Tailoring Properties of Materials at the Nanoscale

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Abstract

The knowledge of growth and characterizing techniques is essential for the preparation of high quality thin films and multilayers. Here, structural properties have been investigated by X-ray reflectivity, X-ray diffraction, and transmission electron microscopy while the composition was determined by Rutherford backscattering spectrometry. For the magnetic studies, magneto-optical Kerr effect and X-ray magnetic circular dichroism have been used.

The structural properties of the metal/insulator multilayer system, Fe/MgO, have been investigated. The coherency of the layers was influenced by the difference of the atomic distance in the Fe and MgO layers, resulting in long range strain fields. As a consequence, the coherency between the layers is not maintained.

The atomic steps can not exist in amorphous materials, due to the absence of well defined atomic distances. Furthermore, the magnetic properties of amorphous materials allow a tuning of magnetic properties such as magnetic anisotropy and ordering temperature. The possibility to imprint arbitrary magnetic anisotropy in nanolaminated magnetic amorphous Co$_{30}$Fe$_{70}$Zr$_{5}$ was demonstrated. The ratio of the orbital to spin moments for both Fe and Co was determined, for both thick and thin layers embedded in amorphous Al$_{2}$Zr$_{30}$ layers. When growing Co$_{30}$Fe$_{70}$Zr$_{5}$ /Al$_{2}$O$_{3}$ the layers exhibit large changes in layer quality with thickness of the layers, ultimately affecting the magnetic properties of the stack.

The use of protective layers is of large importance when performing ex-situ measurements. Most of the materials used were capped by Al$_{2}$O$_{3}$, effectively hindering both the reaction with oxygen and water. The penetration of hydrogen through different thicknesses of alumina was investigated. The experiments confirmed high degree of passivation as well as the possibility to selectively diffuse hydrogen through these layers. The use of element specific diffusion barriers allows the tailoring of magnetic properties of magnetic thin films and multilayers.

Keywords: Multilayers, magnetic anisotropy, amorphous materials

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urn:nbn:se:uu:diva-107425 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-107425)
To my wife, Sanaz,
and
my son, Pooya
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  Hossein Raanaei, Hans Lidbaum, Andreas Liebig, Klaus Leifer and Björgvin Hjörvarsson (2008) Structural coherence and layer perfection in Fe/MgO mulilayers  

II  Hossein Raanaei, Hugo Nguyen, Gabriella Andersson, Hans Lidbaum, Panagiotis Korelis, Klaus Leifer and Björgvin Hjörvarsson (2009) Imprinting layer specific magnetic anisotropies in amorphous multilayers  

III  Thomas Hase, Hossein Raanaei, Hans Lidbaum, Cecilia Sanches-Hanke, Stuart Wilkins, Klaus Leifer and Björgvin Hjörvarsson (2009) Spin and orbital moment in amorphous Co$_{68}$Fe$_{24}$Zr$_8$ layers  
Submitted to Physical Review B

IV  Hans Lidbaum, Hossein Raanaei, Evangelos Th. Papaioannou, Klaus Leifer and Björgvin Hjörvarsson (2009) Structural- and magnetic properties of Co$_{68}$Fe$_{24}$Zr$_8$/Al$_2$O$_3$ multilayers  
Submitted to Journal of Crystal Growth


VI  Gunnar Karl Pálsson, Yuntao Wang, Daniel Azofeifa, Hossein Raanaei, Martin Sahlberg and Björgvin Hjörvarsson (2009) Influence of Titanium and Vanadium on the Hydrogen transport through amorphous alumina films  
Submitted to Journal of Alloys and Compounds

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Comments to my contribution

The level of my contribution in any paper is somewhat reflected by the position of my name in the authors list. I participated in the planning of the experiment and in the manuscript preparation. My participation can be reflected in the following:

I Responsible for the samples preparation, X-ray measurements and manuscript preparation.

II Responsible for the samples preparation, X-ray measurements, MOKE measurements, data analysis, and manuscript preparation.

III Responsible for the samples preparation, participated manuscript preparation.

IV Responsible for the samples preparation, participated in the MOKE measurements and manuscript preparation.

V Responsible for sample preparation and X-ray analysis. Participated in manuscript preparation.

VI Responsible for the samples preparation. Participated in X-ray measurements.
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Introduction

In recent years remarkable improvements, both in fabrication and experimental characterization techniques, have been made to explore the exciting physical properties of nanoscale materials. Low dimensionality and low symmetry are the features of these materials that give rise to unique physical properties which are not found in bulk materials. These features are of much interest in both basic research and nanotechnology. On the technological side, when considering the extensive influences that using nanoscale structures has had on the information technology (IT) industry, it is as if a second "industrial revolution" is taking place.

When ferromagnetic materials are formed in the "small-scale", as for example in the case of thin films or multilayers, they exhibit magnetic and transport properties previously not observed in bulk magnetic layers. The giant magnetoresistance (GMR) effect discovered by A. Fert and P. Grunberg [1, 2] provided the basis for ultra high-density magnetic storage, and is an example of the influence of dimensionality on a materials properties.

Properties of materials in low dimension can be investigated in thin films and multilayers. The physical properties of such systems depend on the layer perfection, thickness variation, crystallinity, and lattice mismatch between the constituents. The growth of metal-insulator systems is of interest because these systems can be utilized in magnetic tunnel junction devices. The interface quality in such systems influences the transport properties and the structural properties can be influenced by the growth temperature. The case of metal/oxide (Fe/MgO multilayers) as a metal-insulator system is discussed in Paper I where it is shown that the coherency of the total structure is strongly affected by the step edges at the interfaces. Papers II, III & IV show that by using amorphous materials the atomic steps at the multilayer interfaces can be removed.

