Doctoral Thesis

Ferromagnetic and antiferromagnetic domain configurations in thin films and multilayers towards a patterned exchange bias system

Author(s):
Czekaj, Slawomir Marcin

Publication Date:
2007

Permanent Link:
https://doi.org/10.3929/ethz-a-005418151

Rights / License:
In Copyright - Non-Commercial Use Permitted

This page was generated automatically upon download from the ETH Zurich Research Collection. For more information please consult the Terms of use.
FERROMAGNETIC AND ANTIFERROMAGNETIC DOMAIN CONFIGURATIONS IN THIN FILMS AND MULTILAYERS – TOWARDS A PATTERNED EXCHANGE BIAS SYSTEM

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

for the degree of
Doctor of Sciences

presented by
SŁAWOMIR MARCIN CZEKAJ
Master of Science, Jagiellonian University of Cracow

born 03.11.1979
citizen of Poland

accepted on the recommendation of
Prof. Dr. Danilo Pescia, examiner
Dr. Frithjof Nolting, co-examiner

2007
Abstract

Magnetic micro- and nanostructures are of high interest for industrial applications. However, many phenomena employed in magnetic devices require better understanding. For instance, the unidirectional coupling of a ferromagnet to an adjacent antiferromagnet, referred to as exchange bias effect, is not fully understood even though it has been known for five decades. Spatially-resolved magnetic, elemental, and chemical information about the ferro-/antiferromagnetic interface is required in order to solve the exchange bias puzzle. X-ray absorption spectroscopy (XAS) and XAS-based magnetic microscopy techniques such as the photoemission electron microscopy (PEEM) are uniquely able to provide this information.

In the present work, the magnetic domain structure of thin films and multilayers is examined. The main aim of this thesis is to study the role of the magnetic domains in the exchange bias effect. In order to address the complexity of this effect, the studies were carried out in three steps: studying the ferromagnetic (FM) system, the antiferromagnetic (AF) system and finally the AF/FM bilayers.

For the FM studies, cobalt and Permalloy films were deposited as a wedge on top of pre-patterned silicon substrates using dc magnetron sputtering and evaporation, respectively resulting in an array of structures surrounded by a continuous film beneath. The FM domain structure as a function of the film thickness of the continuous and the patterned films was studied using the PEEM. In addition, effects of surface roughness
on the magnetic domain structure are discussed. This work provides important information of how various parameters, such as thickness, substrate roughness or patterning, influence the FM domain structure in thin films.

For the AF studies, thin LaFeO$_3$ films were grown using pulsed laser deposition (PLD) on SrTiO$_3$ substrates. Continuous and patterned LaFeO$_3$ films were studied. The patterning was carried out by either growing the films on pre-patterned substrates or post-patterning (i.e. patterning the film after deposition) using either a combination of electron beam lithography and ion-milling or focused ion beam lithography. The PEEM has been used to determine the orientation of individual antiferromagnetic domains in LaFeO$_3$ thin films. We found the antiferromagnetic axes are tilted by 20° out of the surface plane and have a different sign of the x-ray magnetic linear dichroism compared to previous reports on LaFeO$_3$. Using multiplet calculations, we show that this sign depends on the orientation of the magnetization with respect to the crystalline axes. Furthermore, we found that the AF and crystallographic domains in the LaFeO$_3$ films are one-to-one correlated. Finally, we found that the AF domain structure remains unaffected by the patterning.

We have obtained initial results on a LaFeO$_3$/Co exchange bias system. Indications for pinned uncompensated moments in the LaFeO$_3$ film without Co and for free uncompensated moments in the LaFeO$_3$/Co system were obtained. First measurements of the AF/FM domain correlation were carried out and the ability to perform PEEM measurements in applied magnetic fields was proven.

This work highlights the importance of the magnetic domain structure for the understanding of the exchange bias phenomenon. Our findings shed light on the mystery of the magnetic domain formation in thin films and nanostructures.
Zusammenfassung


Für die FM Studien wurden Kobalt- und Permalloy-Schichten keilförmig auf ein vorstrukturiertes Silizium-Substrat mittels „dc magnetro sputtering“ und Verdampfern aufgebracht. Dadurch entstanden strukturierte Schichten, die von einer kontinuierlichen Schicht umgeben sind. Die Muster der FM Domänen wurden als Funktion der


Diese Arbeit hebt die Bedeutung der magnetischen Domänenmuster für das Verständnis des Exchange Bias Effekts hervor und bringt Licht in das Geheimnis der magnetischen Domänenbildung in dünnen Filmen und Nanostrukturen.
# List of acronyms and symbols

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF</td>
<td>antiferromagnetic</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>$E_{ex}$</td>
<td>Exchange bias field</td>
</tr>
<tr>
<td>FIB</td>
<td>focused ion beam</td>
</tr>
<tr>
<td>FM</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>FSE SEM</td>
<td>forward scattered electron scanning electron microscopy</td>
</tr>
<tr>
<td>LAO</td>
<td>LaAlO$_3$</td>
</tr>
<tr>
<td>$m$</td>
<td>index of Kiessig fringe maximum</td>
</tr>
<tr>
<td>MAO</td>
<td>MgAl$_2$O$_3$</td>
</tr>
<tr>
<td>MBE</td>
<td>molecular beam epitaxy</td>
</tr>
<tr>
<td>MFM</td>
<td>magnetic force microscopy</td>
</tr>
<tr>
<td>MOKE</td>
<td>magneto-optical Kerr effect microscopy</td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>neodymium-doped yttrium aluminium garnet</td>
</tr>
<tr>
<td>PEEM</td>
<td>photoemission electron microscope</td>
</tr>
<tr>
<td>PLD</td>
<td>pulsed laser deposition</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly methyl methacrylate (methyl 2-methylpropenoate)</td>
</tr>
<tr>
<td>PRCLA</td>
<td>pulsed reactive cross-beam laser ablation</td>
</tr>
<tr>
<td>Py</td>
<td>Permalloy; alloy with about 20% iron and 80% nickel (Fe$<em>{20}$Ni$</em>{80}$)</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering spectrometry</td>
</tr>
<tr>
<td>RHEED</td>
<td>reflection high energy electron diffraction</td>
</tr>
<tr>
<td>RIE</td>
<td>reactive ion etching</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SPLEEM</td>
<td>spin polarized low energy electron microscopy</td>
</tr>
<tr>
<td>SPSTM</td>
<td>spin polarized scanning tunnelling microscopy</td>
</tr>
<tr>
<td>STO</td>
<td>SrTiO$_3$</td>
</tr>
<tr>
<td>STXM</td>
<td>scanning transmission x-ray microscopy</td>
</tr>
<tr>
<td>$t$</td>
<td>thin film thickness</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TIXM</td>
<td>Transmission imaging x-ray microscopy</td>
</tr>
<tr>
<td>XAS</td>
<td>x-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XMCD</td>
<td>x-ray magnetic circular dichroism</td>
</tr>
<tr>
<td>XMLD</td>
<td>x-ray magnetic linear dichroism</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoemission spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
</tr>
<tr>
<td>XRR</td>
<td>x-ray reflectivity</td>
</tr>
<tr>
<td>2D</td>
<td>two dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>three dimensional</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Bragg reflection angle</td>
</tr>
<tr>
<td>$\theta_m$</td>
<td>position of Kiessig fringe maximum</td>
</tr>
<tr>
<td>$\theta_c$</td>
<td>critical angle of reflecting material</td>
</tr>
</tbody>
</table>
Chapter 1
The Fascination of Magnetic Domains

Magnetism is an old science, since the strange properties of magnetite or lodestone, the magnetic iron ore, have attracted some attention for nearly 3000 years. The earliest writings (800 B.C.) came from the Ancient Greeks, who first reflected upon the wondrous properties of the loadstone, which was mined in the province of Magnesia. The first theories of magnetism were more of a metaphysical rather than scientific nature. In spite of some experimental approaches, this situation lasted for more than two millennia. The history of modern systematic studies on magnetism started with the treatise “De Magnete” by William Gilbert, an English physician to Queen Elizabeth I. Gilbert’s work started an avalanche of new theoretical and experimental findings. Since Gilbert’s times, knowledge of magnetism has improved significantly but is still far from complete. In spite of that, magnetic materials are used in multiple applications. The earliest known is a compass, used for sailing and developed probably by Chinese before 11th century A.D. Today, diverse applications of magnetism are present in every part of our life.
1.1 Introduction

The term magnetic domain was first introduced by Pierre-Ernest Weiss in 1926, which started the history of micromagnetics and domain theory. As in many scientific fields, the research is fuelled both by fundamental interest and technological applications. For instance, in the 1960’s a number of studies of strip and cylindrical domains, known as magnetic bubbles, were followed by Bobeck’s invention of the bubble device, capable of generating, storing and counting units. These bubble devices do not exist anymore and today information can be saved on a computer hard disc by switching tiny domains in ferromagnetic thin films. The pace of the technological development of many devices is breathtaking and often a phenomenon discovered in basic research is turned into an application without fully understanding of its intrinsic origin. A very good example is the exchange bias effect discovered by Meiklejohn and Bean five decades ago, which is central to this thesis and appears as an additional magnetic anisotropy in a ferromagnetic (FM) thin film adjacent to an antiferromagnetic (AF) layer. Despite extensive research, the exchange bias effect is still poorly understood and its intrinsic origin is still unknown. One of many open questions is the magnetic domain configuration on both sides of the interface, i.e. FM and AF layer. Despite the lack of understanding, the effect is already extensively employed in several applications such as hard disk read-heads, magnetic random access memories (MRAMs) or magnetic sensors (see reviews in Ref. 5-11).

The main aim of this Ph.D. Project was to study the magnetic domain structure in magnetic thin films. In particular, we wanted to address the problem of the role of the magnetic domains in the exchange bias effect by studying the FM and AF domain configuration with an x-ray photoemission electron microscope (PEEM). This powerful technique was pioneered by Tonner et al. and combines electron microscopy with x-ray absorption spectroscopy, with the ability to perform spatially, elementally, chemically and magnetically resolved studies. First, the magnetic domain structure was studied in FM and AF thin films separately, which provides better understanding of the domain
configuration in both systems alone. This is essential for comprehensive analysis of the exchange bias results. We will report on measurements of the FM domain structure as a function of the film thickness, measured by means of the PEEM combined with x-ray magnetic circular dichroism (XMCD). These studies were performed both on the FM microstructures and on the continuous films. This showed the importance of local magnetic effects in the determination of the final magnetic domain states in magnetic thin films and small elements. Subsequently, in order to study the AF domain structure we developed a powerful approach to investigate individual AF domains. This method consists of a combination of the PEEM and x-ray magnetic linear dichroism (XMLD). Furthermore, the method allows the determination of the XMLD sign, which is important for the analysis of x-ray spectroscopy measurements. As an example for utilization of this method, we will report on studies of the XMLD sign dependence for thin LaFeO$_3$ films. A spatially resolved correlation between the AF and crystallographic domain structure will be shown, an important result which was never measured before. In addition, determination of the magnetic domain structure in patterned AF thin films will be reported with the conclusion that AF domains are not influenced by the patterning. Finally, initial results on exchange bias systems will be given.

1.2 Exchange Bias – the meeting point of FM and AF domains

Exchange bias refers to the unidirectional pinning of a FM layer by an adjacent antiferromagnet. FM films typically have a preferred magnetization axis, the easy axis, and the spins prefer to align along this axis. There are two equally stable easy spin directions, both parallel to the easy axis, and it is energetically equal to align the spins along either easy direction, e.g. by an external magnetic field. When a ferromagnet is grown on an antiferromagnet, the exchange coupling between the two systems leads to an increased coercivity of the ferromagnet. This is usually attributed to increased
interface anisotropy, resulting from the coupling between the interface moments of the FM and the AF layer [see FIG. 1(a)]. The FM hysteresis loop is still symmetric, indicating two equivalent easy directions. Although, if the AF/FM system is grown in a magnetic field or annealed after growth in a magnetic field at temperatures above the Néel temperature of the AF layer, the hysteresis loop becomes asymmetric and is shifted from zero by a value known as the exchange bias field $E_{\text{ex}}$ [see FIG. 1(b)]. In summary, the key properties of the exchange bias systems are the increased coercivity and the exchange bias field. The following sections will discuss effects related to these properties.

1.2.1 The Fundamental Models

Here, basics of models addressing the problem of the exchange bias effect will be introduced. The increased coercivity and presence of the exchange bias field indicates that additional magnetic moments arise in the total magnetization measured in the

FIG. 1. (a) The principle of the exchange bias effects, an interface effect between FM and AF layers. (b) The FM layer is changed by adjacent AF layer resulting in horizontal hysteresis loop, known as the exchange bias field $E_{\text{ex}}$ and increased coercivity, i.e. the magnetic field $H_c$ at which the magnetization has dropped to zero.
hysteresis loop of the exchange bias system. It is highly probably that these moments are located in the AF layer and in the vicinity of the AF/FM interface. Therefore, the exchange bias is referred to as an interface effect. The clear picture of the AF/FM interface is missing and despite of an active research during the last five decades, the exchange bias effect is still poorly understood (see reviews on the topic by Berkowitz and Nogués). Three main approaches exist, which aim to explain the exchange bias effect: (1) the ideal interface model, (2) the spin flop model and (3) domain models (see FIG. 2). The first was proposed immediately after discovering the effect by Meiklejohn and Bean and it assumes that the AF layer consists of antiparallel magnetization planes and the top plane is exchange coupled to the FM layer. Here, the AF layer is fully uncompensated in the interface plane, which results in creating a large magnetization parallel to the magnetization of the FM layer [see FIG. 2(a)]. The outcome is that the estimated value of the exchange bias field is ≈100 times larger than the measured value. Nevertheless, the model proves that the presence of the uncompensated magnetization in the AF layer is the key to understanding the exchange bias phenomenon. The question is what causes such a small exchange bias field and what reduces the size of the uncompensated moment in order to give the correct field value. The two other theories address this problem in different ways. The spin flop model, invented by Koon, assumes that the AF spins are canted, creating a resultant magnetization which couples to the FM spins. As a result of the coupling, the AF and FM magnetic axes are
mutually perpendicular [see FIG. 2(b)]. The spin flop model estimates a smaller exchange bias field, which is closer to the experimental values. However, the consequences of the spin flop approach are heavily debated in the literature since, for instance, Schulthess et al.\textsuperscript{16} have found that it can predict only the increased coercivity in the exchange bias system but not the exchange bias field. Furthermore, the mutual orientation of the AF and FM axes in the exchange bias systems is still an open question, since many experimental results prove either parallel or perpendicular coupling, and hardly any measurement technique is capable of strictly determining the AF/FM orientation.

The most recent approach to explain the exchange bias effect assumes that the magnetic domain formation, both in AF and FM layer, is the key in understanding the phenomenon. While the knowledge of the FM domains is well established, the lack of knowledge about the AF domain formation is the biggest limitation for the implementation of the domain approach. In general, one could speak about two different approaches to address the problem of the magnetic domain formation depending on whether the domains are formed such that the domain walls are parallel or perpendicular to the interface. In the first case one often speaks about the exchange bias spring, since a $180^\circ$ domain wall is created in the interface plane and can be present either in the AF or the FM layer (see work by Mauri\textsuperscript{17}). Finally, the latest model to explain the exchange bias effect assumes the AF domain formation with domain walls perpendicular to the interface. This approach takes into account the interface roughness or other defects, which results in a random field and as a consequence leads to the break up of the AF layer into domains (see work by Malozemoff\textsuperscript{18}). This model assumes that the imbalance of the AF moments, due to statistical reasons, at the surface of the domains generates uncompensated moments that couple to the FM spins, which results in the exchange bias. However, the origin and localization of the uncompensated moments is still an open question. The models are constantly enriched and tested by many experimental results (see the latest review by Nogués\textsuperscript{19}).

We focus in this thesis on a selection of the exchange bias problems, in particular, those related to the magnetic domain structure. Thus, we will focus on:
Firstly, detailed studies on AF domains and a description of their formation is missing. Secondly, the origin and localization of the uncompensated spins in the antiferromagnet present in the exchange bias multilayer need to be clarified. The question of whether the AF film alone can contain the uncompensated spins or whether these spins are generated in response to the adjacent FM layer is still open. In addition, a different localization of the uncompensated moments can lead to a different domain-size-dependence of the exchange bias. Finally, the increased interest in patterned magnetic multilayers has fuelled studies of patterned exchange bias systems. Effects related to the patterned exchange bias are expected to be a consequence of the magnetic domain structure influence. In the case of FM materials, the understanding of the influence of patterning onto the FM domain structure is well established, however, the field of patterned AF films is hardly explored.

1.2.2 Imaging of Magnetic Domains

In order to address the problem of the role of the magnetic domain structure in the exchange bias effect we have utilized the PEEM technique combined with x-ray magnetic dichroism. A more detailed description of the PEEM method can be found in chapter 2.5. Here, it is sufficient to say that the combination of PEEM, XMCD and XMLD is a very powerful method to investigate the magnetic domain configuration in the surface region. The combination of the spatial resolution and elemental specificity allows the determination of the magnetic domain orientation in the AF and the FM layer of the exchange bias systems, which can be done simultaneously. In addition, ability to measure in applied magnetic field allows detection of spatially and elementally resolved hysteresis loops. This means that the FM spins and the uncompensated moments in the
AF layer, i.e. uncompensated spins, can be detected separately. Furthermore, introduction of the modern elliptical undulators allows full control of the x-ray polarization. For instance, ability to rotate the linear polarization vector (E-vector) from 0° to 90° (between in-plane and out-of-plane) in combination with the PEEM allows studies of individual AF domains and determination of their orientation. This makes PEEM a very unique method, although, it has certainly some limitations. For instance, measurements in applied magnetic fields are limited to relatively small fields (maximum 300 Oe), whereas with other magnetic microscopy techniques measurements in applied magnetic field are limited only by technical issues, such as restricted space around the sample limiting the size of the magnetic coils. Thus, measurements up to several teslas can be done, e.g. magnetic force microscopy (MFM), scanning transmission x-ray microscopy (STXM), transmission imaging x-ray microscopy or magnetic optical Kerr effect microscopy (MOKE). The spatial resolution is also a limiting factor, since the best achieved resolution with PEEM was 20 nm, and other techniques are way much better, e.g. magnetic imaging with transmission electron microscopy (TEM), spin polarized low energy electron microscopy (SPLEEM) or at best spin polarized scanning tunnelling microscopy (SPSTM) with its atomic resolution. Nevertheless, all magnetic imaging methods have their advantages and disadvantages, giving complementary information, for example in terms how magnetic contrast is generated and depth of sensitivity. More detailed reviews on the magnetic imaging techniques can be found in books by Hubert and Schäffer,20 by Hopster and Oepen21 or by Stöhr and Siegmann.22

1.2.3 Antiferromagnetic Domain Orientation

The role of the AF domain configuration in the exchange bias effect is the subject of large discussion. Some researchers suggest it is the key to understand the phenomenon, whereas others claim it is of minor or even negligible importance. Not much is known about the origin of the AF domains and therefore it is not yet possible to
1.2.4 The Role of Uncompensated moments

It is impossible to explain the exchange bias effect without existence of the uncompensated magnetization in the AF layer. An origin of the uncompensated moments, however, remains unclear and the question if it is a product of the canting AF spins or existence of uncompensated AF spins is still open, although, the latest findings
Chapter 1 The Fascination of Magnetic Domains

go in the direction of the latter. Hence, the role of the uncompensated spins in the exchange bias effect needs to be clarified. In addition, the question of the intrinsic origin of these moments has to be answered. Thus more experiments are necessary in order to create a clear model of the structure of the uncompensated spins. It has been shown that the uncompensated spins can be either pinned or are able to rotate freely\cite{40,33,35,41,42}. Thus they have different influence on the FM spins. The pinned spins are expected to be origin of the hysteresis loop asymmetry, i.e. existence of the exchange bias field, whereas the free spins are responsible for increased coercivity in the exchange bias systems. Furthermore, uncompensated spins have been detected at the AF/FM interface (measurements of: NiO/Co by Ohldag et al.\cite{35} and CoO/(Co/Pt) by Kappenberger et al.\cite{40}) as well as in the AF bulk (measurements of CoO/(Co/Pt) by Schmid et al.\cite{43}). The uncompensated spins have been also measured in Ir_{20}Mn_{80}/Co, NiO/Co and PtMn/Co_{90}Fe_{10} using XMCD spectroscopy by Ohldag et al.\cite{33}. In addition, Zaharko et al.\cite{36} have measured the uncompensated moments in Fe/NiO/Co multilayers using soft x-ray resonant magnetic reflectivity. The uncompensated spins were imaged using combination of PEEM and XMLD (see work by Ohldag et al.\cite{35}). However, detailed information about origin and localization of those spins is still missing and the question if the uncompensated spins are localized at the domain walls is still open. For instance, Scholl et al.\cite{44} have studied domain-size-dependent exchange bias in continuous LaFeO$_3$/Co bilayers using PEEM. They have found a statistically significant increase of the width of the bias field distribution with decreasing domain area and an inverse dependence with the domain diameter. This indicates the importance of the AF domain walls in understanding of the exchange bias effect, which suggests that the uncompensated spins are located at magnetic or structural defects.

