitude squared, or \( m \propto \sqrt{I} \) (where \( m \) is the moment amplitude and \( I \) is the measured intensity). As such the induced moment amplitude on a Lanthanide
rare earth \((R)\) \(m_R\) is directly obtained from a magnetic reflection’s intensity \(I_R\) measured at an edge that is sensitive to the \(R\) ions’ unpaired spin states. Similarly, the inducing order’s moment amplitude from a transition metal \(m_{TM}\) can be derived from \(I_{TM}\).

We now wish to determine the magnetic structure induced. For this we make two assumptions. The first assumption is that the local moment at the induced site will be proportional to the size of the inducing field, and along the same direction. This assumption is valid as long as the paramagnetic moment is far from saturation. Therefore we only need to calculate the motif of the magnetic field at the induced sites, and the induced order will be proportional to it. The second assumption we make is that the dominant contribution to the local field is the magnetic dipole field from the inducing ions. The field from one inducing ion would follow the simple magnetic dipole field equation:

\[
h(r) = \frac{1}{4\pi} \left( \frac{3r(m \cdot r)}{r^5} - \frac{m}{r^3} \right)
\]

For consistency with the following steps, \(r\) is defined as the vector from the induced ion to the inducing ion, and \(m\) is the inducing ion’s moment. The field at a given induced site is then calculated as

\[
H = \int_0^R \sum_i h(r) \delta(r - r_i) \, dr
\]

Here the sum is over all inducing ions, and \(\delta\) is a three dimensional Dirac delta function. I express the field in this form to emphasize the cutoff distance \(R\). In principle one should set \(R = \infty\) in order to sum over all ions. However, as \(h\) depends on \(r^{-3}\), the effect of distant ions is negligible and it is reasonable to cut them out for computational efficiency. Another important point is that this procedure is not generally valid, because the dipole sum does not generally converge as the cutoff distance is increased (for example in the case of a ferromagnet). However, in the case of antiferromagnets, the procedure is a valid assumption because most long-range contributions cancel each other out. Those that do not will likely oscillate around a constant value with increasing \(r\). This is explicitly shown in Figure 7.1 for the case of \(\alpha\)-TmMnO\(_3\) (described in the following section): the field induced by the Mn on the Tm sites varies indefinitely by \(\pm 2\%\) around a constant value as the cutoff distance is increased.

In the following we present two cases in which the induced order is measured and used as a tool for better understanding a physical system.
Figure 7.1 – Validity of the induced order approximation: Summed dipole fields at the Tm sites (4c sites in Pbmm symmetry, field values normalized to Mn moment), as functions of the cutoff distance. Two values are shown as two distinct Tm sites are found (detailed in the following section). Even at 20 Å the variation is > ~2% of the final value.

7.1.2 Example: Induced order in o-TmMnO$_3$, resolved with RSXD

In RSXD measurements on o-TmMnO$_3$ samples, a magnetic order is observed at the Tm M edges. In this section we use the model described above to explain this observed order. It will be understood as an order induced from the antiferromagnetically ordered Mn$^{3+}$ ions onto the paramagnetic Tm$^{3+}$ ions. This material is studied in detail Chapter 0. The main motivation there is the unresolved discrepancy regarding the magnetic order of the Mn ions: bulk studies indicate that a commensurate order exists with a wave vector of (0 ½ 0) [72,76], while in films we find an ordering wave vector of (0 $q$ 0) with $q \approx 0.46$. This is shown in Figure 7.2(a) for Mn and Tm resonances. The difference in $q$ values between the two resonances is likely due to a slight change in the index of refraction (the resonances are ~800 eV apart). The parameter $q$ was extracted from the Mn $L_3$ data and the Tm $M_5$ data as a function of temperature. The temperature dependences of $q$ from the two experiments follow each other, as shown in Figure 7.2(b), further evidence that the Tm order is linked to the Mn order.

Figure 7.2 – (a) magnetic diffraction peaks measured at the Mn $L_3$ and the Tm $M_5$ edges. Note the close match in position. (b) Temperature dependence of the reciprocal space position of (0 $q$ 0) reflection shown in (a).
The temperature dependences of the integrated intensities measured from the (0 q 0) at the Mn and Tm resonances are presented in Figure 7.3. The magnetic intensity at the Tm M$_5$ resonance is assumed to be an induced order because previous work has reported that the Tm$^{3+}$ ions order independently only at ~4K [65]. To check this, I shall fit Eq. (7.1) to these data. As mentioned in the previous section, the dipole field is linear with the ordered Mn moment, so the local field may be described as $B \propto \sqrt{I_{Mn}}$, in which $I_{Mn}$ is the intensity of the magnetic (0 q 0) reflection at the Mn L$_3$ edge. Taking the Mn data into account is essential to account for the variation of the inducing field with temperature. Similarly, the intensity measured from this magnetic reflection at the Tm resonance, $I_{Tm}$, fulfills $m_{Tm} \propto \sqrt{I_{Tm}}$, in which $m_{Tm}$ is the induced moment on the Tm$^{3+}$ ions. The best fit of the model to these data is shown as a solid line in Figure 7.3, and is in good agreement with the Tm RSXD data. This indicates that the observed magnetic order of the Tm moments is indeed induced by the ordering of the Mn moments. To indicate the appearance of the structural distortion at $T_c$, the (033) structural reflection is also shown in the Figure 7.3 (measured at 8.45 KeV). As $I_{Mn}$ is observed above $T_c$ and appears to be insensitive to it, this model predicts that the induced Tm order is also insensitive to it.

Figure 7.3 - Temperature dependence of integrated intensities. Blue and black circles represent the (0 q 0) reflection measured with RSXD at the Mn L$_3$ and Tm M$_5$ edges, respectively. These reflections were measured in the same experiment. The solid line is a fit of the Tm RSXD dataset to an induced order moment, using the Mn RSXD dataset to account for the temperature variation in magnetic field. The red triangles are the (033) reflection measured with XRD at 8.45 KeV.

The next step is to use the Tm induced order to test different models of the Mn order. I consider three magnetic structures on the Mn sublattice, and calculate the magnetic field motif they produce at the Tm positions. For simplicity, all structures are calculated as commensurate with $q = \frac{1}{2}$:

1) E-type with c-axis canting, proposed by Garganourakis et al [70], and by this work in Ref. [120].
   This is suggested in analogy to mixed valence PCMO [121].
2) E-type with $a$ and $c$ axis canting, proposed by Mochizuki et al. in Ref. [35].
3) $bc$-cycloid, as found for TbMnO$_3$. [48]
The Tm ions sit at low symmetry crystallographic orbits (Pbnm Wyckoff position 4c), which are defined by two structural parameters: \(x\) and \(y\) (values are taken from Ref. [41]). The fields experienced by these sites will depend on these parameters, regardless of the Mn motif in question. Furthermore, once the magnetic dipole field contributions at each Tm site are summed up from nearby Mn moments (I set a cutoff distance of 20 Å), I find that for the first 2 proposed Mn motifs, these sums all point along the \(c\) axis only.

The option of a \(c\)-axis canted E-type motif for the Mn moments is likely, as this is the expected structure for bulk \(\alpha\)-TmMnO\(_3\) (albeit not with a small incommensurability as found in our films). I therefore discuss it in more detail than the other cases. The Mn canting we describe here alternates in sign from site to site, and is characterized by an angle \(\phi\) from the \(b\) axis towards the \(c\) axis, as in Figure 7.4 (showing the two possible domains). The fields experienced by the Tm sites will depend also on this canting angle. Calculating the mean field at the Tm sites, I find two distinct values, which I label these \(H_1\) and \(H_2\). They are associated with their corresponding Tm position in the doubled units cell in Table 7.1 (also depicted in Figure 7.4). Their dependence on the cutoff distance is shown in Figure 7.1. By systematically varying the \(\phi\) angle in the calculation I find that their dependence on the Mn canting follows:

\[
H_i = h_i \sin(\phi - \delta_i) \tag{7.5}
\]

The constants \(h_i\) and \(\delta_i\) depend on \(x\) and \(y\), for which values are taken from Ref. [41]. The phase constants \(\delta_1\) and \(\delta_2\) are then \(-94.2^\circ\) and \(-59.2^\circ\) respectively. Normalizing the Mn moments to 1 \(\mu_B\), I find that \(\mu_0 h_1\) and \(\mu_0 h_2\) are 0.155 T and 0.113 T respectively. The Mn\(^{3+}\) moment reported for bulk \(\alpha\)-TmMnO\(_3\) at low temperatures is 3.75\(\mu_B\) [65]. This can be adopted to set an upper bounds for the local dipole fields: \(|\mu_0 H_1| \leq 0.581\ T\) and \(|\mu_0 H_2| \leq 0.424\ T\).

![Figure 7.4 – Mn motif of an E-type with a c-axis canting. E1 and E2 are labels given to the two possible domains (not to be confused with E1 or E2 excitation events)](image-url)
Table 7.1 - Expressions for the magnetic field along the c axis at all Tm sites in the commensurate magnetic unit cell, following Eq. (7.3). Expressions are shown for fields induced by Mn domains E1 and E2, shown in Figure 7.4.

The next step would be to test whether the proposed structure agrees with experimental data. For this I calculate the expected azimuthal angle dependence of two magnetic reflections when diffracting off of the proposed motif: (0 ½ 0) and (0 ½ 1). These are accessible at the Tm $M_5$. I plug Eq. (7.5) and Table 7.1 into Eq. (3.33), and deduce explicit expressions for scattered intensity from when using $\pi$ and $\sigma$ linearly polarized incident light. For the (0 ½ 0) reflection, we find

$$
M^{(0 \ 0 \ 0)} = 4 \cos^2 \theta \left(1 + \sin(2\pi y)\right)\left(h_1 \sin(y_1 - \phi) - h_2 \sin(y_2 - \phi)\right)^2
$$

$$
i^{(0 \ 0 \ 0)}_{\pi} \propto M^{(0 \ 0 \ 0)} \times (3 - \cos(2\Psi) - 4 \cos(2\theta) \sin^2 \Psi)
$$

$$
i^{(0 \ 0 \ 0)}_{\sigma} \propto 2M^{(0 \ 0 \ 0)} \times \cos^2 \Psi
$$

The term $M^{(0 \ 0 \ 0)}$ is merely defined for clarity. Doing the same for (0 ½ 1), we reach

$$
M^{(0 \ ½ \ 1)} = \left(\frac{1}{5}\right)\left(h_1^2(1 - \cos 2(y_1 - \phi)) + h_2^2(1 - \cos 2(y_2 - \phi))\right)
\times (1 + \sin(2\pi y))
$$

$$
i^{(0 \ ½ \ 1)}_{\pi} \propto M^{(0 \ ½ \ 1)} \frac{1}{4} \left(49 - 36 \cos 2\theta - 5 \cos 4\theta - 4 \cos^2 \theta (5 \cos 2\theta - 3) \cos 2\Psi
- 16\sqrt{5} \sin 2\theta \sin \Psi\right)
$$

$$
i^{(0 \ ½ \ 1)}_{\sigma} \propto M^{(0 \ ½ \ 1)} \left(11 - 9 \cos 2\theta - 2 \cos^2 \theta \cos 2\Psi + 4\sqrt{5} \sin 2\theta \sin \Psi\right)
$$

The term $M^{(0 \ ½ \ 1)}$ is also just for clarity. For each reflection the proportionality parameter is the same in the $i_{\pi}$ and $i_{\sigma}$ expressions.