In tunneling magnetoresistance (TMR) the possibility to select the anisotropy direction is critical. This anisotropy is typically based on the exchange bias effect. Imprinting uniaxial in-plane anisotropy by imposing an external magnetic field during the deposition makes it possible to create an easy axis in the magnetic amorphous materials. This easy axis can be used as a pinning layer in the TMR. The origin of local anisotropy, as well as induced anisotropy, can be understood by the spin-orbit coupling in such materials. The magnetic properties of magnetic amorphous materials can be tailored by utilizing both composition and extension. Paper II demonstrates how the layer specific anisotropy can be made in amorphous multilayers
and Paper III includes descriptions concerning spin and orbital moment in amorphous Co$_{68}$Fe$_{24}$Zr$_{8}$. In the TMR effect an insulator layer is typically used as a spacer between two ferromagnetic layers. When using magnetic amorphous material as ferromagnetic layers, it therefore becomes important to investigate the growth mode, the layer perfection, and the magnetic properties of the magnetic material (used in Paper II) on the oxide layer. This is discussed in Paper IV.

Hydrogen in metals has been attracting attention in recent years due to both the tunability of a materials properties and the energy carrier. The material properties of a magnetic multilayer can be tuned by exposing the film to hydrogen. The tune of the strength of interlayer exchange coupling caused by changing the hydrogen content in the multilayers is an example of tailoring of material properties [3, 4, 5] and the use of an oxide layer as a transport barrier in hydrogen up-take is one of the routes used to control the hydrogen content in the materials (Paper V). Hydrogen is a clean fuel, however one of the obstacles which needs to be overcome is the storage of the hydrogen on a large scale. Metal hydrides have been found to be able to absorb and store hydrogen for such a purpose. Doping Ti in the Alanates increases both uptake and release of hydrogen, and the role of Ti in Al$_2$O$_3$ on the transport rate and dissociation rate of hydrogen are addressed in Paper VI.

The layout of the thesis is as follows. Chapter 1-5 provide a background to the papers I-IV (as explained below). The background for the paper V and VI concerning to the hydrogen uptake is not provided as my contribution was mainly the growth of the samples for the experiments.

In order to obtain the desired properties in thin films and multilayers, firstly the knowledge of production of such structures is necessary, and is discussed in chapter 1. Secondly, structural investigations such as layer quality and interface properties carried out by X-rays is discussed in chapter 2. There has been extensive development of magnetic properties of thin films for various purposes and understanding such properties requires a basic knowledge of magnetism, which is described briefly in chapter 3. The magnetic characterization techniques required to investigate the magnetic properties of the samples are presented in chapter 4. Magnetic amorphous materials have a large potential to tailor magnetic properties and the anisotropy in such materials is explained in chapter 5. Chapter 6 gives a summary of the papers and finally the full research papers are given at the end of the thesis.
1. Thin films and multilayers

It is not an exaggeration to say that modern life would be very difficult and to some extent impossible without the existence of thin films as magnetic sensors and memory devices [6, 7, 8], which are integral component of computers, are examples of thin films.

Thin film deposition and fabrication techniques together with ultra-high vacuum technology make the growth of thin films in nanoscale possible. In this thesis a magnetron sputtering technique has been used to grow all the thin films and multilayers presented. This technique relies on the formation of plasma and multiple scattering between ions and target material atoms and makes the evaporation of many kinds of materials (metals and insulators) feasible [9, 10, 11, 12]. In this chapter a brief introduction to the sputtering technique and growth process will be discussed, followed by a general discussion of multilayers.

1.1 Sputtering technique

The essence of sputtering techniques lies in the collisions between the ionized atoms and the material atoms which are to be deposited, and this leads to ejection of the target atoms. In order to produce and then accelerate the ionized gas, usually Ar, inside the chamber, an electric potential is applied between the target and the ground where the target is connected to the cathode. This electric field causes electrons to accelerate. The electrons collide with the Ar atoms and these collisions produce ionized Ar atoms and more collisions. The Ar\(^{+}\) finally collide with the target material and atoms are ejected. Some of the ejected atoms arrive at the substrate and here they condense and form a deposited material. The secondary electrons produced by the collision process can be used in the ionizing processes.

In order to achieve a self-sustaining glow discharge a relatively high gas pressure with respect to the vacuum condition is needed. The mean free path of the ejected atoms is approximately proportional to the inverse pressure, thereby in a higher pressure the mean free path becomes shorter because the atoms have more collisions. This results in the fast thermalization of the ejected atoms and the material deposition is therefore decreased by the increasing pressure.

Using a magnetron device the pressure condition can be decreased while the glow discharge is sustained. With this device the secondary electrons experience a Lorentz force confining them close to the target. These electrons
increase the ionizing process. A schematic illustration of magnetron sputtering is shown in Fig. 1.1.

Figure 1.1: Sketch of magnetron sputtering. The ionized Ar$^+$ are accelerated towards the target. The collisions cause the target atoms to be ejected and thereby to be randomly deposited on the substrate.