Further information could be obtained from investigations of the domain-size-dependent exchange bias in patterned multilayers combined with measurement of spatially and elementally resolved hysteresis loops. In addition, studies of exchange bias effect as a function of the number of AF domains can provide the answer to the question of whether the uncompensated spins are situated at the domain boundaries. This is because the exchange bias field would scale with the number of the AF domains within
the single AF/FM microstructure. Finally, using PEEM combined with XMCD we can try to image the uncompensated spins directly.

1.2.5 Patterned Exchange Bias Systems

The increased interest in patterned magnetic microstructures has resulted in numerous studies of patterned exchange bias systems. For instance, it has been found that the size of the exchange bias effect can be influenced by patterning of the AF/FM multilayers and, although only the FM domain structure was measured, it was concluded that this is due to a change in the size and arrangement of the AF domains and domain walls resulting from the patterning.\textsuperscript{45-49} In particular, Chien et al.\textsuperscript{49} have claimed to have unequivocal evidence of changes in the AF domain structure of Py/FeMn by measuring laterally resolved hysteretic behaviour with the magneto-optical indicator film technique, but this supplies spatially resolved information about the magnetization distribution within the multilayer. Furthermore, it was found that patterning can influence the exchange bias effect in various ways, e.g. by changing the coercivity, exchange bias field or the FM switching behaviour. Many results are mutually inconsistent concerning these effects, showing different behaviour in different systems. However, this could be due to incompleteness of the investigations, since very often the focus is on the macroscopic measurements (the collective switching behaviour in arrays of microstructures) or locally resolved measurements of only the magnetization of the multilayer (dominated by the FM), but no measurements on the AF layer are done. Thus, investigating both layers of the exchange bias system, could allow a more detailed understanding of the patterning effects. The influence of the switching behaviour in the FM microstructures by additional interaction with the adjacent AF layer, in particular the magnetic domains, is still unclear. In order to address these problems, we can study both, the AF and the FM domain configuration and hence their mutual interaction. To make this understanding more complete we should investigate each layer in isolation.
1.3 Energy Contributions

In this section the energy contributions, which result in a given magnetic domain state will be discussed. The energy terms are tabulated together with a brief description and magnitude for both FM and AF materials. FM and AF domains will be discussed in turn.

1.3.1 Ferromagnetic Domains

Knowledge of the FM domain formation is pretty well established. Many books and monographs were published on this topic and the most relevant to the present work are those by Hubert and Schäfer,\textsuperscript{20} Mattis,\textsuperscript{50} or by Chikazumi.\textsuperscript{51} Several energy terms contribute to the FM domain state; they are listed in TAB. 1. The main one is the exchange energy, which causes the parallel ordering of the individual atomic magnetic moments. The next energy contribution is a group of anisotropy energies, which have different sources like crystal anisotropy or induced anisotropy. The stray field energy

<table>
<thead>
<tr>
<th>ENERGY TERM</th>
<th>COEFFICIENT</th>
<th>DEFINITION</th>
<th>RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchange energy</td>
<td>$A_{FM}$ [J/m]</td>
<td>Material constant</td>
<td>$10^{-12}$ – $2 \cdot 10^{-11}$ J/m</td>
</tr>
<tr>
<td>Anisotropy energies</td>
<td>$K_u$, $K_c$, … [J/m$^3$]</td>
<td>Material constants</td>
<td>$\pm (10^2$ – $2 \cdot 10^7$) J/m$^3$</td>
</tr>
<tr>
<td>Stray field energy</td>
<td>$K_d$ [J/m$^3$]</td>
<td>$K_d = J_s^2/2\mu_0$</td>
<td>0 – 3$ \cdot 10^6$ J/m$^3$</td>
</tr>
<tr>
<td>Magnetostrictive energy</td>
<td>$C \lambda$ [J/m$^3$]</td>
<td>C – shear modulus (\lambda) - magnetostriction constant</td>
<td>0 –$10^3$ J/m$^3$</td>
</tr>
<tr>
<td>External field energy</td>
<td>$H_{ex} J_s$ [J/m$^3$]</td>
<td>$E_{ex}$ – external field (J_s) – saturation magnetization</td>
<td>Open, depending on field magnitude</td>
</tr>
<tr>
<td>External stress energy</td>
<td>$\sigma_{ex} \lambda$ [J/m$^3$]</td>
<td>$\sigma_{ex}$ – external stress (\lambda) - magnetostriction constant</td>
<td>Open, depending on stress magnitude</td>
</tr>
</tbody>
</table>

TAB. 1. The coefficients of the energy terms contributing to the ferromagnetic state together with definitions and the order of magnitude of these terms in typical materials.
term, also known as shape anisotropy, forces the spins to align parallel to the element edges. For instance, the shape anisotropy is responsible for so-called Landau pattern (see chapter 3.1). Next, the magnetostrictive energy term originates from intrinsic strains of the material and is described by the shear modulus. The last two energy contributions are externally induced by the magnetic field and stress and depend on the magnitude of both.

1.3.2 Antiferromagnetic Domains

The understanding of the AF domain formation in thin films is poor, mainly because of lack of experimental measurements. Not many books or monographs have been published in this field. Thus, the most relevant to the present work are former Ph.D. dissertations from Ohldag\textsuperscript{52} and Regan.\textsuperscript{53} Despite of lack of understanding, AF materials are attracting growing attention, mainly due to their applications in magnetic devices, which results in many experimental and theoretical studies. Development of various experimental techniques based on x-rays or neutrons have improved the knowledge of the AF domains. Although, a clear picture of the energy contributions to the AF domain state is still missing and the intrinsic origin of the AF domain formation is still unknown. Summary of the present knowledge about the energy contributions to the AF domain state is shown in TAB. 2. The main energy contribution is the exchange energy, the same as in FM case but opposite in sign, which causes the antiparallel spin alignment on neighbouring atoms. Furthermore, an AF material has no stray field, i.e. no net magnetization, and one might expect a single domain state to be the thermodynamically stable domain configuration. However, imperfections, such as crystalline grains, defects\textsuperscript{16,54} or structural boundaries, act as pinning centres for domain walls, so that a multidomain state is often observed. Those imperfections and defects can be described by the magnetic anisotropy energy. The multidomain state is caused also by the magnetostrictive energy originating from the lattice strain,\textsuperscript{55} surface roughness, chemical
inhomogeneity\(^5\) and competition between dipolar energy and magnetic anisotropy.\(^6\) Furthermore, one might expect a change in the AF domain configuration in a patterned AF film, since the patterning introduces additional defects and/or a local change of the strain of the film. The multidomain state can even be changed by external strain, as has been shown for single crystalline NiO by Slack.\(^7\) Finally, the AF domain configuration can be changed by applying external magnetic field. However, the necessary field strength very often exceeds the performance of the strongest superconducting magnets.

<table>
<thead>
<tr>
<th>ENERGY TERM</th>
<th>COEFFICIENT</th>
<th>DEFINITION</th>
<th>RANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchange energy (stiffness)</td>
<td>(A_{AF} ) [J/m]</td>
<td>Material constant</td>
<td>(- (10^{-12} - 10^{-11}) ) J/m</td>
</tr>
<tr>
<td>Magnetostrictive energy, e.g.: elastic strain</td>
<td>([J/m^3])</td>
<td>(\lambda) - magnetostriction constant (C) – shear modulus</td>
<td>(10^4 - 10^5 ) J/m(^3)</td>
</tr>
<tr>
<td>frozen strain</td>
<td>(\hat{u} \Lambda\lambda/C)</td>
<td></td>
<td>(10^5 ) J/m(^3)</td>
</tr>
<tr>
<td>Magnetic anisotropy</td>
<td>crystal field, defects, roughness, thickness</td>
<td>Arrangement specific constants</td>
<td>(10^3 - 10^5 ) J/m(^3)</td>
</tr>
<tr>
<td>External field energy</td>
<td>(H_{ex} J_s) [J/m(^3)]</td>
<td>(E_{ex}) – external field (J_s) – saturation magnetization</td>
<td>Open, depending on field magnitude</td>
</tr>
<tr>
<td>External stress energy</td>
<td>(\sigma_{ex}\lambda) [J/m(^3)]</td>
<td>(\sigma_{ex}) – external stress (\lambda) - magnetostriction constant</td>
<td>Open, depending on stress magnitude</td>
</tr>
</tbody>
</table>

TAB. 2. Energy contributions to the AF state, according to the literature. Exchange anisotropy is also known as exchange stiffness.

1.4 Outline of the Thesis

The “Sample Preparation and Characterization” chapter contains a description of the PLD method used for the growth of thin LaFeO\(_3\) films, including the growth issues and solutions achieved. Next, a description of the methods used to characterise the LaFeO\(_3\) films will be given showing the epitaxial growth and the 1:1:3 stoichiometry. In addition, the patterning methods used to structure the FM, AF and nonmagnetic materials will be described, including newly developed structuring approaches. Finally, a
description of the primary measurement technique – photoemission electron microscopy (PEEM) will be presented. The basics of x-ray absorption spectroscopy (XAS) together with XMCD and XMLD effects will be shown, introducing the idea of x-ray magnetic imaging, based on the combination of PEEM and magnetic dichroism spectroscopy.

In the “Ferromagnetic Thin Films” chapter, a detailed study of the magnetic domain configurations in polycrystalline FM thin film wedges of patterned cobalt and Permalloy will be presented. The films were deposited on pre-patterned silicon substrates with micrometer-sized square plateaus and the magnetic domain configuration imaged using PEEM combined with the XMCD effect. This approach allows the observation of the continuous development of magnetic domain states in the micrometer-sized square elements on top of the plateaus as a function of thickness. In addition, one can simultaneously observe the development of the magnetic domains in the continuous film surrounding the plateaus.

In the “Antiferromagnetic Thin Films” chapter detailed studies of the AF domain configurations in continuous and patterned LaFeO$_3$ thin films are reported. Details of our newly developed powerful approach to investigate individual AF domains will be given. This combines the PEEM and the XMLD effect. It is then shown how this method was utilized and what new insight it brings to the better understanding of the AF materials. An important discovery was that the sign of the XMLD effect is sensitive to the AF axis orientation with respect to the crystallographic axes. In addition, the AF domain structure, measured with PEEM, has a one-to-one correlation with the crystallographic domains measured with forward scattered electron-scanning electron microscopy (FSE-SEM). Finally, measurements of the AF domain configuration in the patterned LaFeO$_3$ films are given, showing how the AF structure remains completely unaffected by the patterning.

The final “Exchange Bias Systems: Initial Results” chapter includes initial results obtained for LaFeO$_3$/Co bilayers. Measurements of uncompensated moments in the LaFeO$_3$ film on its own and the bilayer are shown. The findings lead to the conclusion
that the origin of the uncompensated moments in LaFeO$_3$ are the individual uncompensated spins rather than a canting of the spins. Next, initial results on correlating the AF and the FM domain structure will be described. It is shown how after heating the sample the cobalt domain structure changes from the as-grown state and adapts to the AF layer. Finally, measurements in applied magnetic fields and in a remanence using PEEM will be presented indicating a coupling between the FM and the AF domains.
Chapter 2
Sample Preparation and Characterization

Central to this work is an exchange bias system comprised of an AM and a FM layer. We have chosen to investigate layers of LaFeO$_3$ and cobalt, studying their behaviour as separate layers and also combined in an exchange bias system. Although, the LaFeO$_3$/Co bilayer provides a good model system for the study of the exchange bias effect, the exchange bias in the bilayer is low. Firstly, the LaFeO$_3$ system shows an XMLD effect necessary to image the AF domain structure using PEEM (details will be discussed later on, see section 2.5, or see Ref. 29-31). Secondly, the AF domains in thin LaFeO$_3$ films are on the micrometer level.$^{29-31}$ These are one of the largest known in thin films and since they are larger than the spatial resolution of the PEEM, they are ideal for imaging of AF domains using this method. Thirdly, thin cobalt films can provide us with a relatively good FM state, i.e. having in-plane FM domains larger than the spatial resolution of the PEEM, and at the same time they can be thin enough to image the underneath LaFeO$_3$ film (see work by Nolting $et$ $al.$$^{37}$). Finally, the LaFeO$_3$/Co bilayer allows us to take advantage of the PEEM elemental specificity to image the AF and the FM domain structure on the very same sample position, by tuning the x-ray energy to the iron and cobalt edges, respectively.
This chapter contains a description of the PLD method used for the growth of thin LaFeO₃ films, including the growth issues and solutions achieved. Next, a description of the methods used to characterise the LaFeO₃ films will be given showing the epitaxial growth and the 1:1:3 stoichiometry. In addition, the patterning methods used to structure the FM, AF and nonmagnetic materials will be described, including newly developed structuring approaches. Finally, a description of the primary measurement technique – photoemission electron microscopy (PEEM) will be presented. The basics of x-ray absorption spectroscopy (XAS) together with XMCD and XMLD effects will be shown, introducing the idea of x-ray magnetic imaging, based on the combination of PEEM and magnetic dichroism spectroscopy.

2.1 The LaFeO₃ system

The orthoferrite LaFeO₃ is an antiferromagnetic oxide with the highest Néel temperature, $T_N = 740$ K, in the orthoferrites family. In the bulk material, the spins of the iron atoms are aligned parallel to the $a$-axis of the orthorhombic crystal (Space group Pbnm with $a = 5.557$ Å, $b = 5.5652$ Å and $c = 7.8542$ Å). The AF alignment results from the superexchange coupling of the iron cations via the p orbitals of the oxygen atoms (Fe–O–Fe). The buckling of these Fe–O–Fe bonds to about $155^\circ$ induces the orthorhombicity of the unit cell and is, according to Lyubutin et al., responsible for the high Néel temperature. The crystal structure of the LaFeO₃ is shown in FIG. 3.

Thin LaFeO₃ films can be grown epitaxially on various substrates, such as SrTiO₃ (STO), LaAlO₃ (LAO), MgO, and MgAl₂O₄ (MAO). It turns out that the best quality films, i.e. films showing the largest AF domains, have been grown on STO substrates. Furthermore, Lüning et al. have shown that thin LaFeO₃ films grown on the STO(001) substrates, i.e. STO substrates with the (001) surface orientation, consist of twinned crystallographic domains with two mutually perpendicular orientations of the $c$-axis, both lying in-plane. The small tetragonal distortion can be ignored, as it does not affect the magnetic ground state. Therefore it is sufficient for the calculation to use cubic symmetry.
for the crystal field, and indeed from here on we adopt the crystallographic coordinates of the STO(001) substrate to describe the AF axis of the film. The $a$ and $b$-axis are canted 45° out-of-plane, which results in existence of four types of the AF domains with $c$-axis oriented in one of the following directions: $<100>$, $<\overline{1}00>$, $<010>$ or $<0\overline{1}0>$.\textsuperscript{63,62} Therefore the films are the best choice for imaging with the PEEM, since the difference between the linear dichroism signal for the different twins is close to the maximum achievable (see details in section 2.5.4). The LaFeO$_3$ is grown on the STO(001) substrate as the (110) surface, which is shown in a top view [FIG. 3(a)] and in a side view [FIG. 3(b)]. In the bulk material the magnetic axis is parallel to the $a$-axis ($<100>$ direction). However, Lüning et al.\textsuperscript{30} have shown that in LaFeO$_3$(110) films, the spin axis is oriented along the $<1\overline{1}1>$ direction.

FIG. 3. The crystal structure of the LaFeO$_3$ illustrated in a representation of the (110) surface in (a) a top view and (b) a side view. The $a$ and the $b$-axis are titled 45° out-of-plane and $c$-axis lies in-plane.
2.2 LaFeO₃ Growth

Thin LaFeO₃ films with various thicknesses were grown on the STO(001) substrates using pulsed laser deposition (PLD). The principle of the PLD is shown in FIG. 4. A “Quantel Brilliant b” Nd:YAG pulsed laser was used in 10 Hz pulse repetition mode together with a fourth harmonic generator and a power attenuator. The final average power deployed into the growth chamber was ≈200 mW. The laser beam was focused on a target by optical lenses to a spot of ≈0.5 mm in diameter. A single crystalline LaFeO₃ rod-shape target was used (density of 6.63 g/cm³). The base pressure inside the growth chamber was typically ≈10⁻⁹ mbar. Before the growth, the substrates were pre-annealed for one hour at the deposition temperature in an ambient oxygen pressure (≈10⁻⁵ mbar). The substrate heating was realized by passing an electric current through a silicon wafer mounted beneath the STO substrate (typically 6.0 A at 7 V). The deposition temperature was ≈1000 K and the films were deposited in an ambient oxygen pressure (10⁻⁴ mbar). In addition, nitrous oxide gas was injected via a pulsed

FIG. 4. The principle of pulsed laser deposition (PLD). The growth was performed with ambient oxygen pressure (∼10⁻⁴ mbar) and nitrous oxide as a pulsed gas (∼10⁻⁴ mbar). The deposition temperature was ∼1000 K.
valve synchronously with the laser pulse (delay: 250 μs; pulse length: 135 μs), which resulted in a partial pressure of ≈10^{-4} mbar. After the growth, the samples were cooled down to room temperature maintaining an ambient oxygen pressure (≈10^{-5} mbar). In order to reduce charging problems associated with PEEM measurements, the low conducting LaFeO$_3$ films were capped with one nanometre of platinum using magnetron sputtering.

The PLD growth conditions were varied in order to obtain a film with the largest possible AF domains. The growth could be influenced by varying several conditions such as: (1) the laser power and target-substrate distance (changing the deposition rate), (2) the background oxygen and the pulsed nitrous oxide pressure (changing the film oxygen content), (3) the deposition temperature (changing the film crystallinity) and (4) the deposition time (changing the film thickness). As a result of the growth optimization, we have managed to grow a LaFeO$_3$ film with AF domains on the micrometer level. This is comparable with the literature results obtained by molecular beam epitaxy (MBE). However, we could not reproduce the growth conditions and it was only possible to grow further LaFeO$_3$ films with AF domains on the level of a few hundred nanometres, never reaching the micrometer quality again. This could be due to difficulties in controlling the growth parameters such as the deposition temperature, the background oxygen pressure and problems related with the PLD system components such as the pulsed valve malfunctioning or the ablation target decomposition, which had an undefined influence onto the growth conditions. In addition, the PLD system was moved from one location to another, and the laser was shared between different PLD chambers such that the laser alignment was constantly changing with respect to the PLD target. Altogether, the irreproducibility in the sample growth strongly limited the output of high quality samples. Nevertheless, we have sawed the best sample into several pieces, which improved feasibility of experiments. In addition, we have successfully grown LaFeO$_3$/Co/Pt multilayers using the PLD with the target composed of three rod-shaped pieces (a separate piece for each layer) coaxially glued together. The growth was carried out in situ by first depositing the LaFeO$_3$ films at 1000K and then, after cooling to the room temperature, depositing the cobalt and the platinum layer.
respectively. The metallic layers were grown using the same deposition rates as for the LaFeO$_3$ films. The \textit{in situ} growth assures a high quality interface between the layers, which is of a high importance in the studies of exchange bias systems.