The azimuthal dependence of the intensity from these two reflections is presented in Figure 7.5. The corresponding calculated intensities are presented as solid lines (for (0 q 1) the experimental Bragg angle $\theta = 42^\circ$ is used). Excellent agreement is found for (0 q 0), and qualitatively good agreement is found for (0 q 1). The deviations are most likely due to variations in Bragg angle between the two samples used and due to the $q = \frac{1}{2}$ approximation used. This agreement shows that the dipolar field induced order model adequately describes the behavior of the RSXD data at the Tm $M_5$ edge.

Unfortunately, identical results arise when using the a- and c-canted E-type model proposed by Mochizuki et al [35]. A clear statement can, however, be made regarding the comparison with a Mn
A calculation of the expected intensities due to an order induced by a $bc$ cycloid is shown as dashed lines in Figure 7.5. As the data clearly do not agree with the model, a Mn $bc$ cycloid scenario can be ruled out as the cause for the incommensurability.

**Figure 7.5** – variation in RSXD intensity from the $(0 q 0)$ and $(0 q 1)$ reflections upon azimuthal rotation, measured at 10K at the Tm $M_1$ edge ($\sim$1460 eV) with incoming $\sigma$ or $\pi$ polarized linear light. Data are normalized by the sum of intensities from $\sigma$ and $\pi$ light (see figure legend). Triangles and circles correspond to data from [110]-oriented or [010]-oriented samples, respectively. Solid lines are calculations based on Eq. (3.33), (7.6) and (7.7). Dashed lines are the equivalent calculation of an induced Tm order from a Mn $bc$ cycloid.

For completeness, we briefly discuss the difference between the two models that can fit the data. The Mochizuki non-collinear model for Mn order from Ref. [35] also induces local fields at the Tm sites which are also purely along the $c$ direction, and also produces two distinct Tm moment magnitudes ($r_1$ and $r_2$). In this case, however, the fields at the Tm sites differ greatly from each other, and reach values of 1.0 T and 0.5 T which are much higher than in the model with only $c$ axis canting.

Lastly I briefly discuss validity of the individual models with respect to the expected coupling strengths. Adopting the 1.22$\mu_B$ moment reported for the Tm$^{3+}$ ions (at 2K [65]), we find that the interaction strength in the simple $c$-axis canted model does not exceed 0.04meV. This value is at least an order of magnitude lower than the expected Mn-Mn interaction strengths [37,133]. The Tm
moments can thus be regarded purely as spectators, as their effect on the Mn order is negligible. In the case of the Mochizuki model, dipolar interactions then reach over 0.07 meV, which is still small with respect to the expected Mn – Mn interactions.

7.1.3 Example: Induced order in orthoferrite TmFeO$_3$

This section deals with the case of TmFeO$_3$, which was studied for other purposes beyond the context of this thesis. I therefore only briefly discuss this case, to the extent necessary for the example. The goal of this section is give an example of utilizing the induced order calculation using technique other than RXD. In particular I will demonstrate that using this dipole mean field approximation, one can show that the induced order plays a significant role in the macroscopic observables of the material, in contradiction to the available literature.

TmFeO$_3$ is structurally very similar to o-RMnO$_3$ materials. It is also described by the orthorhombic Pbnm symmetry (space group #62). The O ions and R ions (i.e. Tm) all sit at the same crystallographic positions. Furthermore, the Mn ions at the 4b positions are simply replaced by Fe ions at the same positions. Unlike the manganites, TmFeO$_3$ is not known to undergo a symmetry-lowering transition.

The Fe ions of TmFeO$_3$ orders magnetically at ~650K as a G-type antiferromagnet (with \( Q = (001) \)) with a small ferromagnetic moment perpendicular to it. In the range 81K – 94K the system undergoes a reorientation transition in which both the AF and the FM directions turn by 90°. The directions are summarized in Figure 7.6. Furthermore, the magnitude of the net moment reduces by a factor of 2 upon cooling through the reorientation transition. This is shown in Figure 7.7. The values amount to a maximum of \(~\frac{1}{2} \mu_B\) per unit cell, indicating that the Fe moment is mostly AF, and the FM is small fraction of it (in agreement with literature).

Figure 7.6 – Sketch of the magnetic reorientation phase transition in TmMnO$_3$, from Ref. [122]. The Fe ions are shown in black, Tm ions shown in blue. (A) and (C) depict the low and high temperature structures, respectively, and (B) depicts the intermediate state. The arrows associated with the Fe ions represent the AF moment only. The axis systems in the second row depict vectors that represent the directions of the FM moment (“F”) and the axis along which the AF moments align (“G”) for each of the 3 temperature ranges.
The Tm ions do not order magnetically down to 1.6 K [124], and are expected to remain paramagnetic in the whole temperature range discussed. Indeed upon measuring magnetization curves, the magnetization above the coercive field continues to rise with rising magnetic field, suggesting a paramagnetic contribution on top of the hysteretic component.

The mean dipole magnetic field at the Tm positions induced by the Fe order was calculated using the Fe magnetic structures above and below the reorientation. For each case, we calculated the order induced by the AF order and by the FM moments separately. This was done because the actual ratio between the two components is not known. The results are summarized in Table 7.2 and Table 7.3.

<table>
<thead>
<tr>
<th>Field Component</th>
<th>$G \parallel \vec{c}$ (low T)</th>
<th>$G \parallel \vec{a}$ (high T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_x$</td>
<td>$-h_c^{AF}$</td>
<td>$-h_c^{AF}$</td>
</tr>
<tr>
<td>$h_y$</td>
<td>$-h_b^{AF}$</td>
<td>$-h_b^{AF}$</td>
</tr>
<tr>
<td>$h_z$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 7.2 – mean dipole fields induced by the Fe AF order at the Tm 4c sites. The low temperature and the high temperature configurations are shown separately ($G \parallel \vec{c}$ and $G \parallel \vec{a}$ respectively). The results are shown parametrically, and amount to $h_b^{AF} = 84.03 \times 10^{-3}$ and $h_c^{AF} = 16.26 \times 10^{-3}$, in units of $\mu_B M_{AF}/4\pi$ where $M_{AF}$ is the Fe AF moment.

The order induced by the Fe AF order at high temperatures is a ferromagnetic along the $c$ axis, parallel to the FM moment of the Fe, which is in agreement with the large $a$ axis moment observed in Figure 7.7. Below the reorientation temperatures the Fe AF order induces a Tm moment along the $a$ axis of the same magnitude (but antiparallel to the Fe FM moments). An additional AF order is induced in the $b$ direction.

Figure 7.7 - Magnetizations along the $a$ and $c$ directions from Ref. [123]. Open circles represent values obtained by measuring magnetization upon cooling (in a 100 Oe field). Solid symbols indicate value inferred from magnetization measurements at a constant temperature.
Table 7.3 – Mean dipole fields induced by the Fe FM order at the Tm 4c sites. The low temperature and the high temperature configurations are shown separately ($F \parallel a$ and $F \parallel c$ respectively). The results are shown parametrically, and amount to $h_a^{FM} = 2.87 \times 10^{-3}$, $h_b^{FM} = 5.65 \times 10^{-3}$, and $h_c^{FM} = 7.69 \times 10^{-3}$, in units of $\mu_B M_{FM}/4\pi$ where $M_{FM}$ is the Fe FM moment.

Interestingly, the induced order from the Fe FM order may also be important. At high temperatures it induces a trivial FM moment parallel to itself along the $c$ direction. However, at temperatures below the reorientation the Fe FM order induces a net moment antiparallel to itself along the $a$ axis and an AF order along the $b$ direction.

To summarize, the magnetization along the $c$ axis just above the reorientation transition amounts to:

$$M_c = 0.48 \mu_B = 4 \cdot \left( m_{Fe}^{FM} + \chi_{Tm}^c (h_c^{FM} m_{Fe}^{AF} + h_c^{AF} m_{Fe}^{AF}) \right) \quad (7.8)$$

Here the value of $M_c$ is taken from literature [122], $m_{Fe}^{FM}$ and $m_{Fe}^{AF}$ are the FM and AF magnetic moment of the Fe, $\chi_{Tm}^c$ is the $c$-axis component of magnetic susceptibility of the paramagnetic Tm$^{3+}$ ions, and $h_c^{FM}$ and $h_c^{AF}$ are in units of $\mu_B/4\pi$. The value $0.48 \mu_B$ is taken from the data in Figure 7.6.

Similarly, I express the magnetization along the $a$ axis immediately below the reorientation as

$$M_a = 0.25 \mu_B = 4 \cdot \left( m_{Fe}^{FM} - \chi_{Tm}^a (h_a^{FM} m_{Fe}^{AF} + h_a^{AF} m_{Fe}^{AF}) \right) \quad (7.9)$$

Here we use the Tm$^{3+}$ susceptibility along the $a$ axis $\chi_{Tm}^a$, instead of that of the $c$ axis. By direct comparison of Eq. (7.8) and (7.9) one can immediately identify that the reduction in absolute moment observed in Figure 7.7 is due to the change of sign before the contributions from the Tm ions: at high $T$ the Tm contribution is parallel to the Fe FM moment (along $c$), while at low $T$ the Tm is antiparallel to it (along $a$). Furthermore, as the Tm contribution follows the paramagnetic behavior in Eq. (7.1), so it should increase rapidly once temperatures are low (as in Figure 7.3). It is therefore also clear why lowering the temperature further causes the net moment of the sample to shrink. We note that it does not reach a compensation point, unlike ErFeO$_3$, which does.