1.2 Growth process

The film growth process can be explained as follows. An atomic flux reaches the substrate and the atoms are deposited. The deposited atoms can re-evaporate or lose their velocity component normal to the substrate. The adsorbed atoms are not in thermal equilibrium with the substrate, so they can diffuse along the surface, forming clusters. These clusters then collide with the other adsorbed species until they become thermodynamically stable which is called the nucleation stage. This stage depends on the energy of the deposited atoms, the rate of the deposition, the activation energy of the adsorption, thermal diffusion, and the chemical nature of the substrate. Subsequently, the clusters can grow parallel to the substrate by surface diffusion and perpendicular to the substrate by trapping of the deposited atoms; the grown clusters in this step are called islands. In the final step, the islands start to merge with each other to reduce the substrate free surface area and to form a continuous film.

Depending on the surface energy of the substrate, the lattice strain and the thermodynamics of the deposition, the growth process can be simply classified into the following three modes. [13]

- Frank-van der Merwe, layer type, a continuous layer covers the substrate and uniform layer-by-layer growth takes place. [14]
- Volmer-Weber, islands type, a formation of three-dimensional islands occur while some part of substrate is not covered. [15]
- Stranski-Krastanov, mixed type, the growth of a few two-dimensional monolayers take places until the three dimensional islands start to grow.

A schematic representation of the three modes is shown in Fig. 1.2.
Figure 1.2: Schematic representation of the a) Frank-van der Merwe mode, b) Volmer-Weber mode and c) Stranski-Krastanov mode.

The surface energy of the substrate, $\gamma_s$, of the film, $\gamma_f$, and interface energy between film and substrate, $\gamma_i$, play an important role in the wetting process of a surface. When $\gamma_i + \gamma_f < \gamma_s$, the Frank-van der Merwe mode occurs while in the case of $\gamma_i + \gamma_f > \gamma_s$, the Volmer-Weber mode takes place. It should be noted that in the case of lattice mismatch between film and substrate, there is a tendency for the strain to be relaxed; that is forming dislocations which hinder the continuous layer growth. The Stranski-Krastanov mode can happen when $\gamma_i + \gamma_f \approx \gamma_s$ and the lattice mismatch is not big. Once a few two-dimensional monolayers are grown, the strain energy will increase until film relaxation occurs yielding the growth of islands.

The growth of amorphous materials can be likewise dependent on the surface energies. Although there is a difference between the bulk energy for crystalline- and amorphous states, the balance between the energy surfaces, $(\gamma_s, \gamma_i, \gamma_f)$, will allow the formation of islands (dewetting process) or continuous layers (wetting process).

1.3 Multilayers

A multilayer structure consists of two or more different materials which are grown on top of each other and regularly repeated.

A multilayer which shows a long out-of-plane coherence structure is called a superlattice [16]. In the ideal case, the assumption is that a superlattice contains a perfect interface as shown in Fig. 1.3; $d_A$ and $d_B$ are the lattice spacings.

---

1In the case of crystal growth with lattice parameter, $a$, on the crystalline substrate with lattice parameter $a_s$, lattice mismatch is defined as $\varepsilon = \frac{a-a_s}{a_s}$
of materials $A$ and $B$ respectively, and $\Lambda$ and $D$ are bilayer and total thickness respectively. However in a real superlattice there exists a random variation in the number of atomic planes in each material layer-$n_A$ and $n_B$- and in in-plane grain size [17, 18]. Random orientation of the individual grains is another result of deviation from the ideal case [19].

![Figure 1.3: Schematic representation of an ideal superlattice with total thickness $D$ and bilayer thickness $\Lambda$. $d_A$ and $d_B$ are the interplane distances of materials $A$ and $B$ respectively. $t_A$ and $t_B$ are the layer thickness of materials $A$ and $B$ respectively.](image)

The nature of the interface between the layers plays an important role in the layer structure. The structural coherence in the superlattice structures will be destroyed if the disorder at the interface extends a few atomic planes to either side of the interface in such a way that each layer acts as an independent scatterer causing loss of structural information transmitted from layer to layer [20, 21, 22]. In a superlattice with very large lattice mismatch, interfaces are not expected to be coherent. By decreasing bilayer thickness the effect of such non-coherent interface will be dominant, resulting in non-coherent structure of the film.

1.3.1 Fe/MgO multilayers

Fe/MgO/Fe systems are of interest due to the high TMR values reported both theoretically [23] and experimentally [24] and are found to depend on the interface quality on the layers. The use of a multilayer structure is one of the possible routes that can be used to obtain more information about the nature of the interface and the structural coherence of constituent materials. This is done by using X-ray techniques.

---

2Lattice spacing for the cubic symmetry lattice is defined as $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$ where $a$ is the lattice parameter and $(h,k,l)$ are the Miller indices.
In Fe/MgO multilayers the lattice mismatch is huge\(^3\) and \(a_{MgO}/a_{Fe} \approx 1.46\). In order to obtain a common in-plane lattice parameter between two successive different crystal layers, one has to be expanded while the other has to be compressed. The epitaxial relation Fe(001) [110] || MgO(001) [100] shown in Fig. 1.4 results from a lattice match upon a 45° in-plane rotation \([25, 26, 27]\) in such a way that the coherent growth of both Fe and MgO layers will lead to a tetragonal distorted bcc lattice.