2.3 Sample Characterization

2.3.1 Sample Crystallinity and Thickness

Immediately after growth and cooling down, the samples were measured \textit{in situ} using reflection high-energy electron-diffraction (RHEED) in order to confirm an epitaxial growth. FIG. 5(a) illustrates the epitaxial LaFeO$_3$ film grown on the STO(001) substrate: the c-axis is oriented in-plane, and the a and the b-axis are tilted out-of-plane, which is in agreement with the literature studies.$^{63,62}$ Comparison between the RHEED pattern taken on the STO(001) substrate [FIG. 5(b)] and LaFeO$_3$(200nm)/STO(001) [FIG. 5(c)] shows that the film has periodicity of the substrate, i.e. the same main reflexes. In addition, the LaFeO$_3$/STO RHEED pattern exhibits an additional structure with a half length period [reflexes with the smaller intensity between the main STO reflexes in FIG.

![Image](a.png) ![Image](b.png) ![Image](c.png)

FIG. 5. (a) Orientation of LaFeO$_3$ crystalline axes with respect to the STO(001) substrate. The c$_{LFO}$-axis is oriented in-plane along the STO axis. (b) RHEED pattern of the STO(001) substrate. (c) RHEED pattern of the 200 nm thick LaFeO$_3$ film epitaxially grown on the STO(001) substrate. An intermediate structure between the main STO reflexes is due to the double length of the c$_{LFO}$-axis compare to the a$_{STO}$-axis, which causes the doubling of the RHEED pattern.
This is due to the double length of the \( c_{\text{LFO}} \)-axis compared to the \( a_{\text{STO}} \)-axis, which causes a doubling of the electron diffraction pattern. Using RHEED one can distinguish between a flat epitaxial and a clustered 3D film. In the first case the reflexes are elongated [see FIG. 5(c)], due to the electron diffraction on a 2D-like crystal. For a clustered film, the RHEED pattern will have dot structure, which is comparable with the RHEED pattern of a bulk crystal [see FIG. 5(b)].

As previously mentioned, the main issue during the PLD growth was the reproducibility. FIG. 6 shows how nearly the same growth conditions resulted in extremely different films: starting from an epitaxial [FIG. 6(a)] and finishing on a 3D clustered film [FIG. 6(j)]. In particular, one of the intermediate states was the RHEED pattern of the highest quality film [FIG. 6(e)], where the antiferromagnetic domains were on the micrometer level.

FIG. 6. RHEED patterns measured on samples grown with nearly the same growth conditions. Their diversification illustrates how the \( \text{LaFeO}_3 \) growth is highly sensitive to slight changes in the growth conditions. The thin film quality varied between the ideally flat epitaxial (a) and the 3D cluster type (j), with several intermediate states observed (b – i). In particular, one of the intermediate states was the RHEED pattern of the highest quality film (e) with the AF domains on the micrometer level.
In addition to the RHEED measurements, the crystalline quality of the grown films was cross-checked using x-ray diffraction (XRD). In addition, the x-ray reflectivity (XRR) was measured in order to determine the thin film thickness (see FIG. 7). An XRR curve consists of intensity oscillations of the x-rays reflected from the film as a function of the reflection angle, $2\theta$. The intensity oscillations are called Kiessig fringes. The measurements were performed in the standard XRD geometry by measuring $\theta$-$2\theta$ scans, where $\theta$ is the angle between the surface and the incident or the reflected x-rays. The maximum intensities are observed whenever the phase difference between the reflected and refracted beam is a multiple of the x-ray wavelength. The square of the maximum position $\theta_m$ depends linearly on the square of the maximum index $m$ (b). The film thickness is determined from the slope of this dependence. The red line represents the linear regression and $R$ is the correlation coefficient, which determines the quality of the fit in such a way that 1 means perfect correlation and zero no correlation. The value of 0.99965 is considered to be a very good fit.

In addition to the RHEED measurements, the crystalline quality of the grown films was cross-checked using x-ray diffraction (XRD). In addition, the x-ray reflectivity (XRR) was measured in order to determine the thin film thickness (see FIG. 7). An XRR curve consists of intensity oscillations of the x-rays reflected from the film as a function of the reflection angle, $2\theta$. The intensity oscillations are called Kiessig fringes. The measurements were performed in the standard XRD geometry by measuring $\theta$-$2\theta$ scans, where $\theta$ is the angle between the surface and the incident or the reflected x-rays. The maximum intensities are observed whenever the phase difference between the reflected and refracted beam is a multiple of the x-ray wavelength. The square of the maximum position, $\theta_m$, depends linearly on the square of the maximum index, $m$, as given by

$$\theta_m^2 = \theta_c^2 + \left(\frac{\lambda}{2t}\right)^2 m^2$$  \hspace{1cm} \text{eq. 1}$$

where $\theta_c$ is the critical angle of the reflecting material, $\lambda$ is the wavelength of the
incoming x-rays and \( t \) is the thickness of the reflecting film. The film thickness, \( t \), can be obtained from the slope \( s \) of the \( \theta_n^2 \) dependence [FIG. 7(b)]. The Kiessig fringes become denser with the decreasing thickness, which together with the detector angular resolution sets the lower level of the thickness sensitivity. At a certain thickness maximum, however, the fringes are not detectable anymore. The XRR data shown in FIG. 7 correspond to the 25 nm thick LaFeO\(_3\) film.

### 2.3.2 The Surface Roughness Measurements

In an attempt to solve the growth reproducibility issue, the surface quality of differently prepared STO substrates was studied using atomic force microscopy (AFM). First of all, we have investigated the continuous STO substrate as-delivered from CrysTec Kristaltechnologie [see FIG. 8(a)].\(^{66}\) In spite of the irregular structure of the terraces, the surface quality is relatively good with the surface roughness on the atomic level (for the exact values see TAB. 3). We have investigated specially treated STO substrates, i.e. the STO substrates etched with buffered hydrofluoride acid (BHF) followed by two hours of annealing in oxygen atmosphere at 1200 K. This procedure was implemented to improve the surface quality, i.e. the surface roughness and the chemical surface termination, of the substrates [FIG. 8(b)].\(^{67-69}\) however, the mean roughness did not change dramatically, but the maximum height was reduced \( \approx 2.8 \) times (see TAB. 3). In addition, the BHF etching procedure assures a uniform chemical surface termination. Finally, we have implemented this step into the standard sample preparation scheme in order to have better defined surface.

The surface quality of pre-patterned substrates was investigated in order to study how the surface quality was influenced by the patterning. A detailed description of the patterning will be given in section 2.4. Here, it is sufficient to say that the pre-patterned STO substrates consist of elevated and continuous substrate beneath. This surface
relief was produced by ion-milling. During this process, the top surface of the elevated structures was protected with a chromium mask, and the remaining continuous part was etched away by the ions. Afterwards the pre-patterned substrates were etched with the BHF and post-annealed in the oxygen atmosphere for 2h at 1200 K. The surface quality of both the directly ion milled STO surface [FIG. 8(c)] and one protected by the chromium mask [FIG. 8(d)], are comparable with the continuous STO substrates. However, the mean roughness for the protected region is half of the directly milled surface and the maximum height is three times smaller.

Finally, the surface quality of the LaFeO$_3$ films has been examined. The LaFeO$_3$ films grown on the continuous and pre-patterned STO substrate [FIGs. 9(a) and 9(b),
respectively] are comparable in the surface quality. The film grown on the pre-patterned substrate has a smaller mean roughness, which is even more astonishing, since one would expect the opposite behaviour. This indicates that the surface quality of the grown films was determined not only by the substrate. Altogether, the AFM studies have indicated that the lack of reproducibility in the growth of the LaFeO$_3$ was not caused by a different growth parameter and not the surface roughness of the STO substrates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Image</th>
<th>Mean Roughness [nm]</th>
<th>Max. Height [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO – as delivered</td>
<td>FIG. 8(a)</td>
<td>0.167</td>
<td>3.605</td>
</tr>
<tr>
<td>STO – BHF etched</td>
<td>FIG. 8(b)</td>
<td>0.153</td>
<td>1.334</td>
</tr>
<tr>
<td>Pre-patterned STO – Cr protected</td>
<td>FIG. 8(c)</td>
<td>0.155</td>
<td>2.005</td>
</tr>
<tr>
<td>Pre-patterned – etched</td>
<td>FIG. 8(d)</td>
<td>0.266</td>
<td>6.678</td>
</tr>
<tr>
<td>LaFeO$_3$ on as-delivered STO</td>
<td>FIG. 9(a)</td>
<td>0.246</td>
<td>3.117</td>
</tr>
<tr>
<td>LaFeO$_3$ on ion milled STO</td>
<td>FIG. 9(b)</td>
<td>0.131</td>
<td>2.600</td>
</tr>
</tbody>
</table>

TAB. 3. Values of the surface roughness and the maximum height measured for different STO substrates and LaFeO$_3$ films by the AFM. References to the associated images are shown. The BHF etching has clearly improved the STO roughness. As for the LaFeO$_3$ films connection between the magnetic quality and the surface quality is very hard to judge.

FIG. 9. AFM images of continuous thin LaFeO$_3$ films grown on: (a) continuous and (b) pre-patterned STO(001) substrate. The average AF domain size for the continuous films was on the micrometer level, where for the pre-patterned it was below 100 nm and thus not detectable by the PEEM.
2.3.3 LaFeO$_3$ Stoichiometry

The LaFeO$_3$ films were measured using x-ray absorption spectroscopy (XAS) in order to study the elemental composition. The basics of the XAS will be discussed later in section 2.5.1. The XAS measurements were taken using PEEM and the absorption information was gathered from sample areas of $\approx 10 \, \mu m$ in size. An absorption spectrum taken over a large photon energy range is shown in FIG. 10(a). It contains absorption edges of several elements such as carbon, oxygen, iron, cobalt or lanthanum. Thus, the XAS measurement supplies information about the composition of the film and more importantly, information on the iron oxidation state, which has strong influence on the magnetic state of the thin LaFeO$_3$ film. Relative information about the iron oxidation state can be obtained by measuring the absorption spectrum of the Fe-L$_{3,2}$ absorption edge. The example shown in FIG. 10(b) illustrates how the XAS technique is sensitive to different oxidation states of the iron within the film. Here the difference between a typical LaFeO$_3$ film and a deoxidised film which occurred during sputter-cleaning of the sample surface.

![FIG. 10. (a) XAS spectra of Co/LaFeO$_3$ bilayer grown on the STO substrate, taken over large range of the photon energies. Several absorption edges are visible: C, O, Fe, Co, La. (b) XAS spectra of the Fe-L$_{3,2}$ absorption edge of a typical LaFeO$_3$ film (red line) and a deoxidised film which occurred during sputter-cleaning of the sample surface (black line).](image-url)
In order to cross-check stoichiometry of the grown LaFeO$_3$ films, Rutherford backscattering spectrometry (RBS) measurements were performed. The RBS data was measured using an ion beam size of several millimetres. The analysis indicated a La:Fe:O stoichiometry of roughly 1:1:3 with an accuracy of 15% for lanthanum and iron, and 30% for oxygen (see FIG. 11). The large oxygen uncertainty is due to the uncertainty of separating the oxygen signal originating from the LaFeO$_3$ film and the STO substrate. In addition, silicon contamination was detected on some of the samples, which was probably due to the high deposition temperature resulting in evaporation of silicon from the silicon chip used to heat the sample and deposition of the silicon vapour on the sample surface.

![FIG. 11. RBS measurements of thin LaFeO$_3$ films: (a) uncapped and (b) capped with one nanometre of platinum. In both cases, the measurements confirmed that the stoichiometry is roughly 1:1:3. Accuracy in determining content of lanthanum, iron and platinum was $\approx$10%, and in the case of oxygen it was $\approx$30%. The large oxygen uncertainty is due the uncertainty of separating the oxygen signal originating from the LaFeO$_3$ film and the STO substrate. Horizontal axes of the graphs are: channels (bottom) of the ion detector and each channel corresponds to the ion kinetic energy (top).](image)
Chapter 2  Sample Preparation and Characterization

2.4 Patterning Techniques

We have used several complementary approaches to pattern nonmagnetic, FM and AF materials. These approaches differ in the order of the patterning steps and deposition. Therefore, we will distinguish between pre- and post-patterning (both involving etch processes), and lift-off. In the first case, a raw substrate was patterned (i.e. giving pre-patterned substrate) and a material was deposited afterwards. This resulted in an array of elevated structures and continuous material beneath. The post-patterning was carried out directly on the film after deposition. In the lift-off approach, the patterning and deposition occur simultaneously, since the material is deposited onto the patterned resist. All approaches have certain advantages and disadvantages. For instance, in the pre-patterning scheme, damage to the film during any of the etching steps is avoided since the deposition occurs after the patterning processes are complete. However, the increased roughness of the pre-patterned substrate can influence the growth and therefore the film properties. As for post-patterned approach, damaging of the film during the patterning can occur. The advantages of this approach are that the growth can be much better controlled on the unpatterned substrates (i.e. better control of the surface parameters like roughness or chemical termination) and the same sample can be investigated before and after the patterning. A procedure to pattern STO and LaFeO$_3$ was developed during this thesis and it was successfully used to pattern MgO and Fe$_3$O$_4$. Finally, the lift-off approach is the most straightforward patterning approach. However, it is strongly limited due to the resist present during the deposition.
FIG. 12. Different patterning approaches: (a) pre-patterning of the STO substrates, (b) patterning of the thin LaFeO$_3$ film deposited on the STO substrate, (c) pre-patterning of the silicon substrate and (d) the FIB lithography. The lift off patterning is done by performing steps, e.g. 1-4 of the silicon patterning method (c), though, any material can be deposited instead of chromium.
2.4.1 Pre-patterning

(a) Pre-patterned silicon substrates

In this project pre-patterned silicon substrates were used to produce FM structures (see Chapter 3). Pre-patterning of the silicon substrates was carried out combining electron beam (e-beam) lithography with reactive-ion etching (RIE). The scheme is shown in FIG. 12(c). In the first step a 80 nm thick polymethyl methacrylate (PMMA) resist was spin coated on the silicon wafer. Then, the resist was exposed using a Leica LION LV1 e-beam writer and during development the resist was removed in the exposed areas. In the next step, a 20 nm thick chromium mask was evaporated on top of the patterned PMMA resist. Then, the lift-off was performed in acetone, which resulted in a patterned chromium mask on top of the silicon wafer. Next, oxygen plasma cleaning was carried out, which assured removal of any organic residue. In the following step, silicon was etched through the Cr mask using RIE with a mixture of CHF3 and SF6. The final step was the chlorine plasma etching, which removed the Cr mask from the top of the silicon plateaus. In the final pre-patterned silicon substrate, the top surface of the plateaus is smooth but the silicon surface in the valleys is relatively rough due to the plasma etching (see SEM pictures in chapter 3.2).

(b) Pre-patterned STO substrates

Pre-patterning of the STO substrates was performed using a specially developed approach, which consisted of e-beam lithography combined with ion-milling. This involves creating a negative mask with e-beam lithography and later on transferring it into the substrate by ion-milling. The scheme is illustrated in FIG. 12(a). In the first step a chromium mask was evaporated on the substrate. According to our experience the chromium mask thickness should be roughly twice as large (usually 100-150 nm) as the
planned STO structure height. Next, a PMMA resist was deposited on the chromium mask ($\approx 80$ nm). Then, the PMMA layer was exposed using the e-beam writer. After the exposure, the sample was developed and rinsed in demineralised water. Next, a $20$ nm thick aluminium mask was evaporated onto the patterned PMMA resist. In the next step, a lift-off of the PMMA was performed in acetone using an ultrasonic bath, which resulted in a removal of the PMMA together with the unwanted aluminium layer. Next, oxygen plasma cleaning was carried out, which assured removal of any organic residues. The pattern in the aluminium layer was transferred into the chromium using a chlorine plasma etching with rates of about one nanometre per second. At this stage a mask for the ion-milling is ready. For the ion-milling a “Von Ardenne LA440S” sputtering machine was used with one keV argon ions and a fluency of $10^{21}$ cm$^{-2}$. Typical etching rates for different materials are listed in TAB. 4. The remaining chromium was then removed using chlorine plasma etching. The final product, i.e. the pre-patterned substrate, consists of an array of plateaus of various shapes designed during the e-beam lithography step and the continuous substrate beneath.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>ETCHING RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1.7 nm/min</td>
</tr>
<tr>
<td>Al</td>
<td>1.0 nm/min</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>2.5 nm/min</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>1.6 nm/min</td>
</tr>
</tbody>
</table>

TAB. 4. Typical ion-milling etching rates for different materials. Von Ardenne LA440S sputtering machine was used as an ion mill, with 1 keV Ar ions and a fluency of $10^{21}$ cm$^{-2}$.

2.4.2 Post-patterning

(a) Ion-Milling of Thin LaFeO$_3$ Films

Post-patterning of the LaFeO$_3$ films was made using the patterning approach identical to the pre-patterning of the STO substrates and consisted of the combination of e-beam lithography and ion-milling [see FIG. 12(b)]. The process was performed in exactly the same way as the pre-patterning of the STO substrates, however, the LaFeO$_3$
films were deposited onto the substrate before the patterning. In order to obtain isolated structures, samples were ≈10% over-etched. Therefore, the bottom part of each plateau consists of the substrate material and there is no material remaining between the structures [see FIG. 13(a)]. The influence of some patterning steps (like plasma etching or ion-milling) is not well understood. It seems that some materials can be affected, e.g. post-patterning of a cobalt film would probably result in a nonmagnetic or an AF layer of a cobalt oxide. Thus, the post-patterning is the most suitable for materials, which are not sensitive to any of the patterning steps or long exposure to air such LaFeO$_3$. The advantage of this approach is that the same sample can be investigated before and after the patterning.

(b) Focused Ion Beam Lithography

Focused ion beam (FIB) lithography was used to create patterned LaFeO$_3$ films. The FIB consists in ion bombardment of the sample surface using a focused and
accelerated beam (here: gallium ions accelerated to 30 keV). The FIB patterning can be performed either by complete removal or by damaging of the exposed material. This can be controlled by the ion beam fluency varied by changing either the ion current or the exposure time. In the first approach, the fluency is high enough to completely remove the exposed material resulting in pit-like structures [FIG. 13(a)]. The main limiting factor of this approach is a re-deposition process, which occurs around the exposed area and limits the effective LaFeO$_3$ signal detected by the PEEM (see FIG. 35). In the second approach the fluency is such that the exposed area is damaged with the removal of few monolayers from the top surface [FIG. 13(b)]. It was estimated using a SRIM-2006 simulation package$^{71}$ that the gallium ion penetration depth together with secondary processes leads in case of the LaFeO$_3$, to damaging of the material up to 40 nm in depth. The exposed LaFeO$_3$ was found to be nonmagnetic.

2.4.3 Patterning with a Lift-off Process

A lift-off process was used to create patterned metallic layers, e.g. a FM material on top of a continuous AF layer. This approach is a combination of electron beam (e-beam) lithography and a deposition technique, e.g. sputtering, evaporation or MBE. The scheme consists of spin-coating a resist PMMA, e-beam exposure, material deposition and finalized by the lift-off [First four steps of FIG. 12(c)]. The lift-off consists in acetone using an ultrasonic bath, which results in a removal of the PMMA together with the unwanted layer above. The lift-off process is straightforward and does not involve any damaging etch processes. The biggest limitation of the lift-off method is that a thin film has to be deposited on the PMMA mask without destroying it, e.g. by the high deposition temperatures or plasma present during the PLD growth. The lift-off patterning was mainly used as an intermediate patterning step for production of the etching masks.
2.5 Spectromicroscopy

X-ray absorption techniques, both spectroscopy and microscopy, are very important for the study of magnetic systems, because of their experimental simplicity and direct link to the magnetic properties. We have exploited magnetic imaging based on the x-ray dichroism effects in order to study the magnetic structure of both FM and AF materials. Here, the basics of these methods will be discussed.