In principle one can continue along this line and describe the FM and AF induced moments by the small canting angle of the Fe moments away from the G-type structure, whose value could then be obtained (along with moment strengths). However, as this is beyond the purpose of this chapter, I do not pursue this any further.
Lastly, one should recall that the dipole integral does not generally converge. Therefore one must check how stable the calculated value is upon expansion of the sphere in which the inducing ions are counted. In Figure 7.8 two of the parameters induced by the FM moments are presented as functions of this cutoff distance. Clearly the values stabilize to within a few percent well before the limit of the model (10 unit cells in any direction).

Figure 7.8 – Mean dipole fields induced by the Fe FM component, as functions of the cutoff distance of the calculation. The results are shown parametrically, in units of $\mu_0 M_{FM}/4\pi$ where $M_{FM}$ is the Fe FM moment.
7.2 Appendix B: Quantifying structural distortions in o-\(\text{RMnO}_3\)

The goal of this section is to provide specifics regarding calculations done to describe the symmetry lowering effect from \(Pbnm\) symmetry, expected in o-\(\text{RMnO}_3\) alongside the appearance of ferroelectricity. First a simplified phenomenological model will be presented, followed by a more complete description. The motivation here is to use the temperature dependence of charge reflections to estimate the level of distortion that the system undergoes.

7.2.1 Phenomenological model

In this section we wish to quantify the crystal distortion along a single crystallographic direction. This is useful to do in the absence of a known low-temperature crystal symmetry. In our case the symmetry is lowered due to the FE distortion, but the approach is general and can be applied to other scenarios. We use a simple model made possible because \((0\ k\ 0)\) reflections are forbidden by \(Pbnm\) when \(k\) is odd, but allowed when \(k\) is even. Therefore when the symmetry is lowered, the intensity measured at these reflections is used to quantify the level of distortion.

\[
\begin{align*}
\mathcal{F}(\delta) &= f \left( e^{2\pi i Q \delta} + e^{2\pi i Q \left(0 \frac{1}{2} \delta\right)} \right) = f(1 + e^{\pi i k}) \\
F(Q) &= f \left( e^{2\pi i Q \delta} + e^{2\pi i Q \left(0 \frac{1}{2} - \delta\right)} \right) = f(e^{2\pi i k \delta} + e^{2\pi i k \left(\frac{1}{2} - \delta\right)}) \\
&= f(e^{2\pi i k \delta} - e^{2\pi i k \delta}) = 2if \sin(2\pi k \delta) \approx 4\pi f k \delta
\end{align*}
\] (7.10) (7.11)

Figure 7.9 presents a toy model of two identical ions along the \((0 \ 1 \ 0)\) direction in the unit cell. They both sit at high symmetry positions in the unit cell, marked by dotted lines. In this case their structure factor for a \(Q = (0\ k\ 0)\) reflection reads:

Figure 7.9 – Toy model depicting two atoms along the \(b\) direction. Their high symmetry positions are marked by dashed lines, and their low-symmetry positions are marked by solid balls.
In which the last step assumes that $\delta \ll (2\pi k)^{-1}$ (i.e. that $\delta$ is small). Here $\delta$ is in fractional coordinates. From this we learn that the intensity of such a symmetry forbidden reflection should scale with $\delta^2$ for such cases.

To estimate the size of this distortion, we compare such a reflection with a symmetry allowed reflection. Figure 7.10(a) presents the temperature dependence of integrated intensity from the (020) and the (050) reflections ($I_{(020)}$ and $I_{(050)}$), measured from a 400nm [110]-oriented o-LuMnO$_3$ film. Clearly the intensities are separated by several orders of magnitude. Furthermore no variation is observed on the (020) indicating that the structural distortion is small. Under these conditions one can directly relate the corrected$^6$ ratio of the two intensities to $\delta$, as:

$$\frac{I_{(0\bar{1}0)}}{I_{(020)}} \approx \left| \frac{F_{(0\bar{1}0)}}{F_{(020)}} \right|^2 \approx \left| \frac{4\pi f k \delta}{4\pi f k} \right|^2 \rightarrow \delta^2 \approx \frac{I_{(0\bar{1}0)}}{I_{(020)}} \left| \frac{F_{(0\bar{1}0)}}{F_{(020)}} \right|^2$$

(7.12)

where $k$ is an odd integer. In this relation the form factor $f$ must be estimated. A reasonable assumption is to average the form factors of all ions in the unit cell. This is reasonable considering the large number of (light) oxygen ions with respect to the smaller number of (heavy) Mn and Lu ions. Using Eq. (7.12) with the datasets in Figure 7.10(a) we can now produce the temperature dependence of $\delta$, as shown in Figure 7.10(b).

![Figure 7.10](image)

Figure 7.10 – (a) integrated intensities of (020) and (050) as functions of temperature.

We note here that this approach neglects the phase difference between different ions in the structure factor (this phase is explicitly shown in Eq. (3.29)), and as such it will over estimate the size of $\delta$ if it is not a small perturbation.

---

$^6$ Corrections to intensity are described in Appendix D on page 153.
7.2.2 Full structural method

Since the crystal distortion is a weak affect, and this assumed to be a 2nd order phase transition, it is reasonable to assume that the new crystal symmetry is a Maximal non-isomorphic subgroup of Pbnm, of which seven options exist. One such group was suggested by Okuyama et al. [57]. In that study, a single crystal of o-YMnO$_3$ was grown and its structure was solved at 50K and at 23K. The former was expectedly Pbnm (space group #62), and the latter was found to be P2$_1$nm (a nonstandard setting of space group #31, equivalent in its axes to Pbnm). The conversion from the standard setting to the reported setting is listed for both symmetries in Table 7.4.

I note at this point that it is reasonable to suspect that a second structural distortion occurs at lower T’s, as the polarization reported in that study (Figure 7.11) exhibits a second jump at lower temperatures, and 23 K is in fact quite close to the FE transition for this sample. However, under the assumption that our films distort less than a single crystal, it is reasonable to assume the 23K structure reported for this system is an upper limit for the distortion of our films.

![Figure 7.11 – polarization of a single crystal of o-YMnO$_3$ as function of temperature, taken from Ref. [57].](image)

<table>
<thead>
<tr>
<th>Space group #</th>
<th>Standard setting</th>
<th>Nonstandard setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>62</td>
<td>Pnma (abc)</td>
<td>Pbnm (cab)</td>
</tr>
<tr>
<td>31</td>
<td>Pmn2$_1$ (abc)</td>
<td>P2$_1$nm (e'ba)</td>
</tr>
</tbody>
</table>

Table 7.4 – Conversion between standard and nonstandard settings. Both nonstandard settings are equivalent in the axis directions.

In this section we aim to use the published crystal symmetry of o-YMnO$_3$ at 21K to quantify the level of distortion in our films. Adopting this structure is reasonable because the materials in the o-RMnO$_3$ family are all isostructural [41] (with small differences in lattice constants and crystallographic orbits), so their distortion is most likely also similar. The structural parameters reported for $R$=Y are plotted alongside those for the heavy $R$ ions in Figure 7.12. Clearly Y is close to the structure of o-RMnO$_3$ with the heaviest lanthanides. The method of quantifying the distortion allows reaching more meaningful displacement values. In the following I first describe the logic behind the calculation. Afterwards I describe the actual steps taken to adopt the reported P2$_1$mn symmetry.
Figure 7.12 – panels (A) (B) and (C) show the crystallographic orbits of the R ion, O₁, and O₁₁ species. Panel (D) present the reported lattice constants at room temperature (expect for Y, which is at 50K).

We shall assume that, to first order, the ions in the unit cell move along a straight path from their reported positions at 50K to those at 21K. This is reasonable because the low-T structure is reported for a temperature only slightly below the FE transition. With the same line of reasoning I argue that all ions move the same fraction of their path at every temperature. This concept is illustrated in Figure 7.13.

Figure 7.13 – schematic illustrating the symmetry lowering calculation. Blue/red open circles represent 50K/21K positions of 2 ions. Solid circles represent the actual ions’ positions along the path between the two extremes. The total paths and the actual positions are indicated, to express that the fraction of total distance is the same for all ions.
For a given fraction of the distance between the 50K and 21K structures, one can calculate the structure factor for structural reflections. One can then directly compare the ratio of measured reflection intensities to calculated values and estimate the fraction of maximal distortion that the sample has undergone (“maximal distortion” refers to reaching a distortion equal to that in the structure reported for o-YMnO$_3$ at 21 K).

To use the structures reported in Ref. [57], one must first apply a number of corrections to these structures. I now list these technical details:

1) The two structures are assumed to be close. The reported 21K structure must first be shifted by $r_0 = -(0.1286, \frac{1}{4}, \frac{1}{4})$ to roughly align it with the 50K structure (values in f.c.). The value was chosen to minimize the motion of the $R$ ions between the two structures, as they are assumed to move the least due to their mass. Note that this is also reflected by the values of the shift: clearly the $b$ and $c$ axis shifts are purely a matter of definition, as they are commensurate, and $a$ axis shift is nearly commensurate as well (its value is very close to $\frac{1}{6}$).

2) Some reported crystallographic orbits in the 50K structure must be corrected so that the structure aligns with other reports of Pbnm structure for o-RMnO$_3$ (specifically with reference [41]). This amounts to the following corrections:

$$
\begin{align*}
    x(R) &\rightarrow 1 - x(R) \\
    x(O_{II}) &\rightarrow 1 - x(O_{II}) \\
    x(O_{I}) &\rightarrow x(O_{I}) - \frac{1}{2} \\
    y(O_{I}) &\rightarrow y(O_{I}) - \frac{1}{2}
\end{align*}
$$

(7.13)

3) Similar corrections must be applied to the 23 K structure. These are:

$$
\begin{align*}
    x(R_I) &\rightarrow 1 - x(R_I) \\
    x(O_{III}) &\rightarrow 1 - x(O_{III}) \\
    x(O_{II}) &\rightarrow x(O_{II}) - \frac{1}{2} \\
    x(O_{IV}) &\rightarrow y(O_{IV}) - \frac{1}{2} \\
    x(O_{I}) &\rightarrow 1 - x(O_{I}) \\
    y(O_{III}) &\rightarrow y(O_{III}) - \frac{1}{2}
\end{align*}
$$

(7.14)

A direct comparison of the two structures reveals that many of the atoms move symmetrically with respect to one another. As such the actual distortion can be defined by a small number of parameters (small compared to the number of atoms in the u.c. times three dimensions). These parameters are summarized in Table 7.5. One can immediately identify that the shift of the Mn ions is large in all directions, although it is most pronounced in the $b$ direction. The shift of the O ions is most pronounced along the $c$ axis. The $R$ ions shift mostly along $b$ as well, thus it is clear that the distortion is most pronounced along $b$. 