![Tetragonal structure model of the Fe/MgO interface in top view. The epitaxial relation Fe(001) [110] || MgO(001) [100] is fulfilled by a lattice match upon a 45° in-plane rotation.](image)

Although the registry of atomic planes, as seen in Fig. 1.5, makes the high structural coherence in the Fe/MgO system evident, the diffraction pattern did not show any superlattice peaks. The width of the Fe peak was rather wide, corresponding to a coherence length which is equal to the thickness of a single Fe layer. The atomic steps at the interfaces result in a variation in the distance between atomic planes in Fe-Fe and MgO-MgO layers because the (001) lattice distances of Fe and MgO are incompatible. Therefore the lattice mismatch destroys coherency throughout the structure, as is discussed in Paper I. Fig. 1.6 shows the presence of incomplete Fe layers on which MgO layers are accommodated.

1.3.2 Amorphous multilayers

The robustness of the growth of amorphous multilayers depends strongly on interface related effects. For example in the case of metal/oxide system (Paper IV) due to the relatively high interface energy between the metal and the oxide layers, metal materials typically grow in islands on the oxide surface at the initial stage of the growth. The effective interface between metal and

\(^{3}\)The bulk lattice parameter of Fe and MgO are respectively 2.866 Å and 4.213 Å.
Figure 1.5: High resolution micrograph of Fe/MgO multilayer. The film is grown on a MgO(001) substrate. There is high crystal coherence through the layers. The apparent shading is caused by variations of the crystal planes.

Figure 1.6: Schematic illustration of (a) atomic steps of the Fe layers, (b) the 45° rotated side view of the Fe and (c) the MgO lattices. (d) The out-of-plane lattice mismatch between Fe and MgO at the atomic steps. $a_{Fe} = 2.866$ Å and $a_{MgO} = 4.213$ Å, for simplicity it is assumed that $a_{MgO} = \sqrt{2} a_{Fe}$. 
oxide is decreased by increasing the metal surface, thereby minimizing the total energy. In Co$_{68}$Fe$_{24}$Zr$_{8}$/Al$_2$O$_3$ multilayers, Al$_2$O$_3$ grows in an amorphous structure at room temperature [28]. As depicted in Fig. 1.7 the metal islands nucleate on the oxide surface and are isolated from each other. In the thin CoFeZr layer (Fig. 1.7(a)) the holes between the islands are filled by the oxide layer. If the amount of metal grown on the oxide layer is increased until the holes between the islands are filled, continuous metal layers will be formed (Fig. 1.7(b)).

Figure 1.7: TEM images of the Co$_{68}$Fe$_{24}$Zr$_{8}$/Al$_2$O$_3$ multilayers from (a) the thin CoFeZr layer and (b) the thick CoFeZr layer. The islands are formed in the thin CoFeZr layer resulting in discontinuous layers, whereas well-defined continuous layers are observed in the thick multilayer.
2. Structural analyses

One of the broad range of techniques used to explore solid structures is X-ray diffraction. This technique is used to analyze the structural properties of thin films and multilayer such as crystallinity, film stress, interface roughness, and layer quality in multilayers. This chapter briefly introduces crystal diffraction and some X-ray structural characterization techniques used in thin film analyses.

2.1 Crystal diffraction

The crystalline structure relies on the materials periodic atomic planes, therefore the diffraction pattern gives the Fourier transform of the periodic atomic planes. In the kinematic approximation, where the multiple scattering effects are ignored, the structure factor from a unit cell (UC) in a solid is given as [29]

\[ F_{UC}(Q) = \int_{UC} \rho(r) \exp(iQ \cdot r) dr \]  

(2.1)

The integration is extended over the total charge distribution of the UC. \( \rho(r) \) is the charge density in the UC and \( Q \) is the scattering vector. \( Q \) is defined as a difference between the outgoing and incoming wave vectors, \( Q = K_{out} - K_{in} \). The angle between \( K_{out} \) and \( K_{in} \) is \( 2\theta \), (see Fig. 2.1).

Figure 2.1: A sketch showing the relation of scattering vector \( Q \) and wave vectors \( K_{in}, K_{out} \).
If it is assumed that a UC contains $N$ atoms, then the structure factor can be written as

$$F_{UC}(Q) = \sum_{n=1}^{N} f_n \exp(iQ \cdot r_n)$$  \hfill (2.2)

where $f_n$ is the atomic form factor and $r_n$ is the position of the $n$th atom in the UC. In the periodic lattice structure the structure factor can be defined as a contribution of UC times the lattice sum

$$F_{\text{crystal}}(Q) = \sum_{n} f_n \exp(iQ \cdot r_n) \sum_{R_i} \exp(iQ \cdot R_i)$$  \hfill (2.3)

where $R_i$ is the lattice vector which defines unit cell position and can be written in terms of basis lattice vectors, $\vec{a}_1, \vec{a}_2, \vec{a}_3$

$$R_i = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$  \hfill (2.4)

where $(n_1, n_2, n_3)$ are integers.