2.5.1 X-ray Absorption Spectroscopy

Two types of x-ray absorption spectroscopy (XAS) are often distinguished, depending if one deals with resonant or nonresonant absorption. The first is the study of resonances near the absorption edges, and is often called a near edge x-ray absorption fine structure (NEXAFS) or an x-ray absorption near edge structure (XANES). The NEXAFS originates from transitions between a core state and valence states, e.g. for magnetic transition metals these would be dipole transitions from $2p$ to $3d$ valence states.

![Diagram of dipole transitions](image)

**FIG. 14.** (a) Illustration of the dipole transitions between a core states $2p$ and valence states $3d$ of magnetic transition metals. (b) The $L_{3,2}$ absorption edge spectra, which results from the core-valence states transitions.
states (see FIG. 14). The second type of spectroscopy is typically called an extended x-ray absorption fine structure (EXAFS)\textsuperscript{72} starting tens of electron-volts above the absorption edge.

The x-ray absorption intensity is attenuated upon transmission through a sample of thickness \(d\) according to

\[
I = I_0 \exp(-\mu_x d) = I_0 \exp\left(-\rho_a \sigma_{\text{abs}} d\right) \quad \text{eq. 2}
\]

Where \(\mu_x\) is the linear x-ray absorption coefficient with dimensions \([\text{m}^{-1}]\), \(\sigma_{\text{abs}}\) is the x-ray absorption cross-section \([\text{m}^2/\text{atom}]\), and \(\rho_a\) is the atomic density \([\text{atoms/m}^3]\). The x-ray absorption process depends on the properties of the initial and final electronic states. Therefore, measurement of the absorption coefficient can provide us with information related to the electronic structure. XAS measurements are usually performed using three approaches: transmission, electron yield or fluorescence. In the first case, the absorption coefficient is measured by detecting the x-rays transmitted through the sample (photon-in/photon-out). The latter approach consists of detecting the electron yield of electrons emitted from the sample. In the last case the absorption coefficient can be evaluated from the measurement of characteristic light radiating from the material as a consequence of the x-ray absorption process.

The electronic states can be probed with differently polarized x-rays and polarization dependent absorption of light is referred to as dichroism. In fact, polarized x-ray techniques have become of considerable importance for the study of magnetic phenomena and materials, mainly due to their elemental, chemical, and magnetic specificity. The microscopic origin of the dichroic behavior originates from the spatial anisotropy of the charge or the spin. Thus we distinguish natural, i.e. charge dependent and occurring in absence of the spin alignment, and magnetic dichroism, present due to the spin alignment and the spin-orbit coupling. In addition, one discriminates linear and circular dichroism. Altogether, we differentiate between four types of x-ray dichroism:\textsuperscript{22}

(i) X-ray natural linear dichroism (XNLD).
(ii) X-ray natural circular dichroism (XNCD).
(iii) X-ray magnetic linear (XMLD) – is connected with a charge anisotropy
induced by axial spin alignment.

(iv) X-ray magnetic circular dichroism (XMCD) – originates from directional spin alignment.

In the light of this thesis we will concentrate on the x-ray magnetic dichroism, which is employed using x-ray magnetic imaging methods. The x-ray magnetic linear and circular dichroism shall be discussed in turn, but first details of the PEEM technique will be introduced.

2.5.2 Photoemission Electron Microscopy

X-ray magnetic imaging is based on the dichroism effects. Tuning the photon energy to the absorption edges of magnetic elements, for example the L$_3$ or L$_2$ edges of the transition metals or the M$_5$ or M$_4$ of the rare earths, leads to a large dichroism effect. In general, the dichroism effect depends on the photon polarization orientation relative to the magnetic orientation. Therefore, the origin of the x-ray magnetic imaging lies in the x-ray polarization in conjunction with a tunable photon energy. Because of the utilization of these spectroscopy concepts, one often speaks of x-ray spectromicroscopy.

As in electron microscopy, x-ray microscopy has two main approaches: based on either scanning a focussed beam or full-field imaging. Two types of photo-in/photo-out transmission techniques exist: scanning transmission x-ray microscopy (STXM) and transmission imaging x-ray microscopy (TIXM). A detailed description of those methods can be found in the literature (see book by Stöhr and Siegmann$^{22}$). Here, we will focus on the third technique, PEEM, a photon-in/electron-out technique pioneered by Tonner et al.$^{12}$ The principle of this technique is illustrated in FIG. 15. All the PEEM measurements presented in this thesis were performed with an Elmitec PEEM (Ref. 73) at the SIM beamline$^{74}$ at the Swiss Light Source and we will focus our description of the PEEM on this instrumentation. The sample is illuminated by a monochromatic and polarized x-ray beam, which is focused to a 100 micrometer spot. The x-rays impinge on
the sample at a grazing angle of 16°. The photon energy resolution is determined by the x-ray monochromator and the spatial resolution is determined by the electron optics of the PEEM, being limited by spherical and chromatic aberrations of the first lens.

As a result of the x-ray absorption, a broad energy spectrum of emitted electrons is produced in the sample. The electron energies vary from zero up to the energy of the absorbed photons. However, only those electrons with a kinetic energy larger than the work function will leave the sample. In order to collect the electrons into the microscope, a negative potential of 20 kV is applied on the sample. The kinetic energy distribution of the electrons leads to the chromatic aberrations. However, the aberrations are filtered out using a set of slits and hemispherical energy analyzer, which can be tuned to the specific electron energy. The best combination of the spatial resolution and intensity of the measured signal is obtained by tuning the energy filtering to the photo secondary electrons with kinetic energies of ≈1-2 eV. After passing the energy analyzer the 48
electrons pass through a slit, which reduces the energy spread. Finally, the electrons go through a multi-channel plate (MCP) and after multiplication are converted to visible light via a phosphor screen. The light is then detected by a charge-coupled device (CCD) camera. The image being projected on the screen is simple the spatially resolved and magnified map of electrons, which have left the sample surface. The spatial resolution of the PEEM can be at best 30 nm.

2.5.3 X-ray Magnetic Circular Dichroism

The XMCD effect results from directional alignment of magnetic moments. Existence of the net magnetization leads to a different x-ray absorption intensity depending on the orientation of the x-ray angular momentum, i.e. helicity vector of the circularly polarized x-rays, with respect to the magnetization vector. This dependence is $\cos \theta$-like, where $\theta$ is the angle between the helicity and the magnetization vector. Therefore, the XMCD is maximum when the helicity vector is parallel or antiparallel to the magnetization vector and zero in the perpendicular case (see FIG. 16). Finally, the XMCD effect appears only in the presence of nonzero magnetization and spin-orbit coupling, since the photon angular momentum couples to the spin via the orbital angular momentum. This is because the electronic transition is driven by the electric field which does not act on spin but on the orbital angular moment via the charge. Thus the XMCD can be used to measure size and direction of the magnetic moments. Furthermore, the effect is opposite at the L$_3$ and L$_2$ edge (see example of cobalt in FIG. 16), which is due to the opposite sign of the spin component at the two edges, $j=l+s$ at the L$_3$ and $j=l-s$ at the L$_2$ edge.

We shall discuss now the contrast mechanism. As discussed above, the electrons emitted from the sample can be imaged by PEEM, thus the locally resolved absorption coefficient can be measured. This allows utilization of all of the advantages of the XAS technique such as chemical and elemental sensitivity or magnetic specificity. For
instance, tuning the photon energy to 707 eV, the L₃ absorption edge of iron metal, we can emphasize the iron over other elements in the sample. In addition, utilization of the circularly polarized x-rays would emphasize the sample regions with different magnetization directions. Hence, the XMCD effect can be used to image the FM domains. For instance, in order to create the XMCD image of cobalt FM domains, two images at the cobalt L₃ or L₂ absorption edge are collected, one with the plus and second with the minus circular polarization. The XMCD image is result of dividing the first by the second image. The division enhances the magnetic signal and removes all other contributions such as the topography or the chemical signal.

2.5.4 X-ray Magnetic Linear Dichroism

The XMLD effect arises from a nonspherical distortion of the atomic charge caused by the spin-orbit interaction when the atomic spins are axially aligned by the exchange interaction or external magnetic field. Therefore, the XMLD will not appear without the existence of a spin-orbit interaction and nonzero atomic magnetic moments or if those
moments would not be aligned. Therefore, the XMLD effect can appear in any of magnetic materials (like FM, AF, ferrimagnetic or paramagnetic ordered in magnetic field) and it vanishes whenever the magnetic order disappears, e.g. above magnetic transition temperatures (Curie or Néel temperature) or in absence of an external magnetic field. The existence of the magnetic alignment, i.e. existence of the magnetic (spin) axis, leads to different x-ray absorption intensity depending on the orientation of the x-ray polarization vector ($E$-vector) with respect to the magnetic axis. The XMLD has a $\cos^2 \theta$ polarization dependence, where $\theta$ is the angle between the $E$-vector and the magnetic axis. Hence, the XMLD reaches its extrema whenever the $E$-vector is parallel or perpendicular to the spin axis (see FIG. 17). The intrinsic origin of the XMLD effect is the presence of coupled electronic (multiplet) states that are formed under the influence of the exchange and spin-orbit interactions. A typically nonspherical charge distribution of such states can lead to certain energetic separation (removal of degeneration) and as a consequence to a large polarization dependence of individual transitions, hence the XMLD.

The AF domains can be imaged using the XMLD effect associated with the multiplet structure at the absorption edges of certain materials. For instance, the AF domains in the LaFeO$_3$ films can be imaged by recording images at the photon energies corresponding to the A and B peaks of either L$_3$ or L$_2$ absorption edge (see FIG. 17).

![FIG. 17. The principle of imaging using x-ray magnetic linear dichroism (XMLD). Linearly polarized x-rays incident from left with $E$-vector oriented vertically. Assuming the XMLD sign as reported in chapter 4.2, blue spectra (middle) together with white regions (right) correspond to parallel oriented AF axis with respect to the $E$-vector. Red spectra (middle) together with black regions (right) correspond to perpendicular orientation of the AF axis.](image-url)
The XMLD image is created by dividing the first by the second image and it consists of regions with different intensity (i.e. A/B ratio), which indicates different orientations of spin axis with respect to the $E$-vector of incoming x-rays. The extreme cases correspond to either perpendicular or parallel orientation. The principal of the XMLD imaging is shown in FIG. 17 where two types of contrast (bright and dark) can be seen.
Chapter 3
Ferromagnetic Thin Films

Investigation of the FM domain configuration in thin films is an important part of exchange bias studies. The final aim of this thesis was to investigate the effects of patterning on the exchange bias bilayers. Thus, a detailed understanding of the magnetic domain structure in both a FM and an AF layer was necessary. Knowledge of the FM domain formation in thin films is pretty well established. However, the observed FM domain states are very often not the lowest energy configurations since they are very sensitive to variations of different parameters such as thickness, roughness, temperature or external magnetic field. In order to fully reveal effects related to the exchange bias interface it was important to be able to develop an understanding of the factors determining the FM domain structure. Here, we report on studies of the domain configuration in patterned and continuous FM films as a function of thickness. In addition, observed effects of surface roughness will be discussed.
In this chapter, a detailed study of the magnetic domain configurations in polycrystalline FM thin film wedges of patterned cobalt and Permalloy will be presented. The films were deposited on pre-patterned silicon substrates with micrometer-sized square plateaus and the magnetic domain configuration imaged using PEEM combined with the XMCD effect. This approach allows the observation of the continuous development of magnetic domain states in the micrometer-sized square elements on top of the plateaus as a function of thickness. In addition, one can simultaneously observe the development of the magnetic domains in the continuous film surrounding the plateaus.

3.1 Effects of Patterning

The patterning effects in FM thin films are a very complex problem. In this section basic knowledge of the patterning effects will be introduced. Square and rectangular elements are of particular interest as model systems because their basic fourfold symmetry results in simple domain states which have been simulated\textsuperscript{20,75-81} and experimentally observed using various magnetic imaging methods.\textsuperscript{82-87} The magnetic domain configurations present are predominantly determined by the stray field energy associated with the shape boundaries (see details above in section 1.3.1), and a number of key states have been identified which fall into two categories.

The first category contains flux-closure states, including the Landau (or vortex) state [FIG. 18(a)] and the diamond state [FIG. 18(b)], which has a slightly higher energy than the Landau state due to the additional exchange energy associated with additional domain walls and vortices. The second category contains states with a high remanence and incomplete flux closure. These states are found in smaller, thinner elements which have a reduced stray field energy and do not include vortices because of the high exchange energy associated with them. These states include the C state [FIG. 18(c)], the S state [FIG. 18(d)], and the flower state [FIG. 18(e)]. The final magnetic state
observed for a given element depends on the size of the element, film thickness, and the magnetic material, i.e., its magnetization at saturation, exchange length, and the magnetic anisotropies present. In polycrystalline systems the effect of the magnetocrystalline anisotropy is dependent on the size and orientation of the individual crystallites and can be observed as magnetization ripple.

3.2 Experimental details

We have used pre-patterned silicon (001) substrates [for details refer to the chapter 2.4.1]. They were etched to give a plateau height of 125 nm. The top surface of the plateaus is smooth but the silicon surface in the valleys is relatively rough due to the plasma etching [FIG. 19(a)]. An estimation of the roughness from high resolution scanning electron microscope (SEM) images gives the height, width, and center-to-center distance of the small silicon hills of 15, 15, and 40 nm, respectively.

Two different ferromagnetic wedge films were investigated; Permalloy (Ni$_{83}$Fe$_{17}$), deposited by thermal evaporation (base pressure of 4·10$^{-6}$ mbar), and cobalt, deposited

![FIG. 18. Schematic diagrams of the expected PEEM contrast for magnetic configurations in ferromagnetic square elements. The details of the spin structures which occur in real elements, and therefore the measured contrast, will be dependent on the square size, thickness, and material properties.](image)
by dc sputtering (deposition at $1.4 \cdot 10^{-4}$ mbar). The wedge was created by moving a shutter across the substrate during deposition. The saturation at magnetization of the films was determined from hysteresis loops measured using a vibrating sample magnetometer and found to be $880 \cdot 10^3$ A/m for Permalloy and $1300 \cdot 10^3$ A/m for cobalt, which are comparable to the literature values. The preferential growth of the magnetic films on the top surface of the silicon substrate rather than on the plateau edges and self-shadowing effects resulted in the isolation of the square magnetic elements sitting on top of the plateaus from the continuous film in the valleys, as observed with a high resolution SEM and by transmission electron microscopy. The gap between the upper and lower magnetic films is clearly observed up to a film thickness of $t=140$ nm [see FIGs. 19(b) and 19(c)], and even up to 240 nm [FIG. 19(d)] there still appears to be some separation. The thickness of the ferromagnetic wedges was determined from high resolution SEM images of the magnetic film cross sections.

FIG. 19. High resolution SEM images of (a) a 1 μm square silicon plateau and then with a cobalt layer deposited onto the plateau with thicknesses of (b) 40 nm, (c) 110 nm, and (d) 240 nm. The sample is tilted at 45°.
3.3 Results

In this section, results of studies of the FM domain structure in cobalt and Permalloy films will be discussed in turn. First results of patterned and second continuous films will be presented.

3.3.1 Cobalt square elements

The XMCD images of magnetic domain states for the demagnetized cobalt wedge with thickness up to 300 nm are given in FIG. 20. For details on the XMCD imaging refer to section 2.5.3. Due to the difficulty of determining the exact thickness of the films below \( t \approx 10 \) nm with the SEM, we have assumed a zero film thickness at the first square with no magnetic contrast (position indicated with white square frames and labeled "square 0" in the figure) which is in agreement with the absorption spectra taken at this position. This results in an uncertainty in the nanometre range of the low thickness values. From magnetic simulations,\(^{76-78}\) it seems that the lowest energy state for the four and two micrometers square elements should be the Landau state, with a transition to single domain behaviour at very low (around 1 nm) thickness. However, rather than the Landau state we have observed a variety of metastable states not predicted by the simulations. For the four micrometers square elements, we have observed four key thickness regions.

(i) For \( t \approx 2 \) nm (square 1; the squares numbering was defined in FIG. 20), we observe a three-domain state with the domain walls oriented at 45° to the square boundaries [see FIG. 21(a)]. The orientation of the domain walls is similar to that of the continuous film surrounding the plateaus and may therefore be determined by the intrinsic uniaxial anisotropy of the cobalt film.

(ii) For \( t = 4–8 \) nm (squares 2–4), we observe very narrow domains, which seem
FIG. 20. XMCD images of a cobalt wedge deposited on a prepatterned silicon substrate with rows of square plateaus with four, two, and one micrometer edge lengths. The square number (in black) and the cobalt thickness in nm (in white) are indicated.
to result from the piling up of 360° walls [FIG. 21(b)]. Such 360° walls are common in highly dispersed magnetic films which have been demagnetized in a similar manner. The magnetization dispersion is linked to the variation in the orientation of the magnetocrystalline anisotropy axes from crystal grain to grain. Roughness of the square edges may also help to pin magnetic spins, facilitating the formation of the 360° walls.

(iii) For t=10–18 nm (squares 5–18), several different magnetic states are observed which can be divided into two main categories: near-diamond states [FIG. 21(c)] and asymmetric Landau states [FIG. 21(e)]. We also observe one square element with an S state [FIG. 21(d)]. These various states are the results of trapping of magnetic states at local energy minima.

FIG. 21. XMCD images of four micrometers cobalt squares showing (a) three-domain state, (b) piled up 360° walls, (c) near-diamond state, (d) S state, (e) asymmetric Landau state, and (f) centered Landau state.
via pinning of magnetic spins, e.g., in domain walls or vortices, at material defects.

(iv) At a $t=19$ nm (square 19), the elements finally fall into the centered Landau state [FIG. 21(f)] and remain in this state up to the maximum thickness of 300 nm (square 216). It is interesting here to see that the Landau state is maintained by the stray field energy associated with the square shape up to the highest film thickness, despite the fact that the film thickness is 2.5 times thicker than the original etched silicon substrate plateaus.

The study of the magnetic domain configurations in the four micrometers squares as a function of thickness has allowed us to observe how local effects, i.e., pinning and magnetocrystalline anisotropy, compete with the stray field energy associated with the square shape. This results in a series of metastable states existing up to a thickness where the stray field energy dominates and the centered Landau state prevails. For the

FIG. 22. XMCD images of two micrometers cobalt squares with the square number indicated. At low thicknesses a series of metastable states is observed which include a C state (square 1), a thickness range where the magnetocrystalline anisotropy dominates and small domains are present (squares 2–4), a state with white contrast at the borders and a central gray contrast (squares 6 and 11), an S state (square 9), and asymmetric Landau states (squares 7, 8, 10, and 12). The centered Landau state is attained at square 13 ($t=15$ nm), with one last metastable diamond-like state observed in square 28 ($t=25$ nm).
two micrometers squares we see a similar competition (see FIG. 22), with the centred
Landau state first occurring at a film thickness of $t=15$ nm (square 13) and remaining up
to $t=300$ nm, although at a thickness of 25 nm (square 28), one last metastable
diamond-like state occurs. While we see an indication of comparable behaviour from the
XMCD contrast in the one micrometer square elements, we have concentrated our study
here on the four and two micrometers square elements which requires a field of view too
large (i.e. resolution is too low) to determine the details of the magnetic states present in
the smaller elements.

3.3.2 Permalloy square elements

The XMCD images of magnetic domain states for the demagnetized Permalloy
wedge with thickness up to 96 nm are given in FIG. 23. Again, we see different
thickness regions for the four micrometers squares.