[141]
<table>
<thead>
<tr>
<th>Ions species in Pbnm</th>
<th>Shift parameters along $a$</th>
<th>Value (f.c.)</th>
<th>Shift parameters along $b$</th>
<th>Value (f.c.)</th>
<th>Shift parameters along $c$</th>
<th>Value (f.c.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>$\Delta R_{a_1}$</td>
<td>3.0e-5</td>
<td>$\Delta R_{b_1}$</td>
<td>6.2e-4</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>$\Delta R_{a_2}$</td>
<td>4.0e-5</td>
<td>$\Delta R_{b_2}$</td>
<td>8.6e-4</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Mn</td>
<td>$\Delta M_{na}$</td>
<td>8.2e-4</td>
<td>$\Delta M_{nb}$</td>
<td>1.68e-3</td>
<td>$\Delta M_{nc}$</td>
<td>6.5e-4</td>
</tr>
<tr>
<td>O1</td>
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<td>6.0e-5</td>
<td>$\Delta O_{1b_1}$</td>
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<td>4.4e-4</td>
<td>$\Delta O_{1b_2}$</td>
<td>4.9e-4</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>O2</td>
<td>$\Delta O_{2a_1}$</td>
<td>5.8e-4</td>
<td>$\Delta O_{2b_1}$</td>
<td>2.0e-5</td>
<td>$\Delta O_{2c_1}$</td>
<td>7.4e-4</td>
</tr>
<tr>
<td></td>
<td>$\Delta O_{2a_2}$</td>
<td>2.2e-4</td>
<td>/</td>
<td>/</td>
<td>$\Delta O_{2c_2}$</td>
<td>7.6e-4</td>
</tr>
</tbody>
</table>

Table 7.5 – summary of the shift parameters extracted from direct comparison of the structures reported in Ref. [57] for 21K and 50K (in f.c.).

We can now use this model to calculate the structure factor of the system at a given fraction of the maximal distortion. To find actual positions (in spatial units), we use the measured lattice constants of the sample in question, but we do not insert the known bulk crystallographic orbits (in Pbnm), as these vary very little from one R ion to the next (see Figure 7.12), and we cannot relate them to the orbits in the low temperature P2$_1$ nm structure, as they are known only for R=Y.

As an example, Figure 7.14 presents an example in which this procedure was used. The example is chosen because it makes use of reflections with both $k$ and $l$ miller indices, which cannot be used with the previous technique. The measurement was done on [110]-oriented 400nm thick o-LuMnO$_3$. The integrated intensities of the (044) and (054) reflections (allowed and forbidden by Pbnm, respectively) are presented in Figure 7.14(a). The temperature dependence of the (054) indicates that the symmetry lowering effect saturates just within the measured temperature range (at ~10K). The temperature dependence of the (044) shows a weak reduction of intensity upon cooling (the solid line is a linear fit of the data). Running the procedure in question, we can calculate the size of shifts as function of temperature or as function of the intensity ratio. The latter is plotted in Panels (b), (c) and (d) of Figure 7.14. We find that the measured intensity ratio $I_{(054)}/I_{(044)}$ is ~5.7% of the intensity expected from o-YMnO$_3$ at 21K.
Figure 7.14 - (a) the integrated intensity of (044) and (054) as functions of temperature, measured from a [110]-oriented 400nm thick LuMnO$_3$ film. (b,c,d) the shifts from the high to the low temperature symmetry as function of the intensity ratio, for O, Mn and Lu, respectively. Each line in these panels represents on shift parameter, as listed in Table 7.5.
7.3 Appendix C: Multipole analysis of the signals in this thesis

In this section I aim to give an instructive taste of the multipole analysis required to describe the resonant diffraction data in this thesis. The idea behind employing this analysis is to make use of the known crystal symmetry to place constraints on the possible contributions to scattering. While symmetry arguments are often powerful, this type of analysis is not crucial for most arguments in this thesis, but it is sporadically referenced throughout, and therefore presented to add an additional facet to the understanding of the observed data.

Indeed most authors avoid this type of analysis, as it is often perceived as an overkill, or too complicated to apply. The second reason I present this section is to promote the use of this type of analysis, as RXD is an increasingly common tool. I will focus on the first steps, which I perceive as the most difficult to overcome. Furthermore, the results shown here may be useful for future studies, because materials with similar structures are commonly studied (specifically orthorhombic Pbnnm). I will focus in this appendix only on the simplest case of E1-E1 transitions, and mostly on dipolar contributions (K=1).

At the base of the analysis is the same logic as in all diffraction analyses: we want to construct a structure factor for a given set of (hkl) values. That is, an expression of the scattering contribution from all ions, taking into account the phase between them. However, here we focus on the multipole expansion of the electronic cloud at each site (more precisely, an expansion of the outer electrons’ interaction with the EM field, which is, strictly speaking, not the same thing [125]). We aim to distinguish contributions to scattering from different terms of the expansion based on their rank, K (with K=0 being a monopole, K=1 a dipolar contribution etc). In doing so, we take advantage of the commonly-applied separation between the angular and the radial dependences of these terms (spherical harmonics \( Y_Q^K \) and spherical Bessel functions \( j_K \) respectively), because it is only the angular part that defines the anisotropy of the scatterers, and therefore it is the only part that concerns us. The multipoles are labelled generally as spherical tensors \( T_Q^K \) (rank K, projection Q with \(-K \leq Q \leq K\)). For further details it is instructive to follow Ref. [23]. The structure factor is then given by:

\[
F(E1, \tau) = \sum_{KQ} (-1)^Q \chi_Q^K D_{Qq}^K \Psi_q^K
\]

Eq. (7.15) is valid for the case of E1-E1 events (small changes occur for other events), and the sum is over all contributing ranks K. \( \tau \) is the reflection’s momentum transfer (we use \( \tau \) instead of \( q \) or \( Q \) in this section to avoid confusion with the tensor projection parameters). The important concept here is that the term \( \chi_Q^K \) represents the X-rays (given in detail in Ref. [23]), and \( \Psi_q^K \) is the material’s contribution to the structure factor, and contains all the information about the sample. \( D_{Qq}^K \) is a rotation of the tensor \( \Psi_q^K \) to the coordinate system of \( \chi_Q^K \) (also discussed in detail in Ref. [23]). This separation is instrumental, because for understanding the sensitivity of a reflection to specific
multipole terms, all that is needed is knowledge of \( \Psi^K_\varphi \). It is here that I believe a gap in literature exists: contemporary literature covers most aspects of applying the multipole approach, but the first simple steps in constructing \( \Psi^K_\varphi \) are not well-discussed in literature, and are probably the main barrier for novice researchers in applying this approach.

The first requirement is knowledge of the space group and of the sites of the resonant ions. For assistance in understanding the international tables of crystallography, it is instructive to read Ref. [126]. Next the relation between the resonant ions’ sites should be established, in terms of the symmetry operations of the space group. For example, a rotation by \( \pi \) around the \( z \) axis could bring us from ion site 1 to site 2. Once this is known, it should be expressed mathematically by applying these symmetry operations on the multipoles \( \langle T^K_\varphi \rangle \) (triangular brackets indicate a time-average). We can then express any multipole at the \( i \)th site, \( \langle T^K_\varphi \rangle_i \) in terms of the multipole in the first site, \( \langle T^K_\varphi \rangle_1 \). Guidance for this is available in Ref. [23]. However, as I believe that this is the trickiest part, it is spelled out in detail for all reflections in this appendix. Once these relations are spelled out, Eq. (7.16) can be readily employed to construct \( \Psi^K_\varphi \) for a reflection \( \tau \):

\[
\Psi^K_\varphi(\tau) = \sum_d \langle T^K_\varphi \rangle_d e^{i\tau d}
\]

(7.16)

Here the sum is over all resonant ions, and \( d \) is their coordinate in the unit cell. At this point it is sufficient information is present to identify which \( \langle T^K_\varphi \rangle \) components the reflection is sensitive to, and this is often sufficient information. Explicit examples of constructing \( \Psi^K_\varphi \) are given in all sections of this appendix, except the last section (the last section presents examples of calculating the azimuthal dependence of intensity, which is usually an additional next step after constructing \( \Psi^K_\varphi \)).
7.3.1 Case 1: Mn dipoles in o-RMnO₃

The Mn ions sit at high symmetry (“special”) sites (4b) in space group 62 (we use the Pbnm setting). Their positions are listed in Table 7.6. To move from the position of ion 1 to that of ion 2, a rotation of $\pi$ around the $c$ axis is required. Similarly, to get from ion 1 to ion 3, a rotation of $\pi$ around the $a$ axis is required. Both rotations are required to reach a relation between ion 1 and ion 4. These relations are summed up in Table 7.6, based on section 6.3 of Ref [23]. One can also seek guidance from Ref. [127].

Table 7.6 - the 4 Mn ions in o-RMnO₃, their position, and the mathematical relation between multipoles at these positions.