The second sum in Eq. 2.3 has a maximum value if the scattering vector fulfills

$$Q \cdot R_i = 2\pi \times \text{integers}$$  \hfill (2.5)

The reciprocal lattice vector is defined as

$$G = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$$  \hfill (2.6)

where $(\vec{a}_1^*, \vec{a}_2^*, \vec{a}_3^*)$ are reciprocal lattice basis vectors [30] and $(h, k, l)$ are integers. The following equality

$$G \cdot R_i = 2\pi(hn_1 + kn_2 + ln_3) = 2\pi \times \text{integer}$$  \hfill (2.7)

and Eq. 2.5 imply that

$$Q = G$$  \hfill (2.8)

This is the called the Laue condition which gives the condition for observing the diffraction pattern from a crystalline lattice. The Laue condition is exactly equivalent to Bragg’s law$^1$. The crystal diffraction pattern depends on the unit cell structure and the lattice spacing of the $(h, k, l)$ planes. The first sum in Eq. 2.3 is the $F_{UC}(Q)$ which depends on the atomic form factor and the arrangements of atoms in the UC. For example, the $F_{UC}$ for the face centered cubic structure (fcc), with lattice parameter $a$, and assuming all the atoms are identical, is $^2$

$^1$Bragg’s law is defined as $2d \sin \theta = m\lambda$ where $m$ is an integer.

$^2$In the fcc structure a cubic unit cell is chosen. The position of atoms are at

$$r_1 = 0, \quad r_2 = \frac{1}{2}(\vec{a}_1 + \vec{a}_2), \quad r_3 = \frac{1}{2}(\vec{a}_2 + \vec{a}_3), \quad r_4 = \frac{1}{2}(\vec{a}_3 + \vec{a}_1)$$
\[ F_{UC}^{fcc}(Q) = f\left(1 + \exp(i\pi(h+k)) + \exp(i\pi(h+l)) + \exp(i\pi(l+h))\right) \quad (2.9) \]

where the reciprocal lattice vector is of the form \( G = (2\pi/a)(h,k,l) \). If \( h,k,l \) are all even or all odd, then \( F_{UC}^{fcc}(Q) \) has a maximum value, \( 4f \), otherwise it vanishes. In this case the diffraction is said to be forbidden.

Fig. 2.2 shows an X-ray diffraction scan of a layered stack containing Fe and CoO on the Al\(_2\)O\(_3\) substrate. The epitaxial relation between CoO and Fe is Fe\([001]\)\|CoO[110]. The position of the CoO peak at \( 2\theta = 36.6^\circ \) corresponds to the lattice spacing 2.45 Å for the (111) planes. The Fe peak position at \( 2\theta = 44.7^\circ \) agrees very well with the expected lattice spacing of 2.02 Å for the (110) planes.

![Image of X-ray diffraction scan](image)

**Figure 2.2:** The diffraction pattern of the Fe/CoO sample (\( Q = Q_Z \)). The peak positions of CoO(111) and Fe(110) correspond to \( 2\theta_{CoO} = 36.6^\circ \) and \( 2\theta_{Fe} = 44.7^\circ \). The substrate Al\(_2\)O\(_3\)(11\(\bar{2}\)0) peak lies at \( 2\theta_{Al_2O_3} = 37.7^\circ \).

The out-of-plane (\( Q = Q_Z \), c.f., Fig. 2.1) crystal coherence length, \( b \), can be estimated by extracting the full width at half maximum value (FWHM), \( \Delta(2\theta) \), of a diffraction peak by applying *Scherrer’s formula* [31]

\[ b = \frac{0.9\lambda}{\Delta(2\theta)\cos\theta} \quad (2.10) \]
For example, from the Bragg’s peaks of Fe(110) and CoO(111) shown in Fig. 2.2, $b_{CoO} = 291 \text{ Å}$ and $b_{Fe} = 83 \text{ Å}$. In the perfect crystal all the diffracting planes are exactly in registry. In reality, a crystal is often imperfect and contains small crystals which are orientationally tilted with respect to each other. This is called mosaicity. In order to find an estimate of mosaicity, a rocking curve scan around the diffraction point is needed. In a reciprocal space the length of the scattering vector of the rocking curve scan is constant while it is scanned through the diffraction point [32, 33], (see Fig. 2.3).

2.1.1 Superlattice diffraction

The diffraction intensity of an ideal superlattice consisting of material $A$ and $B$ can be written as [34]

$$I(Q_z) = L_N^2(\Lambda) \left( |f_A|^2 L_{nA}^2 (d_A) + |f_B|^2 L_{nB}^2 (d_B) + 2|f_A| |f_B| L_{nA} (d_A) L_{nB} (d_B) \cos(Q_z \Lambda / 2) \right)$$  \hspace{1cm} (2.11)

where

$$L_N(x) = \frac{\sin(Q_z n x / 2)}{\sin(Q_z x / 2)}$$  \hspace{1cm} (2.12)

$L_N^2(\Lambda)$ represents the superlattice peaks arising from one bilayer of thickness $\Lambda$ as a unit cell, if $Q_z = 2\pi j / \lambda$, where $j$ is an integer. The terms between the parentheses are envelope functions; the first and second term are description of contribution to the scattering of the material $A$ and $B$ respectively whereas the last term is a cross term. The shape of the envelope function strongly depends on the lattice spacing of the constituents. In the case where the difference between the lattice spacings of the constituents is huge, the contribution from the
cross term becomes small and the individual layer terms have less overlap. As an example, by using Eq. 2.11 the diffraction pattern of an ideal Fe/MgO superlattice in the case of \( Q = Q_z \) is calculated and illustrated in Fig. 2.4. The frequency fringes between superlattice peaks are resulted from the constructive interface between the total thickness and the average lattice spacing. These fringes are called Laue’s oscillations.