(i) At $t\approx 1–2$ nm (squares 1 and 2; the squares numbering was defined in FIG. 
23), we observe different domain configurations. In square 1 [FIG. 24(a)] we
observe a Landau state, and in square 2 [FIG. 24(b)] we again observe a
three-domain state with the domain walls oriented at 45° to the square
edges.

(ii) For $t\approx 3$ nm (squares 3 and 4), we observe small domains [FIG. 24(c)]. In
this region it seems that the magnetocrystalline anisotropy associated with
the individual crystal grains dominates, resulting in a fine domain structure.

(iii) For $t\approx 4–5$ nm (squares 5 and 6), we observe an S state [FIG. 24(d)].

(iv) For $t=6–10$ nm (squares 7–12), we observe two magnetic configurations:
    either a zigzag configuration [FIG. 24(e)] or a C state [FIG. 24(f)].

(v) For $t=11–16$ nm (squares 13–19), we observe an asymmetric Landau state
    [FIG. 24(g)].
FIG. 23. XMCD images of a Permalloy wedge deposited on a prepatterned silicon substrate with rows of square plateaus with four, two and one micrometer edge lengths. The square number (in black) and the cobalt thickness in nm (in white) are indicated.
(vi) For $t=17–96$ nm (squares 20–112), the elements finally fall into the centred Landau state [FIG. 24(h)].

For the two micrometers Permalloy squares we also observe a similar competition with thickness until the centred Landau state is attained at a thickness of 13 nm (square 15).

### 3.3.3 Continuous cobalt film

In a continuous thin polycrystalline film, we expect to see fairly large domains, which are elongated along the magnetization direction and are several micrometers across, and also the appearance of cross-tie walls over a certain thickness range. For the cobalt film (FIG. 20), we do indeed see cross-tie walls separating large domains with
the film thickness in the range of 26–65 nm (squares 31–91), and large domains continue to be present up to the largest thickness of 300 nm. However, in a thickness range starting sharply just after square 1 \((t\approx 2 \text{ nm})\) and running up to about square 30 \((t\approx 26 \text{ nm})\), we observe small domains which are isotropic in character and increase in size as the cobalt film thickness increases. It seems that in this thickness range, the roughness of silicon substrate, which is produced during the reactive ion etching process used to create the silicon plateaus, plays an important role in determining the domain structure. The local stray fields associated with the resulting film roughness gives a dramatic change in the magnetic domain configuration, providing nucleation sites and pinning centres which favour the formation of small domains. The domain size increases with thickness as the effect of the surface roughness decreases, and at a thickness of 26 nm, the expected large domains appear as the surface roughness becomes insignificant compared with the total film thickness. It is surprising to see that the large domains reappear at lower film thicknesses (just before square 1 at a nominal thickness below \(t\approx 2 \text{ nm}\)). However, if one considers that stray fields become negligible when a ferromagnetic film becomes ultra-thin, a possible explanation for the reappearance of large domains is that the stray field energy associated with the film roughness becomes too small at the lower thicknesses to have an influence on the magnetic domain configuration.

The presence of the square plateaus in the silicon results in square holes or antidots in the continuous films. The effect of the stray field energy associated with the antidots can be most clearly seen in FIG. 20, squares 88–91 and 150–153. Here typical antidot configurations, i.e., whisker domains emanating from the two and one micrometer squares and diagonal domains running between the squares in adjacent rows, can be seen.\(^{90,91}\) Between the four micrometers squares we also observe Landau patterns (between squares 34 and 35) and hexagon-shaped domain configurations, with (black and white contrast between squares 35 and 36) and without (black contrast between squares 37 and 38) the presence of a domain wall, all of which we have outlined with a dashed-white line and are the results of stray field energy associated with the square holes.
For very thick films with a direct exchange interaction (i.e., physical contact between the films), the neighbouring XMCD contrast is expected to be the same. It is also conceivable that there are stray field interactions between the continuous film and the square elements when they are isolated from each other. For the larger film thicknesses, as we have seen, the stray field energy associated with the square shape dominates and results in a Landau state in the square elements. For the thickness range where we observe metastable states in the square elements (film thickness is below 20 nm and vertical separation between the magnetic layers is 100 nm or more), the stray field interactions between the two layers may play a more important role in determining the resulting domain structures.

It should also be noted that, at the lower half of the XMCD image in FIG. 20 between squares 10 and 17, a piling up of 360° walls is observed in the continuous film, indicated in several places by the white arrows, which again is an indication of a high anisotropy dispersion in the cobalt films.89

### 3.3.4 Continuous Permalloy films

For the continuous Permalloy film there is also a large region containing small domains (FIG. 23), which starts at a thickness of \( t \approx 6 \) nm and continues beyond square 33 \( (t \approx 28 \) nm). We do not observe cross-tie walls in the Permalloy films which would normally occur in the region where we observe small domains.
3.4 Conclusions

We have studied the magnetic domain configurations in FM square elements with continuously increasing ferromagnetic film thickness using PEEM. At high film thicknesses, where the stray field energy associated with the shape boundaries dominates, we observe the centred Landau state. Although this is predicted to be the lowest energy state for practically all film thicknesses, we observed that for lower thicknesses the system is trapped in some high energy, more complex configurations. These metastable states include three-domain states, diamond states, zigzag domain states, C states, S states, and asymmetric Landau states, and their presence can be attributed to two causes: First, for low film thickness, material defects such as the surface and edge roughness result in strong local pinning sites and the demagnetizing field is not sufficient to overcome them. Indeed, the lower the thickness the more effective the pinning site will be. Secondly, as the film thickness decreases it becomes more and more difficult to switch between equilibrium states because at lower thickness, the magnetic spins are forced to lie in plane resulting in higher energy barriers between metastable states. In very thin films the observed magnetic spin configuration is almost never the ground state because a few roughness-induced pinning sites suffice to trap the system into high energy equilibrium states, with the coercive field associated with these pinning sites creating a high energy barrier. The presence of local effects, such as magnetocrystalline anisotropy and shape edge roughness, is emphasized by the appearance of small domains or tightly packed 360° walls in a thickness region below 10 nm where these effects appear to dominate.

In the continuous films surrounding the square plateaus, we observe a thickness range with small, isotropic domains which are the results of the surface roughness of the substrate in the valleys due to the etch processes used to pre-pattern the silicon substrate. It seems that creation of small domains results from the stray fields associated with the substrate roughness which provide a dense network of nucleation and pinning centres.
This work is important for the main aim of this thesis, which was studying the magnetic domain structure in exchange bias systems. The knowledge of how various parameters (such as thickness, substrate roughness or patterning) influence the FM domain structure in thin films can be very useful for a complete understanding of the results obtained on the exchange bias systems, where the final FM domain structure is a combination of various effects. In addition, this study of the FM thin films grown onto the pre-patterned substrates, has shown the suitability of this fabrication method for studies of magnetic domain configuration in patterned films. Finally, this work highlights the importance of local magnetic effects in the determination of the final magnetic domain states in magnetic thin films and small elements.

The main part of the above chapter is based on our prior publication.92
Chapter 4
Antiferromagnetic Thin Films

The role of the AF domains in the exchange bias effect is very much a big puzzle. Some researchers claim that the domains are of negligible importance while others expect them to be the key to solve the exchange bias mystery. In any case, an understanding of the origin and formation of AF domains in thin films would allow the debate to be settled. Therefore, studies of bare AF systems and their magnetic domain structure are essential. However, only a few experimental techniques are capable of studying the AF domains. In addition, the existing techniques are usually limited to specific materials and/or require a tremendous amount of work both in the experimental and analysis part. Any major assumption made during the analysis increases the uncertainty of the results. Here, we report on a method which simplifies studies of the AF domain structure and how this can help to solve the problem of the origin of the AF domains.
In this chapter detailed studies of the AF domain configurations in continuous and patterned LaFeO$_3$ thin films are reported. Details of our newly developed powerful approach to investigate individual AF domains will be given. This combines the PEEM and the XMLD effect. It is then shown how this method was utilized and what new insight it brings to the better understanding of the AF materials. An important discovery was that the sign of the XMLD effect is sensitive to the AF axis orientation with respect to the crystallographic axes. In addition, the AF domain structure, measured with PEEM, has a one-to-one correlation with the crystallographic domains measured with forward scattered electron-scanning electron microscopy (FSE-SEM). Finally, measurements of the AF domain configuration in the patterned LaFeO$_3$ films are given, showing how the AF structure remains completely unaffected by the patterning.

4.1 Antiferromagnetic Domains

Determination of the AF domain structure and its origin is of high interest for fundamental and applied research. However, a limiting factor is the lack of experimental results, which are needed to shed more light on the topic. We have developed a new powerful approach to determine the spin orientation of individual domains, based on combining spatially resolved x-ray magnetic linear dichroism (XMLD) images measured using PEEM with rotating the orientation of the linearly polarized x-rays (the $E$-vector). This enables us to determine the magnetic orientation without the need to know the absolute size and sign of the XMLD effect. Here, we will report on temperature dependence studies of the measured dichroic signal confirming its magnetic origin. Next, we report on the studies of the AF axis orientation in thin LaFeO$_3$ films. Using PEEM we found four types of the AF domains having an in-plane fourfold symmetry of the spin axes, which are tilted $20^\circ$ out of the surface plane.
4.1.1 Temperature Dependence

In our studies of the AF domain structure, we have to make sure that the measured linear dichroism is of magnetic origin. Two main contributions to the linear dichroism exist: the XMLD and the crystal field dichroism (see XNLD in chapter 2.5.1). Thus, it is important to determine, which of them, or whether a combination of both, contributes to the measured dichroic signal. It is known in the literature that magnetically ordered materials exhibit a strong temperature dependence.\(^93\) In particular, the AF order disappears at the Néel temperature, \(T_N\). As for the crystal field, no significant temperature dependence is expected, since there is no crystallographic phase transition. Therefore, we have investigated the temperature dependence of the dichroic signal by measuring XMLD images as a function of the temperature; selected XMLD images are shown in FIG. 25(a-d). The XMLD contrast [FIG. 25(a)] vanishes completely above \(T_N\) [FIG. 25(c)] and is completely recovered upon cooling to room temperature [FIG. 25(d)], which indicates that it is of magnetic origin. In addition, multiplet calculations showed that the crystal field does not contribute to the linear dichroism signal of LaFeO\(_3\).\(^95\) We have performed several heating-cooling cycles and the extracted temperature dependence together with a mean field theory fit is shown in [FIG. 25(e)].

The XMLD temperature dependence was fit using mean field approximation by scaling the measured XMLD temperature dependence to match the simulated \(<M^2>\) temperature dependence.\(^21,96\) The scaling factors were \(T_N\) (used as a reduced temperature \(T/T_N\)) and the XMLD signal normalization (proportionality factor between the XMLD and the \(<M^2>\)) under the condition that \(<M^2>\) equals one at zero temperature and equals zero at \(T_N\) (\(T/T_N\) equals one). The scaling was done by self-made code based on the least square method. The determined Néel temperature is 565 K, which is much lower than the bulk value (740 K). Dimensional effects could not explain such decrease, since a thickness of 25 nm is still relatively large. However, the decrease of the XMLD signal could be due to a change in the spin axis orientation and/or a change in the electronic states which contribute to the XMLD effect of LaFeO\(_3\). Therefore, we
determined the spin axis orientation, using our newly developed technique (details will be discussed in the next section), for temperatures between room temperature and $T_N$, and no change in the spin axis orientation or the XMLD shape was observed. The temperature dependence of the XMLD spectrum, taken at iron L$_{3,2}$ absorption edge between dark and bright regions, is shown in FIG. 25(f). The XMLD signal decreases without any changes in the photon energy dependence. Thus, we attribute the reduced $T_N$ to a strain present in the measured thin LaFeO$_3$ films. In conclusion, we have shown that the measured linear dichroism signal is of magnetic origin and that the AF spin axis orientation is constant as a function of temperature.

FIG. 25. XMLD images taken with the $E$-vector oriented in plane. (a) The XMLD contrast is reduced at 400K (b), disappears at 600 K (c) and is completely recovered upon cooling to room temperature (d). Extracted XMLD contrast showing temperature dependence with mean field theory fit (e). (f) XMLD spectra obtained at different temperatures.
4.1.2 Orientation of the Spin Axis

The key property of the AF domain structure is the orientation of the spin axis within an individual domain. Thus, determination of the spin axis orientation is of key importance for the understanding of AF domains. This requires the knowledge of the XMLD size and sign for the data analysis, but often this information is missing, and an assumption concerning the XMLD size and sign has to be made. Hence the determination of the spin axis could be wrong by 90°, which has significant consequences, determining whether a parallel or perpendicular orientation of the magnetic axes is present in an AF/FM system.

FIG. 26. (a) Experimental geometry and definition of the coordinate system. (b) Spatially resolved XAS recorded from a bright and dark area, together with the corresponding difference signal (black dots) and calculated spectrum (solid line) (Ref. 93). The inset shows an XMLD image of LaFeO₃ film taken with the $E$-vector oriented in the plane of the sample.
Here, we report on a new approach, which does not require any initial information regarding either the sign or the size of the XMLD signal. In addition, the XMLD sign can be extracted from experimental data. Finally, it allows the determination of the orientation of individual domains. The basic idea consists of studying the XMLD as a function of the angle between the $E$-vector and AF spins axis.

Determination of the orientation of the AF axis was performed in two steps: first, the in-plane component was measured and second, the out-of-plane component. The intensity at the Fe L$_3$ or L$_2$ absorption edge is given by

$$I = I_0 + I_2 \cos^2 \alpha$$

where the $I_0$ and $I_2$ are constants related to the XMLD signal. The XMLD contribution depends on the angle $\alpha$ between the $E$-vector of incident x-rays and the AF axis. We probe the XMLD signal by first changing the sample angle $\gamma$ about the $z$-axis (i.e. determining the in-plane component), and then changing the angle $\omega$ of the $E$-vector (i.e. determining the out-of-plane component). The cosine of the angle $\alpha$ can be converted

\[ \omega = 90^\circ \]

\[ \text{Sample Angle } \gamma [\text{deg}] \]

\[ \begin{align*}
\text{XMLD signal [a.u.]} \\
2.6 &- 0.8 \\
2.4 &- 1.2 \\
2.2 &- 1.4 \\
2.0 &- 1.6 \\
1.8 &- 1.8 \\
1.6 &- 2.0 \\
1.4 &- 2.2 \\
1.2 &- 2.4 \\
1.0 &- 2.6 \\
0.8 &- 2.8 \\
\end{align*} \]

FIG. 27. Azimuthal dependence of the XMLD signal of different AF domains. The signal was extracted from the XMLD images taken for $\gamma$ rotated from $0^\circ$ to $90^\circ$ in $15^\circ$ steps. The signal is found to be extreme at $\gamma$ equal $0^\circ$ and $90^\circ$, which reveals a fourfold symmetry.
into the coordinate system as follows:

\[
\cos \alpha = (\sin \gamma \cdot \sin \omega + \sin 16^\circ \cdot \cos \gamma \cdot \cos \omega) \sin \theta \cdot \cos \phi + \\
+ (\cos \gamma \cdot \sin \omega - \sin 16^\circ \cdot \sin \gamma \cdot \cos \omega) \sin \theta \cdot \sin \phi + \\
+ \cos 16^\circ \cdot \cos \omega \cdot \cos \theta
\]  \hspace{1cm} \text{eq. 4}

where \( \theta \) and \( \phi \) are the spherical coordinates of the AF axis. Eq. 3 and 4 were used to fit the experimental data, which will be discussed later on. The fit was done using a self-made code written using a ROOT package (see Appendix A). The definition of the coordinate system (x, y and z) is shown in FIG. 26(a). The x-axis is parallel to the in-plane component of the x-rays.

For the determination of the in-plane component of the AF axis, different XMLD images with the \( E \)-vector in-plane were taken for \( \gamma \) rotated from \( 0^\circ \) to \( 90^\circ \) in \( 15^\circ \) steps. The azimuthal dependence of the XMLD signal shows an extreme behaviour at \( \gamma \) equal...

FIG. 28. XMLD images for the two in-plane sample angles \( \gamma = 0^\circ \) and \( 90^\circ \) (top and bottom row, respectively) and \( E \)-vector angle \( \omega = 0^\circ \), 45\(^\circ\), and 90\(^\circ\) (left, middle, and right columns, respectively). Comparison of the domains P1 and P2 shows that they have the same in-plane components, i.e., the same contrast in (d), but a different out-of-plane component, i.e., different contrast in (e). The same holds for Q3 and Q4. Note that for ease of comparison, the images have been rotated.
Chapter 4  Antiferromagnetic Thin Films

0° and 90° (see FIG. 27). This reveals a fourfold symmetry of the in-plane components, also seen as a maximal contrast reversal between the XMLD images shown in FIGs. 28(a) and 28(d). It follows that for the sample angles $\gamma$ of 0° and 90° the in-plane components of the AF axes are either parallel or perpendicular to the $x$-axis.

In order to determine the out-of-plane component of the AF axis, XMLD images with different orientations of the $E$-vector were taken for both 0° and 90° sample angles. The $E$-vector was rotated in steps from in-plane to out-of-plane with respect to the sample surface; note that it is not exactly parallel to the surface normal due to the grazing incidence of 16°. FIG. 28 illustrates the change in the XMLD images for the two in-plane sample angles $\gamma=0°$ and 90° (top and bottom row, respectively) and $E$-vector angle $\omega=0°$, 45°, and 90° (left, middle, and right columns, respectively). Comparing the domains P1 and P2 in FIG. 28, one observes that they have the same orientation of the in-plane component, e.g., the same contrast in FIG. 28(d), but a different out-of-plane component, e.g., a different contrast in FIG. 28(e). This is also the case for Q3 and Q4.

For a quantitative analysis, the peak ratio $A/B$ [see FIG. 26(b)], which we will refer to as the XMLD intensity, was studied as a function of the polarization angle for 70 domains from three different sample regions (some of them are shown in FIG. 29). They can be divided into four characteristic groups of domains, e.g. P1, P2, Q3 and Q4 in FIG. 28. For clarity, we took the average intensity of domains showing the same

![FIG. 29. XMLD signal from individual domains as a function of polarization angle. Results for samples angles (a) 0° and (b) 90° are shown. Four types of dependencies are visible.](image)
Chapter 4  Antiferromagnetic Thin Films

behaviour. Results for sample angles $\gamma$ of $0^\circ$ and $90^\circ$ are shown in FIG. 31(a) and 31(b), respectively.

FIG. 30. (a) Selected virtual orientations of the AF spin axis. Corresponding XMLD signals as a function of the sample angle $\gamma$ (b,c) and the $E$-vector angle $\omega$ (d,e). It is visible how the XMLD signal is changing with the changing spin axis orientation. In particular, four cases (marked with stars) are in agreement with the measured XMLD signal as a function of the sample angle $\gamma$ (see FIG. 27) and $E$-vector angle $\omega$ [see FIG. 31(a)]. For ease of understanding the dependencies were divided into two groups (plots on left and right).
In order to determine the orientation of the out-of-plane component, it is sufficient to find the extremes in the XMLD intensity as a function of the $E$-vector angle $\omega$. As given by eq. 3, the XMLD intensity varies with $\cos^2 \alpha$ and hence all possible values are obtained in the range of $\alpha$ from $0^\circ$ to $180^\circ$. By rotating the $E$-vector, we probe the AF-axis components in the rotation plane. Therefore, for each AF orientation with nonzero components in the rotation plane, we expect to see extremes at a specific $E$-vector angle $\omega$. In addition, we need to know whether a maximum or a minimum of the XMLD intensity corresponds to a parallel alignment of the $E$-vector with the AF axis. This can be derived from FIG. 30. Domains that have their in-plane component of the AF axis in the direction of the $x$-axis will always have their XMLD extremes at an $E$-vector angle of $\gamma=0^\circ$ and $90^\circ$, independent of how much the AF axis is canted. Only domains with an in-plane component of the AF axis perpendicular to the $x$-axis can have extremes different from $0^\circ$ and $90^\circ$ (see FIG. 30).