<table>
<thead>
<tr>
<th>Mn Ion (4b site)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position (Pbnm)</td>
<td>(½ 0 0)</td>
<td>(½ 0 ½)</td>
<td>(0 ½ 0)</td>
<td>(0 ½ ½)</td>
</tr>
<tr>
<td>Relation to 1st ion</td>
<td>$</td>
<td>T^K_{Q1}\rangle$</td>
<td>$</td>
<td>T^K_{Q2}\rangle$</td>
</tr>
</tbody>
</table>

To produce a $\Psi^K_Q$ tensor (the material part of the structure factor in Eq. (7.15)), we follow Eq. (7.16) and sum up all contributions in the following way:

$$\Psi^K_Q (\tau) = \sum_d \langle T^K_{Qd}\rangle e^{i\tau \cdot d} = \langle T^K_{Q1}\rangle e^{i\tau \cdot d_1} + \langle T^K_{Q2}\rangle e^{i\tau \cdot d_2} + \langle T^K_{Q3}\rangle e^{i\tau \cdot d_3} + \langle T^K_{Q4}\rangle e^{i\tau \cdot d_4}$$

$$= \langle T^K_{Q1}\rangle (e^{i\tau \cdot d_1} + (-1)^Q e^{i\tau \cdot d_2}) + \langle T^K_{Q4}\rangle ((-1)^K e^{i\tau \cdot d_3} + (-1)^K + Q e^{i\tau \cdot d_4})$$  \hspace{1cm} (7.17)

From this we can omit the “1” subscript. Inserting $\tau = 2\pi(hk)$ we find:

$$\Psi^K_Q (\tau) = \langle T^K_{Q}\rangle (e^{\pi i h} + (-1)^Q e^{\pi i (h+l)}) + \langle T^K_{-Q}\rangle ((-1)^K e^{\pi i k} + (-1)^K + Q e^{\pi i (k+l)})$$

$$= (\langle T^K_{Q}\rangle e^{\pi i h} + \langle T^K_{-Q}\rangle (-1)^K e^{\pi i k}) (1 + (-1)^Q e^{\pi i l})$$  \hspace{1cm} (7.18)

Eq. (7.18) is a general expression for resonant ions at the 4b sites of Pbnm, and can be used in many other scientific cases of materials with Pbnm symmetry, such as Fe$^{3+}$ ions in orthoferrites, Ni ions in Nickelates etc. The specific case of interest for this thesis is $\tau = 2\pi(0k0)$. For this case, we find:

$$\Psi^K_Q (\tau) = (\langle T^K_{Q}\rangle + \langle T^K_{-Q}\rangle (-1)^K e^{\pi i k}) (1 + (-1)^Q)$$  \hspace{1cm} (7.19)

For the monopole ($K = 0$) and dipole ($K = 1$) terms, we find:

$$\Psi^0_Q (\tau) = 2\langle T^0_{Q}\rangle (1 + e^{\pi i k})$$

$$\Psi^1_Q (\tau) = 2\langle T^1_{Q}\rangle (1 - e^{\pi i k}) = -4i\langle T^1_{Q}\rangle \sin \left(\frac{\pi k}{2}\right) e^{\pi i k}$$

$$\Psi^1_{\pm 1} (\tau) = (\langle T^1_{\pm 1}\rangle - \langle T^1_{\mp 1}\rangle e^{\pi i k}) (1 + (-1)^{\pm 1}) = 0$$

[146]
The \((0\ q\ 0)\) reflection is of magnetic origin, so we are interested in the dipole \((K=1)\) contributions. From Eq. (7.20) we can immediately conclude that a reflection of type \(\tau = 2\pi(0k0)\) with \(K = 1\) can only be sensitive to the \(Q = 0\) tensor, which translates to the \(c\)-axis component of the Mn ion on site 1. I do not show the \(K = 2\) quadrupole terms, as these are not relevant for this thesis, but one should note that it is immediately obvious from Eq. (7.19) that \(\Psi_{1}^{2} = \Psi_{-1}^{2} = 0\).

For completeness, I show here the intensity from each polarization channel, as function of the Bragg angle \(\theta\) and the azimuth \(\psi\) (the azimuthal dependence is explicitly calculated later in this appendix). This is done by plugging Eq. (7.20) into Eq. (7.38) (shown on page 153).

\[
I_{\pi \rightarrow \pi'}^{(0k0)} = 8\sin^{2}(2\theta)\cos^{2}\psi\sin^{2}(\frac{\psi}{\sqrt{2}}k) |\langle \tau_{\pi}^{1} \rangle|^{2}
\]
\[
I_{\pi \rightarrow \sigma'}^{(0k0)} = 8\cos^{2}\theta\sin^{2}\psi\sin^{2}(\frac{\psi}{\sqrt{2}}k) |\langle \tau_{\sigma}^{1} \rangle|^{2}
\]
\[
I_{\sigma \rightarrow \pi'}^{(0k0)} = 8\cos^{2}\theta\sin^{2}\psi\sin^{2}(\frac{\psi}{\sqrt{2}}k) |\langle \tau_{\sigma}^{1} \rangle|^{2}
\]

(7.21)

### 7.3.2 Case 2: Mn ions in \(P2_{1}nm\)

For the case of \(o-RMnO_{3}\) with heavy \(R\) ions, the lattice distortion due to the lowering of crystal symmetry is not negligible. In the following I repeat the calculations for Mn in the previous section, but while taking into account also the lattice deformation. As in previous sections, I base the calculation on the results of Ref. [57], in which the low temperature symmetry was reported as space group 31. In this reduced symmetry two of the 2-fold rotation axes are lost, and only the rotation around the \(a\) axis remains (in a \(Pbnm\)-like setting).

Before the multipole analysis, the setting of the unit cell must be corrected to be directly comparable to the known high-temperature \(Pbnm\) setting. In space group \#31 there is one symmetry operation that includes a 2-fold rotation axis. In the standard setting of the space group (\(Pmn2_{1}\)), the 2-fold rotation axis is parallel to the \(c\) axis, and a normalized vector \((\frac{1}{4}00)\) separates it from the origin. It is then followed by a translation of \((0\ 0\ \frac{1}{2})\). In Ref. [57] the structure is given in the \(P2_{1}nm\) setting, which is equivalent in axis directions to \(Pbnm\). Here the 2-fold rotation axis is parallel to the \(a\) axis, it is separated from the origin by a normalized vector \((0\ 0\ \frac{1}{4})\), and it is followed by a translation of \((-\frac{1}{2}00)\).

Finally, to compare with reported \(Pbnm\) 4b positions, the ions must be shifted by \(-\left(\frac{1}{4}\frac{1}{4}\frac{1}{4}\right)\) . To maintain the same relation between them upon 2-fold rotation, the rotation axis must be shifted by \(+\left(\frac{1}{4}\frac{1}{4}\frac{1}{4}\right)\). The translation does not change when the axes setting changes. Note that if the rotation axis were to be shifted by \(-\left(\frac{1}{4}\frac{1}{4}\frac{1}{4}\right)\), the relation between the ions would be wrong. This is a consequence of the loss of inversion symmetry. Furthermore, the loss of inversion symmetry means that 2 pairs on Mn ions may be related by a 2-fold rotation, but the relation between the pairs is via a mirror plane (inversion). This affects the sign of axial tensors (odd \(K\)), and therefore the following expressions are expressed with two tensors \(\langle T_{Q}^{K} \rangle_{1}\) and \(\langle T_{Q}^{K} \rangle_{2}\) to maintain generality.
The Mn ions in o-RMnO₃, their position in P2₁nm setting of space group #31 (as reported in Ref. [57]), their equivalent position with the origin as in the Pbnm setting of space group #62, and the mathematical relation between multipoles at these positions. The Pbnm-equivalent positions are expressed in terms of parameters that quantify the deviation from the Pbnm symmetry.

\[ \text{Relation} \]

<table>
<thead>
<tr>
<th>Mn Ion (4b site)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reported position (P2₁nm)</td>
<td>( (\frac{1}{2}x - y \frac{1}{2}z) )</td>
<td>( xy - z )</td>
<td>( x y z )</td>
<td>( (\frac{1}{2}x - y \frac{1}{2}z + z) )</td>
</tr>
<tr>
<td>Equivalent Position (Pbnm)</td>
<td>( (\frac{1}{2}+\Delta x, \Delta y, \Delta z) )</td>
<td>( (\frac{1}{2}+\Delta x, \Delta y, \frac{1}{2}-\Delta z) )</td>
<td>( (\Delta x, \frac{1}{2}-\Delta y, -\Delta z) )</td>
<td>( (\Delta x, \frac{1}{2}-\Delta y, \frac{1}{2}+\Delta z) )</td>
</tr>
</tbody>
</table>

A \( \Psi^K_Q \) material tensor for \( \tau = 2\pi(0k0) \) is written as before using Eq. (7.16), as:

\[
\Psi^K_Q(0k0) = \sum_d \langle T^K_d \rangle_d e^{i\tau d} \quad (7.22)
\]

For the monopole (\( K = 0 \)) and dipole (\( K = 1 \)) terms, we find:

\[
\Psi^0_K(\tau) = (\langle T^0_1 \rangle_1 + \langle T^0_2 \rangle_2)(e^{2\pi i k\Delta y} + e^{2\pi i k(\frac{1}{2}-\Delta y)})
\]

\[
\Psi^1_K(\tau) = (\langle T^1_1 \rangle_1 + \langle T^1_2 \rangle_2)(e^{2\pi i k\Delta y} - e^{2\pi i k(\frac{1}{2}-\Delta y)}) \quad (7.23)
\]

To advance further, one must describe the relation between \( \langle T^K_1 \rangle_1 \) and \( \langle T^K_1 \rangle_2 \). These must be decomposed into parity-even and parity-odd contributions. One should also consider the possibility that \( \langle T^K_1 \rangle_1 \) and \( \langle T^K_1 \rangle_2 \) do not represent the same moment value, but any such variation is likely to be very small compared to their average value.

7.3.3 Case 3: R ions in o-RMnO₃ (Pbnm)

The R ions in Pbnm sit at 4c crystallographic orbits (“general positions”) defined by two free parameters “x” and “z” (this notation is a relic of the use of the Pnma setting, which is sometimes confusing when using Pbnm since “z” is along [100] and “x” is along [010]). As before, I spell out the explicit terms through which the sites relate to each other (in Table 7.8):
The general expression for $\Psi_Q^K$ as function of $\tau = 2\pi(\text{hkl})$ is cumbersome. Therefore here I directly write the expressions for reflections which are observed in this thesis.

7.3.3.1. Reflections of type (0 k 0)

For $\tau = 2\pi(0k0)$ one finds:

$$
\Psi_Q^K(0k0) = \langle T_Q^K \rangle (e^{2\pi ikx} + (-1)^0 e^{-2\pi ikx}) + \langle T_Q^\prime^K \rangle (-1)^k e^{i\pi kx} (e^{-2\pi ikx} + (-1)^0 e^{2\pi ikx})
$$

(7.24)

This can be written as:

$$
\Psi_Q^0(0k0) = \langle T_Q^0 \rangle (e^{2\pi ikx} + e^{-2\pi ikx})(1 + e^{i\pi kx}) = 4\langle T_Q^0 \rangle \cos(2\pi kx) \cos(\pi k/2) e^{i\pi kx}
$$

$$
\Psi_Q^1(0k0) = \langle T_Q^1 \rangle (e^{2\pi ikx} + e^{-2\pi ikx})(1 - e^{i\pi kx}) = -4\langle T_Q^1 \rangle \cos(2\pi kx) \sin(\pi k/2) e^{i\pi kx}
$$

(7.25)

$$
\Psi_{\pm 1}^1(0k0) = \langle (T_{\pm 1}^1) + (T_{\pm 1}^\prime) \rangle e^{i\pi kx} (e^{2\pi ikx} - e^{-2\pi ikx}) = 2i \sin(2\pi kx) \langle (T_{\pm 1}^1) + (T_{\pm 1}^\prime) \rangle e^{i\pi kx}
$$

Further reduction of $\Psi_{\pm 1}^1$ would require further knowledge of $\langle T_{\pm 1}^1 \rangle$. The next logical step would be to employ the general relation $\langle T_Q^K \rangle^* = (-1)^Q \langle T_Q^Q \rangle$. For commensurate $k$ values this would imply that $\Psi_{\pm 1}^1$ would be purely real or purely imaginary. However it is already at this point that one should note that for the $R$ ions the (0 k 0) reflection is not the same as for the Mn ions, because for an incommensurate $k$ it is clearly sensitive to all components of the $R$ ions’ dipole.