![Diffraction pattern of an ideal Fe/MgO superlattice in the case of \( Q = Q_z \).](image)

**Figure 2.4:** Diffraction pattern of an ideal Fe/MgO superlattice in the case of \( Q = Q_z \). The peak position of the individual constituents MgO(002) and Fe(002) are \( 2\theta_{\text{MgO}} = 42.9^\circ \) and \( 2\theta_{\text{Fe}} = 65.1^\circ \). The inset shows Laue oscillations between two successive superlattice peaks.

### 2.2 X-ray reflectivity

The propagation of light when it moves from one medium to another is described by Snell’s law.

\[
\eta_A \sin \varphi_A = \eta_B \sin \varphi_B
\]  

(2.13)

where \( \eta_A \) and \( \eta_B \) are the refraction indices of the materials A and B respectively; \( \varphi_A \) and \( \varphi_B \) are the angles between the normal to the surface and the refracted beam in materials A and B respectively.

In the case of an incoming X-ray from a vacuum (\( \eta = 1 \)) with the angle, \( \varphi \), as illustrated in the Fig. 2.5, there is a critical angle, \( \theta_c (\theta = 90^\circ - \varphi) \), below

---

\(^3\)When the difference between lattice spacings is rather small the shape of envelope function will be affected by a large contribution of the cross term. The average lattice spacing \( \bar{d} \) is given as \( \frac{1}{\bar{d}} = \frac{2\sin(\theta)}{\lambda} + i \pi \), where \( \lambda \) is wavelength and \( i \) is an integer [35].
which the incoming ray is totally reflected. Thus, the refraction index, \( \eta \), for X-rays is slightly less than unity [36] and can be written as

\[
\eta = 1 - \delta - i\beta
\]  

(2.14)

where \( \delta \) is in the order of \( 10^{-5} \) and is related to the scattering amplitude and electron density, whereas \( \beta \) is the absorption coefficient. By using Snell’s law the critical angle is found to be \( \theta_c \geq 1^\circ \). In X-ray reflectivity the interference of the reflected beams from the interfaces yields an interference pattern.

When the incident angle \( \theta \) is small a significant reflectivity pattern will be detected. The \( Q \) is close to zero, and hence the probed length scale is bigger than the lattice parameter of the material. Thus X-ray reflectivity is used for investigating interface properties and measuring layer thicknesses as well as total film thickness both in crystalline and amorphous multilayers. The interferences between reflected beams from the film surface and film/substrate interface can be observed as seen Fig. 2.6. This interference pattern contains periodic peaks and troughs which are called Kiessig’s fringes [37]. The probed length scale is in the order of the film thickness and is consistent with the angular distance between the fringes.

The observed constructive fringes from bilayers (multilayer peaks) show high intensity and depend on the difference of electron densities between constituent materials. A reflectivity measurement of Fe/MgO multilayers is shown in Fig. 2.6.

The strong well-defined multilayer peaks originate from chemical modulation of the sample, and the number of multilayer peaks corresponding to the components of the Fourier transform show the layer quality. The angular distance between two successive multilayer peaks corresponds to the bilayer thickness. The bilayer peak position can be calculated by [35]

\[
\sin^2 \theta = \left( \frac{l\lambda}{2\Lambda} \right)^2 - (\eta^2 - 1)
\]  

(2.15)
where \( l \) is the order of the \( l \)-th peak, \( \lambda \) is X-ray wavelength, and \( \bar{\eta} \) is the average refraction index of the multilayers. More details about X-ray reflectivity from thin films and multilayers can be found in Refs. [29, 38, 39]. By using Parrat formalism [40] one can simulate the X-ray reflectivity data. This model relies on a recursive relation containing multiple reflections and refractions. The average single layer thickness and roughness at the interfaces are generally taken to be the fitting parameters. All the reflectivity curves simulated in this thesis have been simulated using the *GenX* program [41, 42], which is an available open source software program written by Matts Björck. The simulation curve of Fe/MgO multilayers is depicted in Fig. 2.6.

In order to experimentally estimate the layer quality and average roughness at an interface, one can utilize a rocking curve through the reflection point. The only difference being that the \( Q \) value is smaller than in the case of diffraction. The rocking curve scan contains two parts, one sharp and one wide, which respectively correspond to the specular and diffuse scattering [43, 39]. Fig. 2.7 illustrates the rocking curve scans through the first multilayer peak for the three multilayers samples \([\text{Co}_{68}\text{Fe}_{24}\text{Zr}_{8}/\text{Al}_{2}\text{O}_{3}]_{10}\) with different CoFeZr thicknesses (10, 20 and 30 Å).

In the rocking curve scan, the high intensity of the specular part with the abruptly decreasing diffuse part (by increasing/decreasing \( \Delta \omega \)) is indications of good layering and small thickness variations at the interfaces in the samples.
Figure 2.7: Rocking curve scans of the three multilayers samples \([\text{Co}_{68}\text{Fe}_{24}\text{Zr}_{8}/\text{Al}_2\text{O}_3]_{10}\) with different CoFeZr layer thicknesses. In the rocking curve scan of the sample 10/20 (the thinnest) the diffuse part is rather constant, whereas for the sample 30/20 a steep decrease of the diffuse part is observed which is a signature of a good layering with respect to the other samples.
3. Thin film magnetism

This chapter is devoted to the principles of magnetism which are discussed in this thesis. First, a brief definition of magnetic interactions is given to explain the origin of spin alignments and magnetic anisotropies. Next, a brief explanation of the Stoner model discussing the origin of ferromagnetism in 3d-elements is presented and finally the physics of the formation of magnetic domains is discussed.