In FIG. 31(a), two pairs of angle dependences of the XMLD intensity for different domains are shown: one pair (P1, P2) with extremes at $\omega=20^\circ$, and $70^\circ$ and a second pair (Q3, Q4) with nearly linear dependence or extremes at 0 and $90^\circ$. Following the above arguments and considering the observed fourfold symmetry, the first pair is oriented perpendicular and the second parallel to the $x$-axis. Hence, from FIG. 31(a) for an $E$-vector angle $0^\circ$ we find that an alignment of the $E$-vector perpendicular to the AF axis (Q3 and Q4) corresponds to a low XMLD intensity. After rotating the sample by $90^\circ$ we find a consistent, reversed behaviour for P1, P2, Q3, and Q4 [see FIG. 31(b)]. The data shown in FIG. 31 were fitted using eq. 3 and 4, and the fits are represented by the solid lines. For clarity we show two XMLD images, the first with $E$-vector oriented in-plane [see FIG. 31(c)] and the second with the $E$-vector canted $45^\circ$ out-of-plane [see FIG. 31(d)]. Our analysis shows that the AF axis of all domains is canted by $20\pm3^\circ$ from the sample surface [see FIG. 31(e)].

The existence of four domain orientations can be explained by considering the crystallographic structure of the films. LaFeO$_3$ is orthorhombic and grows with the $c$-axis in the surface plane and parallel to the STO(001) axes. Our RHEED measurements
indicated that the epitaxial films are crystallographically twinned, resulting in the fourfold symmetry [see introduction to the LaFeO$_3$ system in the section 2.1]. This is in agreement with the studies of Scholl et al.$^{29}$ and Lüning et al.$^{30}$ of LaFeO$_3$ grown by MBE on STO(001), where the crystallographic structure was determined with TEM. In their sample, the AF axis is canted 45° out of the sample surface. We attribute these different orientations (45° vs. 20°) to the growth methods and strain effects.$^{61,94}$ Since the reported magnetic moments are not aligned along easy crystallographic axes, there appears to be a delicate balance that is sensitive to small changes in the environment, which results in the different AF axis orientation compare to the bulk LaFeO$_3$.

In summary, we have reported on our newly developed technique to determine the AF domain configuration based on the combination of the PEEM and the XMLD effect. In particular, we utilized this method to determine the AF domain structure in thin
LaFeO$_3$ films grown on STO(001) substrates. The measured XMLD signal was found to be of purely magnetic origin. Finally, we found existence of four types of twinned AF domains with the in-plane fourfold symmetry of the spin axes, which are canted $20^\circ$ out-of-plane.

4.2 XMLD and the Magnetocrystalline Anisotropy

Comparing our results with the literature and using multiplet calculations we show that the XMLD effect is sensitive to the magnetocrystalline anisotropy and can even change its sign. A change of the XMLD sign has been theoretically predicted$^{98,99}$ for ferromagnetic metals but so far not confirmed by measurements. Here, we report measurements that establish this effect for antiferromagnets for the first time.

As mentioned, using our newly developed technique we can determine the AF spin axis orientation without the need to know either the size or the sign of the XMLD effect. Furthermore, we can determine the sign of the XMLD signal and, interestingly, the observed XMLD has the opposite sign than expected. It has been reported for $\alpha$-Fe$_2$O$_3$ that the peak B of the L$_3$ and L$_2$ edges is maximal when the $E$-vector is parallel to the magnetic axis ($E \parallel M$).$^{27}$ The same is true for studies of LaFeO$_3$ films grown by MBE onto STO(001) substrates (work by Scholl et al.$^{29}$ and Lüning et al.$^{30}$). This is in contrast with our result (see above in section 4.1.2), as can be seen in FIG. 32, where the spectra of a bright and dark domain are compared. We have shown that the dark domain is perpendicular to the $E$-vector, yet the B peak is maximal, while Lüning et al. have shown the opposite.

Since the crystal field also can contribute to the linear dichroism, it is in principle possible that a quadrupole moment in the ground state, induced by a noncubic crystal field, gives rise to an additional, or even opposite, linear dichroism. Indeed, Haverkort et al.$^{100}$ showed using multiplet calculations that for NiO on Ag, the linear dichroism of
magnetic and crystal field origin have opposite signs. However, we showed the XMLD signal of LaFeO$_3$ to be of purely magnetic origin using temperature dependence studies and multiplet calculations (see above in section 4.1.1).

The sign reversal between the XMLD in our study and those of Scholl et al.$^{29}$ and Kuiper et al.$^{27}$ must therefore have a different origin than purely the crystal field. The multiplet calculations by G. van der Laan in the presence of a cubic crystal field revealed indeed a reversal of the XMLD [see FIG. 26(b)]. Here, the dichroism depends on the magnetic orientation; it changes sign when the AF axis rotates from the (100) to either the (111) or the (110) directions, with the reversal occurring around 30°. The absolute sign can be retrieved from Ref. 25. The spectra for Fe d$^5$ in an octahedral field of $\Delta=2$ eV are very similar to those for the isoelectronic Mn d$^5$ in FIG. 26(e) of Ref. 93. It shows that

---

**FIG. 32.** XMLD images and corresponding intensity of the iron L absorption edge for bright and dark AF domains of thin LaFeO$_3$ films. Sketches illustrate the opposite sign of the XMLD signal reported by (a) Lüning et al.$^{30}$ and by Czekaj et al.$^{31}$ (see above in section 4.1.2). The XMLD image for the data reported by Lüning et al. was inverted compared to the published data where they used the peak ratio B/A, while we use the peak ratio A/B.
for an alignment of the $E$-vector parallel to the magnetic orientation (in this case along the tetragonal axis, i.e., $E \parallel M \parallel [001]$) the peak B is lower than for $E \perp M$. This also remains true if M is at a moderate angle ($< 30^\circ$) with one of the $<100>$ axes. However, if the magnetization direction is near the $<110>$ or $<111>$ direction, then the situation is reversed, so that peak B is higher for $E \parallel M$. This is exactly the case for the studies of Scholl et al.\textsuperscript{29} and Kuiper et al.\textsuperscript{27} In the study of Scholl et al., the magnetic axis is at 45° with respect to the [001], while for our case it is 20°. In hematite ($\alpha$-Fe$_2$O$_3$) the spin axis is trigonal,\textsuperscript{27} i.e. along the [111]. A similar sign reversal between [001] and [111] for Fe metal was also reported by Kuneš and Oppeneer.\textsuperscript{98} However, their investigation was more restrictive since the magnetization was taken only along the crystallographic axes. Using multiplet calculations we verified the sign reversal for the magnetization and incident light in arbitrary directions.

To summarize, we found that the measured XMLD signal of the LaFeO$_3$ films has the opposite sign compared to the one reported by Lüning et al.\textsuperscript{30} Furthermore, using the multiplet calculations we showed that the XMLD effect is sensitive on the orientation of the magnetic axis with respect to the crystalline axes. In particular, the XMLD will change its sign when the AF axis rotates from the (100) to either the (111) or the (110) directions, with the reversal occurring around 30°.

![Illustration of the XMLD reversal in LaFeO$_3$. A change in the orientation of the spin axis with respect to the crystallographic axes causes a change of the dichroic signal. In particular, around 30° out of (001) plane the XMLD changes its sign. This is seen by comparing results from Lüning et al.\textsuperscript{30} and Czekaj et al.\textsuperscript{31}](image)
4.3 Patterned thin LaFeO$_3$ films

According to the literature, the influence of patterning on the AF domain structure has never been studied until now. This is mainly because a lack of experimental techniques which can be used to determine the AF domain configuration. Here, we present the AF domain configuration of LaFeO$_3$ films patterned with three complementary approaches: (1) the LaFeO$_3$ films were grown on pre-patterned STO substrates, (2) the LaFeO$_3$ films were post-patterned using e-beam lithography combined with ion-milling and (3) the LaFeO$_3$ films were damaged by FIB (for details see section 2.4).

For the pre-patterned films no difference between the AF domains in the structure and the surrounding areas is visible. An example of a 2 $\mu$m circular structure is given in FIG. 34(a), where it can be seen that the AF domains are much smaller (around 300 nm) than the structure. The effects of structuring might become visible when they have a

![FIG. 34. XMLD images of patterned thin LaFeO$_3$ films. The pattern was created by: (a) thin film deposition on pre-patterned STO substrate prepared by electron beam lithography with ion-milling, (b) post-patterning using electron beam lithography with ion-milling and (c,d) FIB lithography. In all cases, the AF domain configuration remained unaffected by the patterning.](image)
comparable size. However, for the pre-patterned sample it was not possible to grow films with larger AF domains, which was probably due to an increased surface roughness of the substrate produced during the ion-milling.

For the post-patterned films, we could obtain much larger AF domains with $>1 \mu m$ sizes (as seen in FIG. 34(b) which has a square structured by ion milled post-patterning). Measurements of various structure sizes, from 300 nm up to several micrometers, have shown consistently that the AF domain configuration in these samples is unaffected by the patterning. In the third patterning approach, employing FIB, the AF film was patterned by ion damaging rather than removal of the surrounding regions. In FIG. 34(c) the lines correspond to the damaged nonmagnetic LaFeO$_3$ material between the structures, i.e. we have found that the XMLD signal of these areas was reduced to zero. The bright and dark regions everywhere else, which are different AF domains of $>1 \mu m$ sizes, are unaffected by these lines. In addition to these structures, we also produced an array of periodic, nonmagnetic defects, often referred to as antidots, with different periods and sizes. The antidots shown have a period of $1 \mu m$ and size of $0.5 \mu m$ [FIG. 34(d)].

In addition to the FIB damaging approach, we tried to pattern the LaFeO$_3$ films using the FIB to remove the material (see the section 2.4.2). However, re-deposition of the removed material, which occurs in area close to the patterned areas (see FIG. 35), has made the PEEM measurements not feasible. The re-deposited material has

![FIG. 35. The PEEM images of different regions of thin LaFeO$_3$ film patterned by FIB with various doses. (a) Patterning by damaging the film and (b) patterning by the removal of the film. Re-deposition in the latter process is visible as a shadow around the FIBed structures, which reduces the underneath LaFeO$_3$ signal measured with the PEEM.](image)
reduced the XMLD signal of the underneath LaFeO$_3$ film to zero, which precluded the AF domain imaging. The comparison between the XMLD images of the LaFeO$_3$ film patterned by FIB using either damaging or removal is shown in FIG. 35. The AF domain configuration in these samples was unaffected by the patterning.

In order to exclude that the domain configuration after patterning is trapped in a local energy minimum, i.e. that there is an influence of the patterning which could be seen if the energy barrier were overcome, we heated the sample above the Néel temperature (565 K). In FIG. 36 it is shown how the XMLD contrast measured in a post-patterned film (left) vanishes at 600K (middle) and is completely recovered upon cooling to room temperature (right). Therefore the AF domain configuration remains unaffected even after heat treatment. In addition to the domain configuration, we have determined the AF spin orientation and it was found to be the same as that obtained for the initial continuous layers (see chapter 4.1.2 or Ref. 31). We measured four orientations of the AF domains; their spin axes exhibit four-fold in-plane symmetry and are canted 20° out-of-plane (see FIG. 37).

FIG. 36. XMLD images taken during heating-cooling cycle: at 300K in a post-patterned state (left), above Néel temperature at 600K (middle) and back at 300K after cooling down (right). The XMLD contrast disappears above $T_N$, and is completely recovered upon cooling to room temperature.
In summary, we found that the AF domain structure of thin LaFeO$_3$ films remained unaffected by the patterning. This is an intriguing observation in view of the reported results on patterned exchange bias systems, where many researchers attribute the observed effects to changes in the AF domain configuration (see details above in section 1.2.5).

4.4 Correlating AF and Crystallographic Domain Structure

With the aim to determine the effects responsible for the AF domain formation, we studied the correlation between the AF and crystallographic domain structure in thin LaFeO$_3$ films. A comparison of the orientation contrast image taken with a FSE-SEM (forward scattered electron-scanning electron microscopy) and XMLD image taken with the PEEM is given in FIG. 38. Similar studies were performed comparing PEEM and TEM images, but they could not measure the same sample position with both microscopes. With the help of the structures in one of the post-patterned LaFeO$_3$ films,
we were able to measure the orientation contrast image and XMLD image at the very same sample position. The orientation contrast imaging was carried out using an SEM with a quadrant ring detector. The sample was tilted by $70^\circ$ and the angular distribution of the forward scattered electrons was detected. Thus the image consists of the difference in the angular distribution of the forward scattered electrons as a function of the sample position.

The orientation contrast image shown in FIG. 38(a) consists of bright and dark regions which are reversed after a $90^\circ$ rotation around the surface normal. In the case of thin LaFeO$_3$ films grown on STO(001), the origin of the orientation contrast are twinned crystallographic domains with mutually perpendicular $c$-axis orientations, both lying in-plane (see above in section 4.1.2). In the XMLD image shown in FIG. 38(b), bright and dark regions represent two mutually perpendicular in-plane projections of the spin axis. Outlines in FIGs. 38(a) and 38(b) emphasize the fact that there is a one-to-one correlation between both images, providing experimental proof for the direct correspondence between the antiferromagnetic and the crystallographic domains in LaFeO$_3$.

To summarize, we studied the correlation between the AF and the crystalline domain structure. We found that there is one-to-one correlation between the both
structures. Therefore, we conclude that the AF domains in the thin LaFeO₃ films are of crystallographic origin.

4.5 Conclusions

We have shown that PEEM combined with the XMLD effect can be used to determine the orientation of individual antiferromagnetic domains. In LaFeO₃ thin films grown using PLD, four domain orientations were detected with a fourfold symmetry in the plane of the surface, each having their antiferromagnetic axis canted 20° out of the sample surface. This is in contrast to previous literature studies for LaFeO₃ grown with MBE, and we attribute this discrepancy to different strains in the films. Comparing our results with the literature, we observed that the XMLD can change its sign. We showed using multiplet calculations that this is because the sign depends on the orientation of the magnetization with respect to the crystalline axes. This reversal of the XMLD sign has significant implications for the interpretation of XMLD spectra. It is therefore essential that either the relative orientation of the AF axis with respect to the crystalline axes is known or, as reported here, that a technique is employed that allows the determination of the XMLD sign. This information is particularly important for the analysis of the coupling between ferromagnetic and antiferromagnetic films in exchange bias systems.

Furthermore, we showed that patterning of thin LaFeO₃ films does not influence the AF domain configuration, even when the patterns are of comparable size. In addition, we revealed by comparing FSE-SEM and PEEM images that the AF domains are directly coupled to the crystallographic structure. Therefore for thin LaFeO₃ films, the crystalline domains are the intrinsic origin of the AF domains, which explains why no change in the AF structure in patterned LaFeO₃ films was observed. Extrapolating our results to patterned exchange bias systems, our findings clearly show that for LaFeO₃, it
is not modifications to the AF domains resulting from the patterning that will drive any changes in the magnetization reversal. Quite the opposite; the crystalline domains will try to maintain the already existing antiferromagnetic domain structure. This magnetization reversal is rather determined by the domain configuration in the ferromagnet, which is not only governed by the stray field energy associated with the element size and shape, but also very importantly by the domain configuration of the antiferromagnet to which the ferromagnet is coupled. Therefore in order to understand the magnetization reversal, not only should the stray field energy associated with the ferromagnet be taken into account, but also the interaction with the existing AF domains. In order to determine the energetics of these complex multilayer systems, it is therefore important to comprehend the magnetic behavior of the individual layers. However, while the patterned ferromagnets are well understood not much is know about patterned antiferromagnets. Our work is an important step towards closing this gap.
Chapter 5
Exchange Bias Systems: Initial Results

The final aim of this thesis was to study the interplay of AF and FM domains in patterned exchange bias system. In particular, we chose to study the LaFeO$_3$/Co bilayer and its magnetic domain configuration using PEEM. The aim was to address specific questions related to the exchange bias such as the role of magnetic domains, the nature of the uncompensated moments in the AF layer and the effect of patterning in the exchange bias system. Therefore, it was necessary that the sample would contain both AF and FM domains with sizes which allowed them to be measured with the PEEM. We have tried various approaches to produce the LaFeO$_3$/Co bilayer. First, the AF layer was grown using PLD. Next, a cobalt layer was deposited on top either in situ by PLD or ex situ using dc sputtering or evaporation. The patterning was carried out using pre-patterned, post-patterned and lift-off approach (see details in section 2.4). Unfortunately, we were unable to grow bilayers where both the AF and FM domains could be resolved with PEEM. In a final attempt, we took the LaFeO$_3$ film used for the AF studies (see Chapter 4). Since the film was capped with one nanometre platinum, the capping layer had to be carefully removed with sputtering before a cobalt film could be grown in situ. The results presented here are very preliminary due to the lack of time available and various technical problems.
This chapter includes initial results obtained for LaFeO$_3$/Co bilayers. Measurements of uncompensated moments in the LaFeO$_3$ film on its own and the bilayer are shown. The findings lead to the conclusion that the origin of the uncompensated moments in LaFeO$_3$ are the individual uncompensated spins rather than a canting of the spins. Next, initial results on correlating the AF and the FM domain structure will be described. It is shown how after heating the sample the cobalt domain structure changes from the as-grown state and adapts to the AF layer. Finally, measurements in applied magnetic fields and in a remanence using PEEM will be presented indicating a coupling between the FM and the AF domains.

5.1 Experimental Details

As mentioned, the best LaFeO$_3$ film (with large AF domains and employed for the studies in Chapter 4) was capped with one nanometre of platinum. This capping layer prevented the growth of a cobalt layer directly on top. However, after sawing the sample into several pieces we were able to perform trials to carefully remove the platinum capping layer by sputtering. In order to control the platinum removal a truly surface sensitive technique was required. Therefore, we have utilized the ability of the PEEM to perform x-ray photoemission spectroscopy (XPS) studies. This can be done by tuning the photon energy to an energy slightly above the core level and measuring the XPS spectrum with the PEEM. Here we used photons with energy of 150 eV. The platinum surface content was determined by comparing platinum 4f electronic states with lanthanum 4d electronic states (see FIG. 39). Since the XPS signal originates from a few monolayers of the top surface, interpretation of the XPS data has to be done very carefully, e.g. a platinum free surface [red line in FIG. 39(a)] can be easily mistaken with a highly contaminated surface [black line in FIG. 39(b)]. In the latter case the platinum layer was covered by the surface contamination and the platinum 4f peak was not
detected, however, after a sputter-cleaning it appeared again in the XPS spectra [see red line in FIG. 39(b)]. The 4d peak of lanthanum is visible even in presence of the contamination, which is due to the strong kinetic energy dependence of the escape depths of photoelectrons. Finally, we have performed the sputter-removal of the platinum layer in a very careful way, i.e. relatively soft sputtering conditions (fluency ≈$10^{14}$ cm$^{-2}$) with an etch rate of roughly one nanometre per hour. After several sputtering cycles the Pt(4f)/La(4d) ratio decreased to zero [see FIG. 39(a)] and the platinum layer was removed.

FIG. 39. XPS studies of the sputter-cleaned surface: (a) removing the platinum layer and (b) removing the contamination.

FIG. 40. Overview XAS data for the absorption L$_{3,2}$-edges of iron and cobalt for the LaFeO$_3$/Co bilayer. (a) Deposition of cobalt in steps of increasing thickness. (b) The final LaFeO$_3$/Co bilayer.
Next, a cobalt layer was evaporated on top of the sputter-cleaned LaFeO$_3$ film \textit{in situ} in the preparation chamber of the PEEM system. The cobalt was deposited in steps of increasing thickness until FM domains were visible in the cobalt layer. As the cobalt thickness increased, it was found that the LaFeO$_3$ signal decreased [see FIG. 40(a)]. According to the evaporator calibration and in agreement with the XAS spectra, the cobalt film was roughly two nanometre-thick [see FIG. 40(b)].