For completeness I also write the quadrupolar terms.

$$
\Psi_Q^2(0k0) = \langle T_Q^2 \rangle (e^{2\pi ikx} + e^{-2\pi ikx})(1 + e^{i\pi kx}) = 4\langle T_Q^2 \rangle \cos(2\pi kx) \cos(\pi k/2) e^{i\pi kx}
$$

$$
\Psi_{\pm 1}^2(0k0) = \langle (T_{\pm 1}^2) - (T_{\pm 1}^\prime) \rangle e^{i\pi kx} (e^{2\pi ikx} - e^{-2\pi ikx}) = 2i \sin(2\pi kx) \langle (T_{\pm 1}^2) - (T_{\pm 1}^\prime) \rangle e^{i\pi kx}
$$

(7.26)

$$
\Psi_{\pm 2}^2(0k0) = \langle (T_{\pm 2}^2) + (T_{\pm 2}^\prime) \rangle e^{i\pi kx} (e^{-2\pi ikx} + e^{2\pi ikx}) = 2 \cos(2\pi kx) \langle (T_{\pm 2}^2) + (T_{\pm 2}^\prime) \rangle e^{i\pi kx}
$$

From inspection one immediately sees that for any commensurate $k$ value $\Psi_Q^0 = 0$. Terms of the form $\langle T_{\pm 1}^1 \rangle$ were suggested in Ref. [87] to be the cause for (0 2q 0) charge reflections, as they can relate to quadrupolar charge fluctuations that would not appear in simpler models. Indeed here it is shown from an explicit calculation that these terms do not cancel out (such reflections require special treatment to account for the loss of translational symmetry).
7.3.3.2. Reflections of type (0 k 1)

For reflections of the form $\tau = 2\pi(0kl)$ one finds:

$$\Psi_Q^K(0kl) = e^{\frac{i}{2}inl} \left[ \langle T^K_0 \rangle (e^{2\pi ink} + (-1)^{q+1}e^{-2\pi ink}) + \langle T^K_{-1} \rangle (-1)^{k}e^{ink}(-e^{-2\pi ink} + (-1)^{q}e^{2\pi ink}) \right] \quad (7.27)$$

For brevity, I limit the discussion to odd $l$ values, which are of interest in this work. Eq. (7.27) then reduces to:

$$\Psi_Q^K(0kl) = i(-1)^{l+1} \left[ \langle T^K_0 \rangle (e^{2\pi ink} + (-1)^{q}e^{-2\pi ink}) + \langle T^K_{-1} \rangle (-1)^{k}e^{ink}(-e^{-2\pi ink} + (-1)^{q}e^{2\pi ink}) \right] \quad (7.28)$$

The contributing terms up to the dipolar order are (note that the prefactor $i(-1)^{l+1}$ is omitted for clarity in Eq. (7.29)):

$$\Psi^0_0(0kl) = \langle T^0_0 \rangle (e^{2\pi ink} - e^{-2\pi ink})(1 + e^{ink}) = 4i\langle T^0_0 \rangle \sin(2\pi lk) \cos(nk/2) e^{\frac{i}{2}ink}$$

$$\Psi^1_0(0kl) = \langle T^1_0 \rangle (e^{2\pi ink} - e^{-2\pi ink})(1 - e^{ink}) = 4\langle T^1_0 \rangle \sin(2\pi lk) \sin(nk/2) e^{\frac{i}{2}ink} \quad (7.29)$$

$$\Psi^1_{\pm 1}(0kl) = \left( \langle T^1_{\pm 1} \rangle + \langle T^1_{\mp 1} \rangle e^{ink} \right) (e^{-2\pi ink} + e^{2\pi ink}) = 2\left( \langle T^1_1 \rangle + \langle T^1_{-1} \rangle e^{ink} \right) \cos(2\pi lk)$$

7.3.3.3. Reflections of type (h k 0)

Lastly, as the (1 q 0) reflection was also observed, I also spell out the terms for reflections of type $\tau = 2\pi(hk0)$. The general expression would be:

$$\Psi_Q^K(hk0) = \langle T^K_0 \rangle (e^{2\pi ichz+\kappa k} + (-1)^q e^{-2\pi ichz+\kappa k}) + \langle T^K_{-1} \rangle \langle e^{2\pi ichz+\kappa k} + (-1)^q e^{-2\pi ichz+\kappa k} \rangle \quad (7.30)$$

Since the interest is only in odd integer $h$ values, Eq. (7.30) can be slightly simplified, although an explicit dependence on the value of the orbit “z” is maintained:

$$\Psi_Q^K(hk0) = \langle T^K_0 \rangle (e^{2\pi ichz+\kappa k} + (-1)^q e^{-2\pi ichz+\kappa k}) + \langle T^K_{-1} \rangle \langle e^{2\pi ichz+\kappa k} + (-1)^q e^{-2\pi ichz+\kappa k} \rangle \quad (7.31)$$

The contributing terms up to the dipolar order are:

$$\Psi^0_0(hk0) = 2\langle T^0_0 \rangle \left( \cos(2\pi(hz + \kappa k)) - e^{ink} \cos(2\pi(hz - \kappa k)) \right)$$

$$\Psi^1_0(hk0) = 2\langle T^1_0 \rangle \left( \cos(2\pi(hz + \kappa k)) + e^{ink} \cos(2\pi(hz - \kappa k)) \right)$$

$$\Psi^1_{\pm 1}(hk0) = 2i\left( \langle T^1_{\pm 1} \rangle \sin(2\pi(hz + \kappa k)) + \langle T^1_{\mp 1} \rangle e^{ink} \sin(2\pi(hz - \kappa k)) \right) \quad (7.32)$$
7.3.4 Case 3: Co ions in CoCr₂O₄

Now I focus on the Co ions in CoCr₂O₄. These sit on 8 diamond sites (2 fcc sublattices). The relation between the ions within each of the fcc sublattices can be expressed by simple 2-fold rotations around the principle axes. Site 1 relates to sites 2, 3 and 4 by rotations of π around the x, y and z axes, respectively. In the same manner, site 5 relates to sites 6, 7 and 8 through the same rotation around the x, y and z axes, respectively. In this brief account I treat these two sublattices separately, as the relation between then involves a nontrivial operation (for example, a rotation by π around a diad parallel to [110]).

<p>| Table 7.9 – relations between the ions in the first fcc sublattice of Co in CCO. |</p>
<table>
<thead>
<tr>
<th>Co Ion (8a site)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position (Fd3m)</td>
<td>(0,0,0)</td>
<td>(½, 0, ½)</td>
<td>(½, ½, 0)</td>
<td>(0, ½, ½)</td>
</tr>
<tr>
<td>Relation to 1ˢ ion</td>
<td>(\langle T^K_Q \rangle_1)</td>
<td>(\langle T^K_Q \rangle_2 = (−1)^K\langle T^K_Q \rangle_1)</td>
<td>(\langle T^K_Q \rangle_3 = (−1)^K\langle T^K_Q \rangle_1)</td>
<td>(\langle T^K_Q \rangle_4 = (−1)^Q\langle T^K_Q \rangle_1)</td>
</tr>
</tbody>
</table>

<p>| Table 7.10 – relations between the ions in the second fcc sublattice of Co in CCO. |</p>
<table>
<thead>
<tr>
<th>Co Ion (8a site)</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position (Fd3m)</td>
<td>(½, ½, ⅔)</td>
<td>(⅔, ½, ⅔)</td>
<td>(⅔, ⅔, ½)</td>
<td>(⅔, ⅔, ⅔)</td>
</tr>
<tr>
<td>Relation to 1ˢ ion</td>
<td>(\langle T^K_Q \rangle_5)</td>
<td>(\langle T^K_Q \rangle_6 = (−1)^K\langle T^K_Q \rangle_5)</td>
<td>(\langle T^K_Q \rangle_7 = (−1)^K\langle T^K_Q \rangle_5)</td>
<td>(\langle T^K_Q \rangle_8 = (−1)^Q\langle T^K_Q \rangle_5)</td>
</tr>
</tbody>
</table>

We deal here with the cubic case of CCO. A reflection of the general form \(\tau = 2\pi hkl\) would produce the following contribution from the first Co fcc sublattice

\[
\psi^K_{Q, first} (\tau) = \langle T^K_Q \rangle_1 + (−1)^K\langle T^K_Q \rangle_1 e^{πi(h+l)} + (−1)^K\langle T^K_Q \rangle_1 e^{πi(h+k)} + (−1)^Q\langle T^K_Q \rangle_1 e^{πi(h+l)}
\]

\[
= \langle T^K_Q \rangle_1 (1 + (−1)^Q e^{πi(h+l)}) + (−1)^K e^{πi(h+k)}(\langle T^K_Q \rangle_1 e^{πi(h+l)} + (−1)^Q e^{πi(h+k)})
\] (7.33)

And the following contribution from the second Co fcc sublattice.

\[
\psi^K_{Q, second} (\tau) = \langle T^K_Q \rangle_5 e^{½πi(h+k+l)} + (−1)^K\langle T^K_Q \rangle_5 e^{½πi(h+k+l)}
\]

\[
+ (−1)^K\langle T^K_Q \rangle_5 e^{½πi(h+k+l)} + (−1)^Q\langle T^K_Q \rangle_5 e^{½πi(h+k+l)}
\]

\[
= e^{½πi(h+k+l)} \left[ \langle T^K_Q \rangle_5 (1 + (−1)^Q e^{πi(h+k)}) \right] + (−1)^K e^{πi(h+k)} (\langle T^K_Q \rangle_5 e^{πi(h+k+l)} + (−1)^Q e^{πi(h+k+l)})
\] (7.34)

To simplify this, the interest in this section is for reflections with an ordering wave vector of the form \(\tau = 2\pi (q, q, 0)\). The two equations then simplify to the nearly identical forms:

\[
\psi^K_{Q, first} (qq0) = \langle T^K_Q \rangle_1 (1 + (−1)^Q e^{πi(q)}) + (−1)^K e^{πi(q)}(\langle T^K_Q \rangle_1 (1 + (−1)^Q e^{πi(q)})
\] (7.35)

and

\[
\psi^K_{Q, second} (qq0) = e^{πi(q)} \left[ \langle T^K_Q \rangle_5 (1 + (−1)^Q e^{πi(q)}) + (−1)^K e^{πi(q)}(\langle T^K_Q \rangle_5 e^{πi(q)} + (−1)^Q e^{πi(q)}) \right]
\] (7.36)
7.3.5 Azimuthal scans around (0 k 0) and (0 k 1)

This section gives a brief overview of the work required to calculate variations in intensity as the sample is rotated around \( \tau \). Specific equations will be derived for use in specific cases of previous subsections of this appendix. Detailed guidance for this process is given in the appendixes of Ref. [128], and I encourage readers to follow this for greater detail.