3.1 Magnetic interactions

This section presents a brief introduction of interactions in the solid state. The spins play an important role in the magnetism; in order to understand magnetic interactions, one needs to consider the Pauli equation [44] containing the spin term

\[ [\mathcal{H}_e + \mathcal{H}_{so}] \psi(r,t) = E \psi(r,t) \]  

(3.1)

The first term on the left, \( \mathcal{H}_e \), represents the kinetic energy of the electrons and all the Coulomb interactions in the atomic system, whereas the second term, \( \mathcal{H}_{so} \), represents the spin contribution to the energy. These terms are responsible for the exchange and spin orbit interaction respectively which are explained below:

1. **Exchange interaction**: The emission spectra of the He atom is a good exemplar to introduce the concept of exchange interaction. The Pauli exclusion principle\(^2\) (PEP) implies that the total wave function of the electrons in two-electron systems must be anti-symmetric [45]. This gives rise to the splitting of excited states in He atoms into singlet and triplet states. The Heisenberg paper [46] is one of the classic works used to interpret such splitting. It should be noted that the exchange interaction arises from the Coulomb interaction taking PEP into account. PEP gives rise to either parallel or anti-parallel spins and the exchange interaction is associated with the coupling of spins. *Heisenberg* Hamiltonian is based on the concepts of the exchange interaction and is defined by

\[ \mathcal{H} = -2 \sum_{i<j} J_{ij} \vec{S}_i \cdot \vec{S}_j \]  

(3.2)

\(^1\)In principle, the Dirac equation, which contains the relativistic effects, would give us a more accurate picture.

\(^2\)The Pauli exclusion principle states that two electrons cannot be in identical states.
where \( J_{ij} \), the coupling energy constant, is positive for ferromagnetic coupling and negative for antiferromagnetic coupling. In the semiclassical view, and for the purpose of macroscopic calculation, the average value of Eq. 3.2 can be written as [47]

\[
E_{ex} = -2 \sum_{i<j} J_{ij} S^2 \cos \theta_{ij}
\]  

(3.3)

where \( \theta_{ij} \) is the angle between two adjacent spins and has to be small. By using the expansion \( \cos \theta_{ij} = 1 - \frac{\theta_{ij}^2}{2} + \cdots \), the exchange energy per unit volume may be expressed by

\[
\frac{E_{ex}}{V} = A \left( \frac{\partial \theta_{ij}}{\partial x_{ij}} \right)^2 = A \left( \nabla M \cdot M \right)^2
\]  

(3.4)

where \( M \) is the magnetization and \( A \) is the exchange stiffness constant and is a macroscopic measure of the stiffness of coupling in the spin system and is given by

\[
A = \frac{S^2 a^2 J N_v}{2}
\]  

(3.5)

where \( N_v \) is the number of the nearest-neighbor atoms per unit volume and \( a \) is the distance between the spins.

2. **Spin-orbit interaction**: As the name suggests, the spin-orbit interaction describes the coupling between the spin and the angular momentum, \( \vec{l} \), leading to the total angular momentum, \( \vec{j} = \vec{s} + \vec{l} \). The second term in the Pauli equation, \( H_{so} \), represents the magnetic induction due to the relative motion of the electron and the nucleus in the atom, which is proportional to \( \vec{s} \cdot \vec{B} \), where \( \vec{B} \) is the magnetic induction. This magnetic induction is interpreted by using Maxwell’s equations and Lorentz transformations [48, 49]. By using the definition of the quantum mechanical orbital angular momentum, \( \vec{r} \times \vec{p} = \hbar \vec{l} \), and after some mathematical computations, the spin-orbit Hamiltonian can be written as: [50, 45]

\[
H_{so} = \zeta_{nl} \vec{s} \cdot \vec{l}
\]  

(3.6)

where \( \zeta_{nl} \) is the spin-orbit coupling parameter. The spin-orbit interaction energy for the 3d-transition metals is in the order of 10-100 meV, whereas the exchange energy is significantly larger, having a value in the order of 1 eV [51, 52], for the rare earths, the spin-orbit is considerably larger.

3. **Zeeman interaction**: This interaction is caused by the action of the magnetic field, \( \vec{H} \), on the spin and orbital angular momentum leading to energy
splitting in the atom. The Zeeman Hamiltonian, \( \mathcal{H}_{\text{Ze}} = \frac{\mu_B}{\hbar} \mathbf{H} \cdot (\mathbf{\hat{l}} + 2\mathbf{\hat{S}}) \), can be derived from the Dirac equation. Thus, the magnetic moment is [53]

\[
\mathbf{m} = \frac{\mu_B}{\hbar} (\mathbf{\hat{l}} + 2\mathbf{\hat{S}})
\]

(3.7)

where \( \mu_B \) is the Bohr magneton. The twice weighted factor for spin contribution is called the Lande g-factor \(^3\).

Application of the Zeeman effect is seen both in the research and even in everyday life. The Zeeman effect is applied to investigate magnetic properties of magnetic materials; for example, observing spin-orbit coupling, measuring magnetization loop and coercivity, and finding the easy axis in ferromagnetic materials. When we save or write information on a computer, it is the Zeeman interaction originating from the current induced from the recording head, which is utilized.