5.2 Results

5.2.1 Uncompensated Moments in LaFeO$_3$

The existence and the intrinsic origin of uncompensated magnetic moments in AF films are still open questions. They can be either a result of a canting of the AF spins or individual uncompensated spins in the AF layer. In either case, they are expected to be the key in the understanding of the exchange bias effect. In addition, the uncompensated spins are either pinned or can freely rotate. It should be possible to detect the pinned spins in the as-grown state assuming that they are pointing in the same direction producing signal of size detectable by PEEM. However, the free uncompensated spins are expected to be randomly oriented and so cannot be measured in as-grown state with the limited resolution of the PEEM. However, measurements in an applied magnetic field or low temperatures should reveal their existence. Here, we will focus on the possibility to measure the uncompensated moments with PEEM.

Assuming that uncompensated moments are present in the LaFeO$_3$ film, it should be possible to detect them using the combination of the PEEM and the XMCD effect (see the section 2.5.3). This can be done by collecting an XMCD image at the metallic iron absorption L$_{3,2}$-edge [denoted as A peak in FIG. 26(b)], assuming that uncompensated moments are originating from the metallic iron of the LaFeO$_3$ layer.$^{102}$
Chapter 5  Exchange Bias Systems: Initial Results

The uncompensated moments in the AF materials are a product of either a canting of the AF spins or the existence of individual uncompensated spins. Assuming certain AF spin axis orientation one can estimate an expected XMCD signal for the two cases. The model XMLD contrast together with the corresponding XMCD contrast for the case of the canted AF spins and the uncompensated spins is shown in FIG. 41(a) and (b), respectively. In the case of canted antiferromagnet bright (dark) AF regions go with bright or dark (grey) XMCD regions [see FIG. 41(a)], while for the antiferromagnet with individual uncompensated spins it is reversed dark (bright) AF regions go with bright or dark (grey) XMCD regions [see FIG. 41(b)].

We have made several trials to measure the uncompensated moments in bare LaFeO$_3$ films. Since any signal would be very small it is important to obtain a good signal to noise ratio by using long exposure times. In order to correct for the sample drift.
we used one of our post-patterned LaFeO$_3$ films to align a sequence of the images from the same sample position, which significantly improved signal-to-noise ration of the XMCD image. Finally, we have detected a very small XMCD contrast correlated with the XMLD image of the AF domains in the bare LaFeO$_3$ film. The XMLD and the XMCD image are shown in FIG. 42(a) and 42(b), respectively. The XMCD contrast is very weak and any conclusions are rather speculative. There seems to be a one-to-one correlation of the FM domains and the domains of the uncompensated moments. Furthermore the correlation of the contrast appears to correspond to the existence of the case of individual uncompensated spins: dark (bright) AF regions go with bright or dark (grey) XMCD regions.

FIG. 42. PEEM images of a thin LaFeO$_3$ film measured using (a) XMLD and (b) XMCD at the Fe-L$_{3,2}$ absorption edge. However, the uncompensated magnetic moments measured with the XMCD image could not be detected by local spectroscopic studies, which would be sufficient confirmation of their existence. This could be due to very small signal to noise ratio of the measured XMCD signal for the LaFeO$_3$. 
In addition, we have measured the uncompensated moments in the LaFeO$_3$ layer after deposition of the cobalt layer on top. The XMLD image of the AF domains in the LaFeO$_3$, the XMCD image of the uncompensated moments in the LaFeO$_3$ and the XMCD image of the FM domains in the cobalt are shown in FIGs. 43(a), 43(b) and 43(c), respectively. The Fe-XMCD signal in the bilayer is a few orders of magnitude bigger compare to the bare LaFeO$_3$, which means that the number of uncompensated moments is a few orders of magnitude larger compare to the case of the bare LaFeO$_3$. In addition, the Fe-XCMD image is one-to-one correlated with the Co-XMCD image showing a parallel coupling between the uncompensated moments of the LaFeO$_3$ and the FM moments of the cobalt. Interestingly, the AF and the FM domains are not correlated in the as-grown state.

Although, the quality of the measured Fe-XMCD signal for both the single LaFeO$_3$ layer and the LaFeO$_3$/Co bilayer did not allow any final conclusion, our measurements can be explained as follows. Firstly, the correlation between the Fe-XMCD signal and
the AF domains in the single LaFeO\textsubscript{3} layer is similar to the one modelled for the individual uncompensated spins [see FIG. 41(b)]. Secondly, after the cobalt deposition the amount of the uncompensated moments increased by a few orders of magnitude. This indicates that in the case of the LaFeO\textsubscript{3} on its own only the pinned uncompensated spins were measured, since the free uncompensated spins are either not present in the bare LaFeO\textsubscript{3} or are pointing in random directions and do not contribute to the XMCD signal. The addition of the cobalt layer caused either creation of the free uncompensated spins or aligning of the existing free uncompensated spins, which cannot be distinguished in our measurements. The observed Fe-XMCD contrast not only indicates the existence of pinned and free uncompensated moments, but there are two additional pieces of information:

(a) The fact that the uncompensated moments form domains, with the spins pointing in one direction, can explain the exchange bias field.

(b) The alignment of the free uncompensated moments with the cobalt domains indicates that they are susceptible to field and hence can lead to increased coercivity of the exchange bias system.

5.2.2 Antiferro-/Ferromagnetic Coupling and Domain Correlation in LaFeO\textsubscript{3}/Co

One of the aims of this thesis was to determine whether there is correlation between AF and FM domains in LaFeO\textsubscript{3}/Co bilayers. In this section initial results of the correlation studies will be reported. We found that AF domains of the LaFeO\textsubscript{3} film and FM domains of the cobalt layer are not correlated in the as-grown state, see images in FIG. 44(a) and (d), respectively (measured at room temperature). After heating the sample the FM domain configuration of the cobalt layer suddenly changed at \(\approx 400\) K. On increasing the temperature above 400 K the new FM domain configuration in the cobalt
Chapter 5  Exchange Bias Systems: Initial Results

layer did not change further, even as the temperature was increased above the Néel temperature [see FIG. 44(e)] and after cooling down to room temperature [see FIG. 44(f)] no further changes of the FM domain pattern were observed. The final state of the cobalt domain configuration seems to be correlated with the AF domains of the LaFeO$_3$ layer [compare images shown in FIGs. 44(c) and 44(f)]. The quality of these images (FIG. 44) is low due to relatively large field of view and therefore low pixel resolution.

Further investigations were not possible, because the sample broke in the vacuum chamber. However, some speculation is still possible. The cobalt layer was grown on top of the sputtered surface of the LaFeO$_3$. In general, ion bombardment of the surface can lead to changes in the chemical composition, increased roughness or ion implantation. Hence, the LaFeO$_3$/Co interface could be far from ideal resulting in lack of

---

**FIG. 44.** PEEM images of continuous LaFeO$_3$/Co bilayer taken during a heating-cooling cycle: at 300 K in the as-grown state (left column), above the Néel temperature at 590 K (middle column) and back at 300 K after cooling down (right column). The XMLD images of the AF domains in LaFeO$_3$ (upper row) and the XMCD images of the cobalt FM domains (lower row) are shown. In the as-grown state, the FM domains of cobalt seem not to be correlated with the AF domains of LaFeO$_3$ [compare images (a) and (d)]. During heating the cobalt, the XMCD contrast evolves into a different domain state (compare images (d) and (e)). Above $T_N$, the XMLD contrast of the LaFeO$_3$ disappears (b) and is fully recovered after cooling down to room temperature [compare images (a) and (c)]. The FM domains of cobalt in their changed state appear to be correlated with the LaFeO$_3$ domains [compare images (c) and (f)]. Any further investigations were impossible due to technical problems.
coupling between the AF and the FM layer (as observed). The change in the FM domain pattern of cobalt occurred after heating was started. After the new FM domain state was reached it was not changing thereafter. This suggests that the FM domain structure either adapts to the surface roughness or couples to the AF layer, which in either case would result in a new FM domain structure. Thus, more detailed experiments are required in order to determine the exact cause of the observed FM domain structure change.

Finally, an intriguing question concerning the magnetic domain structure of the LaFeO$_3$/Co bilayers is whether the AF domain structure is changing as a response to adjacent ferromagnet, as has been reported for NiO/Co.$^{34}$ Ideal, we would have determined the AF spin axis orientation in the LaFeO$_3$ before and after depositing the cobalt layer (see chapter 4.1). However, further investigations of the LaFeO$_3$/Co bilayer were impossible due to technical problems. Nevertheless, we utilized patterned regions of the LaFeO$_3$ to correlate the AF domain pattern before and after the cobalt deposition (see FIGs. 45(a) and 45(b), respectively). We found that the AF domain pattern stays the same following the cobalt deposition. However, a full determination of the spin structure is required before we can say for certain that there is no effect on the AF domain structure.

FIG. 45. XMLD images of the patterned thin LaFeO$_3$ films measured with the $E$-vector oriented in-plane. The same sample position was imaged before (a) and after (b) cobalt deposition. As it is visible, by comparing both images, the AF domain patterned of LaFeO$_3$ remained the same and did not respond to the presence of the FM cobalt layer.
In summary, we found that the FM and the AF domains are not correlated in the as-grown LaFeO$_3$/Co bilayer. However, the FM domains structure changed when heating the FM film to $\approx 400$ K. However, at this stage we can not say whether this is due to roughness effects or a development of coupling with the LaFeO$_3$ layer. In addition, the AF domain pattern before and after the cobalt deposition did not change.

### 5.2.3 Measurements in Applied Magnetic Field

In order to directly observe the switching processes spatially resolved measurements in an applied magnetic field are required. The PEEM technique is strongly limited, because the slow electrons emitted from the sample would be deflected by the magnetic field. Nevertheless, we have developed a special sample holder with a small magnetic coil, which allowed us to measure in applied magnetic fields up to 100 Oe and in remanence up to 300 Oe. Measurements in remanence can be used to study the change in the FM domain configuration after applying a magnetic field in specific systems (e.g. see antidot studies by Heyderman et al.$^{90}$).

Here, we report on initial measurements of a LaFeO$_3$/Co bilayer carried out in applied magnetic field. A two nanometre-thick cobalt layer was grown ex situ on top of the PLD grown LaFeO$_3$ film. In order to prevent oxidation, the LaFeO$_3$/Co bilayer was capped with one nanometre-thick platinum layer. The LaFeO$_3$ film was of a low quality, i.e. the spectroscopic studies revealed that it was antiferromagnetic but the sizes of the AF domains were below the spatial resolution of the PEEM and hence they could not be resolved. However, a strong magnetic contrast was observed in the cobalt layer and it was possible to image the FM domains of the cobalt film. The sample was mounted on the magnetic sample holder and series of images in an applied magnetic field and at remanence following application of the magnetic field were taken (see FIG. 46). We have found that individual FM domains in the cobalt layer were switching. The fact that the FM domains are stationary and small implies that they are coupled to the AF
domains of the LaFeO\textsubscript{3} layer. Since, the AF domains were much smaller than the cobalt domains an individual cobalt domain would have to be coupled to a group of AF domains. However, the observed FM domain structure can originate from effect of surface roughness on the FM domain structure (see chapter 3.3.3). Although the effect is similar, it is not surface roughness which causes the decoupling of the small Co domains. It also can be seen in chapter 3.3.3, that surface roughness generates a very narrow domain size distribution while for LaFeO\textsubscript{3}/Co we observe a broad size distribution of the Co domains, which originates from the AF/FM coupling.

FIG. 46. XMCD images of the cobalt FM domain structure in the Co/LaFeO\textsubscript{3} bilayer as a function of the magnetic field. The images were measured in the applied magnetic field (b-c) and in the remanence (e-g). Only the FM cobalt domains could be measured. Although the LaFeO\textsubscript{3} was antiferromagnetic, the AF domains were to small to be measured with PEEM (probably below 50 nm in lateral size). The images were taken in: (a) as-grown state, (b) 0.2 Oe, (c) 68 Oe, (d) 140 Oe, (e) 200 Oe, (f) 300 Oe and (g) -300 Oe. Individual cobalt domains are switching while applying a higher magnetic field (see outlines). This is an indication for coupling between the cobalt and LaFeO\textsubscript{3} layer.
To summarize, we have carried out measurements in applied magnetic fields and in remanence using PEEM. Furthermore, we measured the cobalt domain structure in the LaFeO$_3$/Co bilayer and found that they were coupled to the AF domains. However, the AF domains were too small to image directly with the PEEM.

5.3 Conclusions

We have obtained initial results on the LaFeO$_3$/Co bilayer. However, further investigations are necessary to clarify our interpretation. We found that in the as-grown state the FM domains of the cobalt layer are not correlated with the AF domains of the LaFeO$_3$ film. Furthermore, we found that the cobalt domain pattern evolved immediately after heating the sample and later on was stable even above the Néel temperature. In addition, existence of the uncompensated moments in the LaFeO$_3$ layer was found in the as-grown state. The uncompensated moments are one-to-one correlated with the FM moments of the cobalt layer and are coupled parallel. In addition, we found an indication of uncompensated moments in the single LaFeO$_3$ films. Differences in the size of the Fe-XMCD signal from the single LaFeO$_3$ and the LaFeO$_3$/Co bilayer indicates that in the case of the AF layer alone only the pinned uncompensated spins were measured, whereas in the case of the bilayer, free uncompensated spins were aligned by the adjacent ferromagnet and as a consequence contributed to the Fe-XMCD signal. Next, we have found that the LaFeO$_3$ domain pattern is not influenced by deposition of the cobalt layer. Finally, we have reported on initial results on direct observations of the switching behaviour of the cobalt domains in the LaFeO$_3$/Co bilayer. The results indicate that the FM domains of the cobalt are coupled to the AF domains, even if the latter were not large enough to be imaged with the PEEM.
Conclusions

The ultimate motivation of this thesis was to understand the role of magnetic domains in patterned exchange bias systems. In order to achieve this ambitious aim we have focused our endeavours on LaFeO$_3$/Co. The magnetic domain configuration was studied using a combination of PEEM and X-ray magnetic dichroism (i.e. XMCD and XMLD). In addition, multiple experimental and modelling techniques were involved in the process of sample preparation and evaluation of the obtained results. In order to disentangle the complex interplay of the properties, in particular the domain formation in the ferromagnet and the antiferromagnet in an exchange bias system, the thesis was divided into three main tracks. First, the magnetic domain formation in the ferromagnet and in the antiferromagnet on their own was investigated. Finally, the role of the magnetic domains in the exchange bias multilayer of LaFeO$_3$/Co was examined. Continuous and patterned systems were investigated in all cases and in the studies of the ferromagnet and the antiferromagnet, we were able to answer some intriguing and important questions. In the case of the exchange bias bilayers, promising preliminary results were achieved and gave first indications of the importance of the understanding the domain formation of the FM and the AF film on their own in order to reveal the effects due to the coupling. The information given in this thesis is summarized below and can be put in a nutshell as follows:
Conclusions

- Thickness and roughness dependence of the FM domain structure in cobalt and Permalloy continuous films and patterned elements
- Determination of the spin structure of individual AF domains in thin LaFeO$_3$ films
- Dependence of the sign of the XMLD effect on the magnetocrystalline anisotropy in thin LaFeO$_3$ films
- No influence of patterning on the AF domain structure in thin LaFeO$_3$ films
- Revealing the crystallographic origin of AF domains in thin LaFeO$_3$ films
- Progression of the uncompensated moments from the LaFeO$_3$ film on its own to an exchange bias LaFeO$_3$/Co bilayer

The FM domain configuration was investigated in continuous and patterned films of cobalt and Permalloy. We have gained knowledge about how various parameters such as thickness, substrate roughness and patterning influence the FM domain formation. This work highlights the importance of local magnetic effects in the determination of the final magnetic domain states in magnetic thin films and structures. This information is very useful for a complete understanding of the results obtained on the exchange bias systems. For example it enabled us to distinguish whether the Co domain structure was due to surface roughness or due to coupling to the antiferromagnet.

The individual AF domains in the thin LaFeO$_3$ films were examined using a newly developed and powerful approach combining the PEEM and the XMLD effect. We found four orientations of the AF domains having an in-plane fourfold symmetry of the spin axis, which are tilted $20^\circ$ out of the surface plane. Remarkably, we found that the XMLD sign depends on the orientation of the magnetization with respect to the crystalline axes. Furthermore, we found that the AF domain structure in thin LaFeO$_3$ films remains unaffected by the patterning, which we could explain by the crystalline origin of the AF domains. Our results are very important for understanding of the exchange bias effect. Firstly, our newly developed method to study the individual AF domains is very useful for tracking changes in the AF domain configuration in the exchange bias systems. Secondly, determination of the XMLD sign is essential for answering the question of whether the AF-FM coupling is parallel or perpendicular. This is because without this
knowledge it is not possible to distinguish parallel coupling with a positive (negative) sign and perpendicular coupling with a negative (positive) sign, i.e. this would give the same contrast. While the sign of the XMCD effect is well established, we showed here for the first time how to determine this sign for the XMLD effect experimentally and that the sign can change even for the same system. Finally, extrapolating our results to patterned exchange bias systems, our findings clearly show that for LaFeO$_3$, it is not modifications to the AF domains resulting from the patterning that will drive any changes in the magnetization reversal. Quite the opposite; the crystalline domains will try to maintain the already existing antiferromagnetic domain structure. Therefore in order to understand the magnetization reversal, not only should the stray field energy associated with the ferromagnet be taken into account, but also the interaction with the existing AF domains.

The magnetic domain structure was examined in the LaFeO$_3$/Co bilayer. Unfortunately, due to various technical reasons these studies are very preliminary but a few results could be obtained. The uncompensated moments in LaFeO$_3$ were measured both for LaFeO$_3$ without Co and with Co on top. Comparing the AF domain structure with the distribution of the uncompensated moments we conclude that these moments are not due to a spin canting. In addition, we found first indications for domains of pinned and free uncompensated moments in LaFeO$_3$ which are coupled parallel to the FM moments of the cobalt. Interestingly, we found that the FM domain structure in the cobalt layer can be in a metastable state after evaporation and that a Co domain can be coupled to several AF domains. These are starting points for further studies and in addition, a key accomplishment was the ability to perform PEEM measurements on the bilayer in an applied magnetic field.

Finally, further studies of the exchange bias effect can be carried out using the information supplied in this thesis. Building on the initial interesting results on the LaFeO$_3$/Co bilayers, suggestions for the continuation of these studies are as follows. First, the measurements of the uncompensated moments of the LaFeO$_3$ films should be confirmed by magnetometry measurements, at best in applied magnetic fields and/or at low temperatures. Secondly, studies of the AF/FM domain correlation and coupling and
105

Conclusions

how they change from the as-grown state on various parameters such as temperature or an applied magnetic field can supply very important information shedding light on the mystery of the exchange bias effect. Thirdly, detailed studies of the patterned LaFeO$_3$/Co would be very interesting, since the influence on the exchange bias effect from different patterned elements can be studied. These studies can answer many questions related to the exchange bias effect such as the role of magnetic domains, the origin of the uncompensated moments and understanding of the effects observed in patterned exchange bias multilayers.

While we are still far away from a complete comprehension of the mechanisms acting in a patterned exchange bias system, we have improved our understanding of the magnetic behaviour of the individual layers. This will help to determine the energetics of these complex multilayer systems, since it is important to comprehend the magnetic behavior of the individual layers. While the patterned ferromagnets are well understood not much is know about patterned antiferromagnets. This work is an important step towards closing this gap.
Appendix A

Fitting procedure for Spin Axis Determination

A code used for fitting the linear polarization angle dependence of the XMLD signal (see chapter 4.1.2) was written in the C++ language using ROOT package. The code consists of three files:

1) Makefile – a file used to compile the code
2) fit_function.h – a library file containing a definition of the fitting function
3) linrot_fit_full.cxx – a main file containing the main code

The content of each file can be found below. The code was never optimized and it can take a while to understand it fully. However, the main idea is that a single class was made containing all needed variables and functions for fitting, testing and simulating the linear polarization angle dependence of the XMLD signal using Eqs. 3 and 4.