Here I will focus only on K=1 contributions, as only these are relevant to this thesis. However it should be noted that the results in this subsection are correct for any sample with orthonormal axes (cubic, tetragonal, orthorhombic), irrespective of the internal symmetry.

Explicit forms of the X-ray term \( X^K_0 \) are now required for this. These can be calculated for any geometry (e.g. by employing \( X^1 = \frac{i}{\sqrt{2}} (e' \times e) \)), but it is instrumental to use the geometry defined in Figure 3 of Ref. [23] (they are also tabulated therein), because most examples in literature follow it, and one can then cross-check results. This geometry dictates that \( \tau \) must be along \(-\hat{x}\), which means that the sample must be rotated accordingly from its local coordinates (\( abc \)). However, this leaves one degree of freedom, which we satisfy by rotating the sample to an arbitrary azimuth defined as \( \psi = 0^\circ \).

This initial rotation is described by the operation \( R_\psi (\alpha, \beta, \gamma) \), in which the angles are Euler angles. After this, a second rotation is applied azimuthal rotation \( R_\psi (\alpha, \beta, \gamma) \). For correct rotation the use of tabulated \( d^K_{M M'} \), values is required, which are available on page 119 of Ref. [129].

7.3.5.1. Azimuthal scans around \( \tau = (0 k 0) \)

To calculate the azimuthal dependence of reflections of the form \((0 k 0)\), the rotation angles are given by \( R_\psi (0,0,\pi/2) \) and \( R_\psi (\psi/2,\psi, -\pi/2) \). In this scenario, \( \psi = 0^\circ \) is defined when the \( a \) axis is made parallel to \( \hat{y} \) in the experimental coordinates in Figure 3 of Ref. [23].

The full explicit forms of the intensity from the reflection then take the forms:

\[
I^{(0k0)}_{\pi-\pi} = \frac{1}{2} \sin^2(2\theta) \left( \cos^2 \psi |\Psi_0^1|^2 \right) \\
+ \frac{1}{2} \sin^2 \psi \left( |\Psi_1^1|^2 + |\Psi_{-1}^1|^2 - (\Psi_1^1)(\Psi_{-1}^1)^* - (\Psi_{-1}^1)(\Psi_1^1)^* \right) \\
+ 2^{-3/2} \sin 2\psi \left( (\Psi_0^1)(\Psi_1^1)^* + (\Psi_1^1)(\Psi_0^1)^* - (\Psi_{-1}^1)(\Psi_0^1)^* - (\Psi_0^1)(\Psi_{-1}^1)^* \right) \\
- (\Psi_0^1)(\Psi_{-1}^1)^* \\
\]

(7.37)
\[ I^{(0k0)}_{\pi \rightarrow \sigma'} = \frac{1}{4} \cos^2 \theta \left( 2 \sin^2 \psi |\Psi_0^1|^2 + (\tan^2 \theta + \cos^2 \psi) \left(|\Psi_1^1|^2 + |\Psi_{-1}^1|^2\right) 
- \sqrt{2} \sin \psi \left((\Psi_0^1)(\Psi_1^1)^* (i \tan \theta + \cos \psi) + (\Psi_0^1)(\Psi_{-1}^1)^* (i \tan \theta - \cos \psi) \right) 
+ (\Psi_0^1)(\Psi_1^1)^* (-i \tan \theta + \cos \psi) + (\Psi_0^1)(\Psi_{-1}^1)^* (-i \tan \theta - \cos \psi) \right) 
+ (\Psi_1^1)^* (\Psi_{-1}^1)^* (\tan^2 \theta - \cos^2 \psi + 2i \tan \theta \cos \psi) \right) 
+ (\Psi_1^1)^* (\Psi_{-1}^1)^* (\tan^2 \theta - \cos^2 \psi - 2i \tan \theta \cos \psi) \right) \]

\[ I^{(0k0)}_{\sigma \rightarrow \pi'} = \frac{1}{4} \cos^2 \theta \left( 2 \sin^2 \psi |\Psi_0^1|^2 + (\tan^2 \theta + \cos^2 \psi) \left(|\Psi_1^1|^2 + |\Psi_{-1}^1|^2\right) 
- \sqrt{2} \sin \psi \left((\Psi_0^1)(\Psi_1^1)^* (i \tan \theta + \cos \psi) + (\Psi_0^1)(\Psi_{-1}^1)^* (i \tan \theta - \cos \psi) \right) 
+ (\Psi_0^1)(\Psi_1^1)^* (-i \tan \theta + \cos \psi) + (\Psi_0^1)(\Psi_{-1}^1)^* (-i \tan \theta - \cos \psi) \right) 
+ (\Psi_1^1)^* (\Psi_{-1}^1)^* (\tan^2 \theta - \cos^2 \psi + 2i \tan \theta \cos \psi) \right) 
+ (\Psi_1^1)^* (\Psi_{-1}^1)^* (\tan^2 \theta - \cos^2 \psi - 2i \tan \theta \cos \psi) \right) \]

Clearly these terms are not given in their most compact form, but in a form that one can easily plug in \( \Psi_Q^1 \) terms and identify which contributions cancel out. In fact, it is instructive to recall that many specific cases in this thesis involve contributions only from moments along the \( c \) axis. This translates into \( \Psi_Q^0 \), and all other terms are zero. Eq. (7.37) then shrinks to:

\[ I^{(0k0)}_{\pi \rightarrow \sigma'} = \frac{1}{2} \sin^2 (2 \theta) \cos^2 \psi |\Psi_0^1|^2 \]

\[ I^{(0k0)}_{\sigma \rightarrow \pi'} = \frac{1}{2} \cos^2 \theta \sin^2 \psi |\Psi_0^1|^2 \]

\[ I^{(0k0)} = \frac{1}{2} \cos^2 \theta \sin^2 \psi |\Psi_0^1|^2 \]  \hspace{1cm} (7.38)

Clearly the only parameter that changes the azimuthal scans’ shape is the Bragg angle \( \theta \). Even with no explicit knowledge of \( \Psi_Q^1 \), or even of the ions’ positions, this is enough to reproduce many of our experiments. Figure 7.15 presents azimuthal scans of (0 \( q \) 0) alongside calculations with using Eq. (7.38) with \( \theta \) values close to experimental ones.
Figure 7.15 – Azimuthal scans around \((0 q 0)\) with different \(\theta\) values. Solid lines are calculations of Eq. (7.38) using \(\theta = 20^\circ\) and \(50^\circ\), which are close to experimental values for the Mn \(L\) edges and the Tm \(M_5\) edge with \(q = {\frac{1}{2}}\). Open circles represent data from \(o\)-TmMnO\(_3\) and closed circles represent data from \(o\)-LuMnO\(_3\). All data are normalized to the sum of intensities from incoming \(\sigma\) and \(\pi\) polarized light.

7.3.5.2. Azimuthal scans around \(\tau = (0 k l)\)

This rotation is slightly more involved, because \(\tau\) is not along a principle axis. However, it does lie in the \(bc\) plane, which simplifies the algebra. A detailed explanation of the algebra is given in Ref. [128] for a nearly identical case. To calculate the azimuthal dependence of reflections of the form \((0 k l)\), a number of definitions are required. A rotation to the experimental geometry Ref. [23] with \(\psi = 0^\circ\) is given by \(R_{\tau}(0, \beta, \pi/2)\), in which \(\psi = 0^\circ\) is defined when \(\hat{a}\) axis is parallel to \(\hat{y}\). \(\beta\) is an angle defined by the direction of \(\tau\), and is given by \(\sin \beta = -\tau_c\) and \(\cos \beta = \tau_b\). It is now noteworthy that \(\tau\) is a unit vector defined as

\[
\tau = (\tau_a, \tau_b, \tau_c) = \left(\frac{h}{a}, \frac{k}{b}, \frac{l}{c}\right) / \sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}
\]

Subsequent azimuthal rotations are again given by \(R_{\psi}(\pi/2, \psi, -\pi/2)\). The addition of the two rotations is greatly simplified by adding the following definitions (see specific description of the addition theorem in Ref. [128] and Ref. [23]):

\[
\cot \alpha_0 \equiv \cot \beta_i \sin \psi
\]

\[
\cos \beta_0 \equiv \cos \psi \cos \beta_i
\]

The full explicit descriptions of the intensity from the reflection then take the forms:
\[ I_{\pi \to \sigma}^{(0k\ell)} = \frac{1}{2} \sin^2(2\theta) \left( \cos^2 \beta_0 |\Psi_0^1|^2 ight. \\
+ \frac{1}{2} \sin^2 \beta_0 \left[ |\Psi_{-1}^1|^2 + |(\Psi_{-1}^1)(\Psi_{-1}^1)^* e^{-i\alpha_0} - (\Psi_{-1}^1)(\Psi_{-1}^1)^* e^{2i\alpha_0} \right] \\
+ 2^{-3/2} \sin 2\beta_0 \left( (\Psi_0^1)(\Psi_{-1}^1)^* e^{i\alpha_0} + (\Psi_{-1}^1)(\Psi_0^1)^* e^{-i\alpha_0} - (\Psi_{-1}^1)(\Psi_0^1)^* e^{i\alpha_0} \\
- (\Psi_0^1)(\Psi_{-1}^1)^* e^{-i\alpha_0} \right) \]

\[ I_{\pi \to \sigma'}^{(0k\ell)} = \frac{1}{4} \cos^2 \theta \left( 2 \sin^2 \beta_0 |\Psi_0^1|^2 + (\tan^2 \theta + \cos^2 \beta_0) \left( |\Psi_1^1|^2 + |\Psi_{-1}^1|^2 \right) \\
- \sqrt{2} \sin \beta_0 \left( (\Psi_0^1)(\Psi_{-1}^1)^* e^{-i\alpha_0} (i \tan \theta + \cos \beta_0) \\
+ (\Psi_{-1}^1)(\Psi_0^1)^* e^{i\alpha_0} (i \tan \theta - \cos \beta_0) \\
+ (\Psi_0^1)(\Psi_1^1)^* e^{-i\alpha_0} (-i \tan \theta + \cos \beta_0) \\
+ (\Psi_1^1)(\Psi_{-1}^1)^* e^{i\alpha_0} (-i \tan \theta - \cos \beta_0) \right) \]  

(7.41)

\[ I_{\sigma \to \sigma'}^{(0k\ell)} = \frac{1}{4} \cos^2 \theta \left( 2 \sin^2 \beta_0 |\Psi_0^1|^2 + (\tan^2 \theta + \cos^2 \beta_0) \left( |\Psi_1^1|^2 + |\Psi_{-1}^1|^2 \right) \\
- \sqrt{2} \sin \beta_0 \left( (\Psi_0^1)(\Psi_{-1}^1)^* e^{-i\alpha_0} (i \tan \theta + \cos \beta_0) \\
+ (\Psi_{-1}^1)(\Psi_0^1)^* e^{i\alpha_0} (i \tan \theta - \cos \beta_0) \\
+ (\Psi_0^1)(\Psi_1^1)^* e^{-i\alpha_0} (-i \tan \theta + \cos \beta_0) \\
+ (\Psi_1^1)(\Psi_{-1}^1)^* e^{i\alpha_0} (-i \tan \theta - \cos \beta_0) \right) \]  

As before, there terms are not given in their most compact form so that relations between different terms are easily observed. Unlike the previous example, however, it is not possible to reproduce the experimental results of (0 q 1) when only the c component contributes (see Figure 7.5). This is because the induced order on the R ion is comprised of two inequivalent sublattices, so more information is required.
7.4 Appendix D: Miscellaneous calculations

7.4.1 Thin film calculations

In the following a number of calculations are presented which are specific for the case of diffraction from thin films.

7.4.1.1. Limit on azimuthal dependence for off-specular reflections

When following a reflection that is not specular, the angle between the light and the surface varies upon azimuthal rotation. We now define the angle $\chi_0$, which is the angle between the momentum transfer $Q$ and the film normal.

![Figure 7.16 – Experimental geometry of diffraction from a film, following a non-specular reflection.][1]

This is shown in Figure 7.16. For low $\chi_0$ values, a full azimuthal rotation can still be recorded. The critical angle, beyond which the light is blocked by the substrate for certain azimuths, is $\chi_0 = 90^\circ - \theta$, where $\theta$ is the Bragg angle. We now aim to calculate the range of accessible azimuthal angles for a given $\chi_0 > 90^\circ - \theta$.

We choose a coordinate system in which $\hat{\psi}$, $\hat{z}$ points upwards and $\hat{x}$ is in the film plane when $\psi = 0^\circ$ (and $180^\circ$). In this axis system the film normal is expressed as along the film

$$\hat{n} = (0 \cos \chi_0 \sin \chi_0)$$

(7.42)

The wave vectors $\hat{k}$ and $\hat{k}'$ are expressed in this coordinate system as

$$\hat{k} = (-\cos \theta \ - \sin \theta \ 0)$$

$$\hat{k}' = (-\cos \theta \ \sin \theta \ 0)$$

(7.43)

Azimuthal dependence can be expressed with a simple rotation matrix around $Q$, written as $R(\psi)$. The normal can then be written as $\hat{n}(\psi) = R(\psi)\hat{n}(\psi = 0)$. The conditions for blocking the beam are then given by $\hat{n} \cdot \hat{k} = 0$ and $\hat{n} \cdot \hat{k}' = 0$. As an example, the first case is explicitly written out as

[156]
\[
\hat{k} \cdot \hat{n} = (-\cos \theta - \sin \theta) \begin{pmatrix} \cos \psi & 0 & \sin \psi \\ 0 & 1 & 0 \\ -\sin \psi & 0 & \cos \psi \end{pmatrix} \begin{pmatrix} 0 \\ \cos \chi_0 \\ \sin \chi_0 \end{pmatrix} = 0
\] (7.44)

From this we reach the final solution: the accessible range is defined by \( \pm \psi_{\text{max}} \) and \( 180^\circ \pm \psi_{\text{max}} \), with

\[
\psi_{\text{max}} = \sin^{-1} \left( -\frac{\tan \theta}{\tan \chi_0} \right)
\] (7.45)

### 7.4.1.2. Correction for SD data

In the experiments conducted at the SD station (see section 3.2.2.2 on page 37), two corrections must be made.

- The first accounts for the sample volume. As our experiments are far from resonance, the penetration depth in the energies used (\( E > 8 \text{ KeV} \)) is several microns. We can assume that the whole film thickness is probed, and so we only correct for the spot size by multiplying the intensities by a factor of \( \sin \alpha \) (\( \alpha \) is the angle between the surface and the beam, shown in Figure 3.6)

- The second accounts for the polarization of light. The light in the beamline is always linearly polarized, with the electric field in the synchrotron plane. However, our scattering plane moves around with the detector, so the polarization channel is no purely \( \sigma \) or \( \pi \). This correction is applied by dividing the intensity by a factor of \( \sin^2 \eta' + (\cos \eta' \cos 2\theta)^2 \). Here \( \eta \) is the angle of polarization relative to the scattering plane (defined below).

The Lorenz factor is automatically accounted for in the software (data are recorded as function of position in reciprocal space), and is therefore not corrected.

In the following I calculate \( \eta' \) and the Bragg angle. The geometry for the calculations is given in Figure 7.17.
The $\gamma$ rotation is a simple rotation around the $\hat{z}$ axis. The $\delta$ rotation is around an axis that moves with $\gamma$. This axis can be written as $(\sin \gamma \ - \cos \gamma \ 0)$. Using these tools, one can show that the Bragg angle is given by

$$\theta = 90^\circ - \cos^{-1}(\mathbf{k} \cdot \mathbf{Q}) = 90^\circ - \cos^{-1}\left(\frac{1}{\sqrt{2(1 - \cos \gamma \cos \delta)}}\right)$$

(7.46)

To calculate the polarization angle relative to the scattering plane, we must define the polarization in the lab frame. This is given by the polarization vector $\mathbf{e} = (0 \ \sin \eta \ \cos \eta)$, and $\eta$ is the polarization angle of linear light with respect to the synchrotron plane ($0^\circ$ in our case). The normal to the scattering plane is given by $\hat{n} = \hat{k} \times \hat{k}'/|\hat{k} \times \hat{k}'|$. The linear polarization angle relative to the scattering plane is given by

$$\eta'(\gamma, \delta, \eta) = 90^\circ - \cos^{-1}(\mathbf{e} \cdot \hat{n}) = 90^\circ - \cos^{-1}\left(\frac{-\sin \eta \sin \delta + \cos \eta \sin \gamma \cos \delta}{\sqrt{\sin^2 \delta + \sin^2 \gamma \cos^2 \delta}}\right)$$

(7.47)

This expression simplifies slightly for $\eta = 0^\circ$, as is the case for our experiments.

### 7.4.2 Probe depth

The probe depth is a measure of the depth through which the X-rays can enter and exit the sample upon scattering. For this thesis we are specifically interested in this quantity around the energies of transition metal L edges. More than one flavor of the probe depth calculation exists. In the following, we are interested in the depth for which the outgoing intensity weakens by a factor of $1/e$ (see figure).

The penetration depth of X-rays can be calculated using readily available tools (see http://henke.lbl.gov/optical_constants/atten2.html), however these calculations do not take into account the effects of the crystal (e.g. the crystal field), and are therefore incorrect around the absorption edges. To account for this, a measured absorption spectrum of the material is required. In this section we break this calculation down into simple steps.

The absorption spectrum is usually not in units of length. Therefore it must be normalized with values from the atomic calculation (online). Figure 7.18 presents an absorption spectrum of TbMnO$_3$, with specific parameters used for terminology. Our aim is now to scale the vertical axis into units of length. This is done by scaling the absorption $A_1$ and $A_2$, which are at energies $E_1$ and $E_2$ (that are sufficiently far from the resonance), with the calculated atomic attenuation lengths at these energies. For a calculation done for a normal incident angle, the result must be multiplied by $\frac{1}{2} \sin \theta$ ($\theta$ is the Bragg angle). Now that the vertical axis has been scaled to attenuation lengths, the attenuation length at the resonance energy ($E_3$) can be estimated. Table 7.11 presents calculated values of the probe depth of $(0 \ q \ 0)$ at the Mn edge for bulk o-RMnO$_3$. 

[158]
Figure 7.18 – (left) illustration of the probe depth. (right) Absorption spectrum of TbMnO$_3$, adapted from Ref. [130]. We use only the red curve.

Table 7.11 – The probe depth of the (0 $q$ 0) reflection at Mn L$_3$ edge (642 eV). Data are shown for bulk values of o-RMnO$_3$ with $R$=Tb..Lu. Calculations are made using the data in the figure above, under the assumption that the absorption spectrum on Mn changes very little between the materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm$^3$)</th>
<th>$q$ (r.l.u.)</th>
<th>Probe depth (642 eV) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TbMnO$_3$</td>
<td>7.60</td>
<td>0.27</td>
<td>37.1</td>
</tr>
<tr>
<td>DyMnO$_3$</td>
<td>7.76</td>
<td>0.36</td>
<td>44.2</td>
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<td>HoMnO$_3$</td>
<td>7.88</td>
<td>0.41</td>
<td>44.3</td>
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<tr>
<td>ErMnO$_3$</td>
<td>8.02</td>
<td>0.43</td>
<td>39.2</td>
</tr>
<tr>
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<td>0.5</td>
<td>38.5</td>
</tr>
<tr>
<td>YbMnO$_3$</td>
<td>8.30</td>
<td>0.5</td>
<td>32.4</td>
</tr>
<tr>
<td>LuMnO$_3$</td>
<td>8.41</td>
<td>0.5</td>
<td>25.5</td>
</tr>
</tbody>
</table>
8 Bibliography


[106] K. Dey, S. Majumdar and S. Giri, "Ferroelectricity in spiral short-range-ordered magnetic state of spinel


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