Content of the Makefile:

```
ROOTCFLAGS    = $(shell root-config --cflags)
ROOTLIBS      = $(shell root-config --libs)
ROOTGLIBS     = $(shell root-config --glibs)

linrot_fit_full: linrot_fit_full.cxx
    g++  -o linrot_fit_full linrot_fit_full.cxx $(ROOTCFLAGS) $(ROOTLIBS) $(ROOTGLIBS)
```

Content of the fit_function.h:

```
// :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
// /        S T A R T
//----------------------------------------------------------------------------
double r2d(double rad) //radians to degrees
{
```
Appendix A Fitting procedure for Spin Axis Determination

    return rad*TMath::RadToDeg();
}  
//----------------------------------------------------------------------------

double d2r(double rad) // degrees to radians
{
    return rad/TMath::RadToDeg();
}

double calc_angle(double T1, double P1, double T2, double P2)
{
    double x1, x2, y1, y2, z1, z2, angle,tmp ;
    x1 = sin(d2r(T1))*cos(d2r(P1)) ;
    y1 = sin(d2r(T1))*sin(d2r(P1)) ;
    z1 = cos(d2r(T1)) ;
    x2 = sin(d2r(T2))*cos(d2r(P2)) ;
    y2 = sin(d2r(T2))*sin(d2r(P2)) ;
    z2 = cos(d2r(T2)) ;
    tmp = x1*x2 + y1*y2 + z1*z2 ;
    if(tmp < 0) tmp = -1*tmp ;
    angle = r2d(acos(tmp));
    return angle ;
}

double Intensity_G0(double *t,double *p) //y=0
{
    double A, B, T, F, x, a16, cos_tmp ;
    x = d2r(t[0]) ;
    T=d2r(p[0]); F=d2r(p[1]); A = p[2] ; B = p[3] ; a16 = d2r(16) ;
    cos_tmp = sin(a16)*cos(x)*sin(T)*cos(F)+sin(x)*sin(T)*sin(F)+cos(a16)*cos(x)*cos(T) ;
    return A + B*cos_tmp*cos_tmp ;
}

double Intensity_G90(double *t,double *p) //y=90
{
    double A, B, T, F, x, a16, cos_tmp ;
    x = d2r(t[0]) ;
    T=d2r(p[0]); F=d2r(p[1]); A = p[2] ; B = p[3] ; a16 = d2r(16) ;
    cos_tmp = sin(a16)*cos(x)*sin(T)*cos(F)-sin(x)*sin(T)*sin(F)+cos(a16)*cos(x)*cos(T) ;
    return A + B*cos_tmp*cos_tmp ;
}
double Intensity_mG90(double *t, double *p) //y=90
{
    double A, B, T, F, x, a16, cos_tmp;
    x = d2r(t[0]);
    T = d2r(p[0]);
    F = d2r(p[1]);
    A = p[2];
    B = p[3];
    a16 = d2r(16);
    
    cos_tmp = -sin(x) * sin(T) * cos(F) + sin(a16) * cos(x) * sin(T) * sin(F) +
                cos(a16) * cos(x) * cos(T);
    return A + B * cos_tmp * cos_tmp;
}

double Intensity_diff(double *t, double *p)
{
    return Intensity_G90(t, p) - Intensity_mG90(t, p);
}

Content of the linrot_fit_full.cxx:
#include <stdlib.h>
#include "Riostream.h"
#include <TROOT.h>
#include <TApplication.h>
#include <TCanvas.h>
#include <TH1.h>
#include <TH2.h>
#include <TH3.h>
#include <TGraph.h>
#include <TGraph2D.h>
#include <TStyle.h>
#include <TGraphErrors.h>
#include <TF1.h>
#include <TStyle.h>
#include <TAxis3D.h>
#include <TPad.h>
#include <TLatex.h>
#include "fit_function.h"
// #include "filename.h"

#define z_x z1
char *Z_name = "D1";
int SA2 = -90; // z1 z2 => 90 ; z3 z4 => 0
double dAngT = 1; // for angles Theta
double dAngP = 1; // for angles Phi
double dCon = 2000; // for constants A B

double temp;

TROOT api();

// D1 D2 => 90 ; D3 D4 => 0

void simulate(char *file);
void draw_and_fit(char *file);
void draw_slices(int padnum, TPad *pp, int value, double *data, char * name);
void draw_fit_function(int value, int padnum, int dr);
void fit_slices(int value, int padnum);
void read_data(char *file);
void make_pads_sets(TPad *p, int set = 3);
Appendix A  
Fitting procedure for Spin Axis Determination

```cpp
pad->Draw();
fitting_procedure::make_pads_sets(pad,13);

j++ ; num++ ;
fitting_procedure::draw_fit_function(1000,j,0);

j++ ; num++ ;
fitting_procedure::draw_fit_function(1000,j,0);

j++ ; num++ ;
fitting_procedure::draw_fit_function(1000,j,0);

j++ ; num++ ;
fitting_procedure::draw_fit_function(1000,j,0);

j=0 ;
j++ ; num++ ;
fitting_procedure::draw_fit_function(90,j+4,1);

j++ ; num++ ;
fitting_procedure::draw_fit_function(90,j+4,1);

j++ ; num++ ;
fitting_procedure::draw_fit_function(90,j+4,1);

j++ ; num++ ;
fitting_procedure::draw_fit_function(90,j+4,1);

j=0 ;
j++ ; num++ ;
fitting_procedure::draw_fit_function(-90,j+8,2);

j++ ; num++ ;
fitting_procedure::draw_fit_function(-90,j+8,2);

j++ ; num++ ;
fitting_procedure::draw_fit_function(-90,j+8,2);

j++ ; num++ ;
fitting_procedure::draw_fit_function(-90,j+8,2);
}

//-------------------------------------------------------------------------------
void fitting_procedure::draw_and_fit(char *file)
{
    j = 0 ; num = 0;
    fitting_procedure::read_data(file);

    c1 = new TCanvas("c1","Main",0,0,1000,800);
    c1->SetFillColor(10);    // color white
    pad = new TPad("pad","",0,0,1,1);
    pad->Divide(2,2);
    pad->Draw();
    fitting_procedure::make_pads_sets(pad,5);
```
j++;
fitting_procedure::draw_slices(j,pad,SA2,z1,"D1");
fitting_procedure::fit_slices(SA2,j);

j++;
fitting_procedure::draw_slices(j,pad,SA2,z2,"D2");
fitting_procedure::fit_slices(SA2,j);

j++;
fitting_procedure::draw_slices(j,pad,0,z3,"D3");
fitting_procedure::fit_slices(0,j);

j++;
fitting_procedure::draw_slices(j,pad,0,z4,"D4");
fitting_procedure::fit_slices(0,j);

// Post-fitting summary:
ofstream out;
out.open("out_parameters.txt");
for(int a = 0 ; a < 16 ; a++)
{
    out << par_out[a] << endl ;
}
out.close() ;
cout << "nFit Results were saved in file <out_parameters.txt> !!!\n";
double T1,T2,P1,P2,T3,P3,T4,P4;
T1 = par_out[0] ; P1 = par_out[1] ;
T3 = par_out[8] ; P3 = par_out[9] ;
cout << "tAngle between domains :\n" ;
cout << "\tD1 <-> D2 : " << calc_angle(T1,P1,T2,P2) << endl ;
cout << "\tD1 <-> D3 : " << calc_angle(T1,P1,T3,P3) << endl ;
cout << "\tD1 <-> D4 : " << calc_angle(T1,P1,T4,P4) << endl ;
cout << "\tD2 <-> D3 : " << calc_angle(T2,P2,T3,P3) << endl ;
cout << "\tD2 <-> D4 : " << calc_angle(T2,P2,T4,P4) << endl ;
cout << "\tD3 <-> D4 : " << calc_angle(T3,P3,T4,P4) << endl ;
cout << endl ;
}
//------------------------------------------------------------------
void fitting_procedure::draw_slices(int padnum, TPad *pp, int value, double * data, char * name)
{
    pp->cd(padnum);
    char *tmp, *xtitle ;

}
Appendix A    Fitting procedure for Spin Axis Determination

gr[padnum] = new TGraph();
int m = 0;
xtitle = "Liner Polarization Angle [deg]";
tmp = "Sample Angle cut at";

    for(int k = 0 ; k < i ; k++)
    {
        if(x[k]==value)  { gr[padnum]->SetPoint(m++,y[k],data[k]); }
    }

gr[padnum]->GetHistogram()->SetXTitle(xtitle);
gr[padnum]->GetHistogram()->SetYTitle("Intensity [a.u.]");
gr[padnum]->GetYaxis()->SetTitleOffset(2);

char tekst[30] ;
sprintf(tekst, "%s %d for %s", tmp, int(value),name) ;
gr[padnum]->SetTitle(tekst);
gr[padnum]->SetMarkerStyle(3);
gr[padnum]->Draw("AP");

void fitting_procedure::draw_fit_function(int value,int padnum, int dr)
{
    par[0] = par_all[0+(j-1)*4] ;

    pad->cd(padnum);
    char TFun[10];
    // gr[padnum] = new TGraph();
    sprintf(TFun, "fun%d", num) ;
    if(value == 0) { fun[num] = new TF1(TFun,Intensity_G0,0,90,4); }
    if(value == 90) { fun[num] = new TF1(TFun,Intensity_G90,0,90,4); }
    if(value == -90) { fun[num] = new TF1(TFun,Intensity_mG90,0,90,4); }
    if(value == 1000) { fun[num] = new TF1(TFun,Intensity_diff,0,90,4); }

    fun[num]->SetParameters(par);
    fun[num]->SetParNames("Theta","Phi","A","B");

    switch(dr) {
        case 0 : fun[num]->Draw() ; fun[num]-> SetLineColor(2) ; break ;
        case 1 : fun[num]->Draw() ; fun[num]-> SetLineColor(3) ; break ;
        case 2 : fun[num]->Draw() ; fun[num]-> SetLineColor(4) ; break ;
    }
Appendix A  Fitting procedure for Spin Axis Determination

} // gr[padnum]->Fit(TFun,"r");

} //-------------------------------------------------------------------------------------------------
Appendix A  Fitting procedure for Spin Axis Determination

```cpp
par_out[3+(j-1)*4] = fun[j]->GetParameter(3);
}

void fitting_procedure::read_data(char *file)
{
  i=0;
  ifstream in3;
  in3.open("parameters.txt");
  while(1)
  {
    if(!in3.good()) break;
  }
  in3.close();

  ifstream in;
  in.open(file);
  while(1)
  {
    in>>temp>>temp>>temp>>temp>>temp>>temp; // 6 columns
    if(!in.good()) break;
    i++;
  }
  in.close();
  x = new double[i+1];
  y = new double[i+1];
  z1 = new double[i+1];
  z2 = new double[i+1];
  z3 = new double[i+1];
  z4 = new double[i+1];

  i=0;
  ifstream in2;
  in2.open(file);
  while(1)
  {
    in2>>x[i]>>y[i]>>z1[i]>>z2[i]>>z3[i]>>z4[i]; // 6 columns
    z1[i]=double(z1[i]/1);
    z2[i]=double(z2[i]/1);
    z3[i]=double(z3[i]/1);
    z4[i]=double(z4[i]/1);
  }
```
if(!in2.good()) break;
    i++;
}
in2.close();
}

void fitting_procedure::make_pads_sets(TPad *p, int set)
{
    for(int a=1; a<set; a++)
    {
        p->cd(a);
        gPad->SetFillColor(10);
        gPad->SetLeftMargin(0.15);
        gPad->SetTopMargin(0.08);
        gPad->SetBottomMargin(0.12);
        gPad->SetBorderMode(0);
    }
}

int main(int argc, char **argv)
{
    if(argc == 1)
    {
        cout << "Give filename to read as parameter!!!\n" ;
        exit(0) ;
    }
    char *tmp ;
    tmp = argv[1] ;
    fitting_procedure a ;

    // ROOT part :
    TApplication theApp("App",&argc,argv);
    gROOT->Reset();
    a.draw_and_fit(tmp) ;
    a.simulate(tmp) ;
    theApp.Run(); // running till Exit Root
Appendix A Fitting procedure for Spin Axis Determination

    return 0;
}

//------------------------------------------------------------------
//------------------------------------------------------------------
//------------------------------------------------------------------
Bibliography

Bibliography


Bibliography


64 P. R. Willmott and J. R. Huber, Rev. Mod. Phys. 72, 315 (2000).


66 SrTiO$_3$ substrates: orientation (001); tolerance <0.5$^\circ$; edge parallel to (010); one side epipolished; size: 10×10 mm; thickness: 0.5 mm.; manufactured by CrysTec GmbH (www.crystec.de).


95 Private communication with G. van der Laan (to be published).

96 R. Baierlein, Thermal Physics (Chapter 16.4, Cambriuge University Press, 1999).

97 The ROOT package is based on the C++ language and can be downloaded from the website: http://root.cern.ch/


Acknowledgments

First of all, I would like to acknowledge tremendous work of Laura Heyderman – my unofficial supervisor from Laboratory for Micro- and Nanotechnology at Paul Scherrer Institut. All I know in the field of patterning and structuring came directly from her. In addition, I have inherited from her the way of organizing and solving problems and much more small things making the work efficient. Her great ability to teach in connection with inexhaustible patience made these improvements possible. Her contribution to the quality of my English is unquestionable and priceless. Finally, Laura’s approach is a proper combination of humanity, professional and commanding skills resulting in an excellent environment for a co-worker or an employee of her. It was a great pleasure to work with Laura. I am grateful to Laura for all the patience and hard work she has done in order to make this thesis possible.

The major part of the knowledge I have gained during this thesis came from Frithjof Nolting – my official supervisor from Swiss Light Source at Paul Scherrer Institut. I am very grateful for all time that we have spent together. Frithjof taught me everything what he could and I appreciate it a lot. I am impressed by his ultimate patience and devotion for excellence, which is combined with a very nice character. Altogether, all these years spent with him were very enriching from both personal and professional point of view. I am grateful to Frithjof for all that hard work he has done while working with me and trying to understand my way of thinking and being.
Acknowledgments

I would like to acknowledge the input from Danilo Pescia – my official supervisor at Eidgenössische Technische Hochschule Zürich. We were always in touch and even if he did not interfere much I knew I always could come and discuss or ask him for help. I believe that this is the best what a student could have from the supervisor.

I would like to thank the following people from Swiss Light Source at Paul Scherrer Institut:

Jan Rothe, Blagoj Sarafimov and Fritz Dubi for their technical support at the SLS and other occasions.

Urs Staub for interesting discussions and advices with some scientific problems.

Christoph Quitmann for being such as nice beamline boss and official supervisor in the beginning of my thesis.

Jörg Raabe and Arantxa Fraile-Rodriguez for their help with solving PEEM problems.

Phillip Willmott for his support in the PLD and allowing me to use one of his PLD chambers – NYAH. Without his setup sample production would be even harder that it was.

Roger Herger and Christian Schlepuetz for supporting me with the NYAH PLD chamber during many hours of technical problems.

I would like to thank the following people from Laboratory for Micro- and Nanotechnology at Paul Scherrer Institut:

Anja Weber for a lot of work with evaporation of aluminum and chromium layers in the Clean Room facility at the LMN and for being such a nice office mate.

Eugen Deckardt, Fredy Glaus, Bianca Haas, Jana Lehman and Korad Vogelsang for their technical assistance at the LMN.

Stefan Stutz for his efforts with polishing single crystals.

Rolf Scheldorfer for AFM measurements carried out on my various samples.

Elisabeth Müller for TEM measurements carried out on my samples.

I would like to thank the following people from Laboratory for Neutron Scattering at...
Acknowledgments

Paul Scherrer Institut:

Michael Horisberger for His tremendous work on sputter-deposition of cobalt and platinum layers in various combinations. Without His exact and efficient work it would not be possible to fight with charging problems.

Kazimierz Conder and Ekaterina Pomjakushina for the annealing in oxygen carried out on my various samples and for the growth of the single crystal of LaFeO₃.

Hans Grimmer for his support with XRD measurements and allowing me to use his powder diffractometer – Seifert.

I would like to thank Max Döbeli from ETH Zürich for the RBS measurements carried out on my samples.

I am grateful to Karsten Kunze from ETH Zürich for the FSE-SEM measurements carried out on my samples and for fruitful discussions, which resulted with a very nice discovery of the origin of AF domains in thin LaFeO₃ films.

I would like to thank Gerrit van der Laan from CCLRC Daresbury from for the fruitful discussions and his contribution in understanding of the XMLD and hence explanation on the mysterious experimental finding concerning the XMLD sign.

I am grateful to Andreas Scholl ALS Berkeley for explaining how to fit the temperature dependence of the XMLD signal in LaFeO₃.

I would like to thank Michael Krüger from ETH Zürich (currently at University of Freiburg, Germany) for FIB lithography on my samples.

I would like to thank my sister Izabela Czekaj from Department of General Energy at PSI for supporting images of crystallographic structure of LaFeO₃ and support with understanding the XPS measurements and analysis. Without her help the final goal would not be achieved at all.

I am grateful to Tomasz Bryś and Peter Fierlinger – my flat mates from Sommerhldenstr. 13B and Ph.D. students at UCN/EDM Group at PSI. My time at PSI would not be the same without them. In addition, without their support I would not learn ROOT so fast, which was very useful in my thesis.

I would like to thank to Rolf Bertschinger for evaporating cobalt films on a very short notice.
Acknowledgments

I am grateful to Thomas Lippert and Stela Canulescu for allowing me to use their PLD chamber and sharing their experience in the topic.

I would like to thank Andrej Buellesmer for his efforts on polishing and cutting various samples.

I would like to thank my office mates (Ana, Anja, Berndt, Dirk, Elena and Maxi) for all discussions and everything we have done together. In particular, I would like to thank Maxi for always screaming at me whenever I was not responding for my phone while listening to music (i.e. heavy concentrated while working) and for reminding me to put this very paragraph onto the acknowledgments.

I would like to thank my parents Janina and Józef Czekaj, and my brother Robert Rupi Czekaj. Without their help and support I would not have written this dissertation or either have finished the studies in Cracow at the first place.

Finally, I would like to acknowledge financial support from Swiss National Science Foundation and Paul Scherrer Institut.
Curriculum Vitae

**Personal Details**

Born in Cracow, November 3rd, 1979

**Education**

1987–1994 Grammar School No. 1 Skawina, Poland
- Multiple Chemistry, Physics and Mathematics Contests
- Prize winner of the Regional Chemical Contest

1994–1998 General High School Skawina, Poland
- Examination for the secondary school (Polish, Chemistry, English)
- Multiple Chemistry and Physics Contests

1998–2003 Jagiellonian University Cracow, Poland
**Diploma Studies**
- Specialization: Solid State Physics, Master degree with distinction mark
- Diploma Thesis in Laboratory for Experimental Computer Physics
- Subject: "Resistometric studies of atomic ordering kinetics in Fe-Pd binary system" supervised by Dr hab. Rafal Abdank-Kozubski

2003–2007 Paul Scherrer Institut Villigen PSI, Switzerland
**Ph.D. Studies at PSI/ETHZ**
- Shared PhD Student between Swiss Light Source and Laboratory for Micro- and Nanotechnology
- PhD Thesis Supervisor: Prof. Danilo Pescia (ETHZ)
- PSI Supervisors: Dr. Frithjof Nolting (PSI-SLS) and Laura Heyderman (PSI-LMN)

**Traineeship**

Summer 2002 Paul Scherrer Institut Villigen, Switzerland
**Construction, operation and optimization of Helmholtz stabilization system**
- Supervisor: Dr. Reinhold Henneck, Laboratory for Particle Physics UCN/EDM Project
- Programming in Matlab 6.1
- Final mark: very good

**Hobby**

Books (sci-fi, fantasy, philosophical), hiking, snowboarding, cycling, basketball, volleyball, tennis, badminton, snooker, model-making, computers (operating systems, programming, networks, development of technology and science)