### 3.2 Itinerant ferromagnetism

The measured values of the atomic moments of Fe, Co and Ni are \( m_{\text{Fe}} = 2.16 \mu_B \), \( m_{\text{Co}} = 1.71 \mu_B \), and \( m_{\text{Ni}} = 0.61 \mu_B \). It can be seen that these values are odd fractions of the Bohr magneton and much smaller than the values obtained by Hund’s rules\(^4\). This difference originates from the fact that 3\(d\)-electrons are not localized. The delocalizaton of 3\(d\)-electrons may be expressed by the Stoner model [54, 55]. In this model both spin-up and spin-down electrons have their own band energy. The energy difference between these two sub-bands makes a difference between spin-up and spin-down electrons populations resulting in a net magnetic moment. It is assumed that the occupation number of the spin-up and spin-down electrons is expressed as

\[
N^{\uparrow\downarrow} = \int_0^{E_F} D^{\uparrow\downarrow}(E) dE
\]

(3.8)

where \( D^{\uparrow\downarrow}(E) \) is the spin-up and spin-down electron density of states. The exchange interaction energy can be defined by [53]

\[
E_{\text{ex}} = -\frac{I}{4} (N^\uparrow - N^\downarrow)^2
\]

(3.9)

where \( I \) is the Stoner parameter and contains Coulomb- and exchange interaction. The existence of spontaneous magnetization is defined by the Stoner criterium [53]

\[
D(E_F) \geq 1/I
\]

(3.10)

Fe, Co and Ni are the only elements that fulfill the Stoner criterium [53].

---

\(^3\)In higher order relativistic corrections, \( g = 2.0023 \ldots \).

\(^4\)Hund’s rules suggest that the magnetic moment of Fe, Co and Ni are 6, 6 and 5 \( \mu_B \) respectively.
Although the Stoner criterium predicts the existence of the magnetic order it does not give the magnitude of the magnetic moments. In order to predict the magnetic moments the population of the spin-up and spin-down electrons has to be considered, on the other hand a distinction between the strong and week ferromagnetism is needed. Co and Ni are strong ferromagnets as their $3d$ spin-up sub-bands are fully filled, whereas for Fe the $3d$ spin-up sub-band is partially filled which is considered as a week ferromagnet.

### 3.3 Magnetic anisotropy

In principle, magnetic anisotropy is defined as the energy which is needed to turn the magnetization direction, $\mathbf{M}$, from the easy to the hard axis. The anisotropy energy density must be unchanged when the the magnetization is reversed, i.e., $E_{\text{ani}}(\mathbf{M}) = E_{\text{ani}}(-\mathbf{M})$. Thus the anisotropy energy has to be an even function of the angle, $\theta$, confined by the magnetization vector and the magnetic axis. One may expand the energy density

$$E_{\text{ani}} = k_1 \sin^2 \theta + k_2 \sin^4 \theta + k_3 \sin^6 \theta + ... \quad (3.11)$$

where $k_i (i = 1, 2, 3, ...)$ are anisotropy constants. One way to determine the anisotropy constant is to turn $\mathbf{M}$ from the easy axis (magnetic axis) by applying an external magnetic field, which acts as a torque to rotate the magnetization vector. In the case of uniaxial anisotropy, where all anisotropy constants are zero with exception of $k_1$, the derivative of Eq. (3.11) with respect to $\theta$ means that the torque acts on $\mathbf{M}$; on the other hand the torque is equal to $\mathbf{M} \times \mathbf{H}_{\text{ani}} = M \mathbf{H}_{\text{ani}} \sin \theta$, thus

$$\mathbf{H}_{\text{ani}} = \frac{2K_1}{M} \cos \theta \quad (3.12)$$

In principle, $H_{\text{ani}}$ is the effective field required to rotate the magnetization. This provides a description for the existence of anisotropy. Fig. 3.1 shows the rotated magnetization with respect to the easy axis of the thin film. The anisotropy constant, $K_1$, can contain two anisotropies; the first is a contribution from magnetocrystalline anisotropy, $K_{\text{crys}}$, originating from spin-orbit coupling, and the second is a contribution from shape anisotropy, $K_s$. In the following subsections, these anisotropies will be discussed briefly.

#### 3.3.1 Shape anisotropy

In shape anisotropy the magnetization direction depends on the shape of the ferromagnetic material. When a material with a volume, $V$, is magnetized in a space, the magnetization, $\mathbf{M}$, is discontinuous and falls suddenly to zero.

---

5 The magnetic axis or easy axis of the thin film can be out-of-plane or in-plane, depending on the competition between the anisotropies in the thin films.
Figure 3.1: The magnetization vector is rotated in-plane with respect to the magnetic axis. In principle, $\mathbf{M}$ is the saturation magnetization which is rotated by $H_{ani}$, see Eq. (3.12). In this case, where there is strong in-plane uniaxial anisotropy, the magnetic axis is defined as the in-plane easy axis.

at its surface. By using $\nabla \cdot \mathbf{B} = 0$ and the divergence theorem close to the surfaces, one can conclude that there is an effective surface charge density, $\sigma_M$, on the surfaces [49]. These charges act as a source of the demagnetization field, $\mathbf{H}_d$, which is opposite to the magnetization. Strictly speaking, $\mathbf{H}_d$ is a magnetostatic field generated by the divergence of the magnetization\(^6\). In the body of the material it is given by

$$\mathbf{H}_d = -\mathbf{N} \cdot \mathbf{M} \quad (3.13)$$

where $\mathbf{N}$ is a demagnetization tensor, which depends on the shape of the material. The field generated out of the magnetic material by the magnetization is called a stray field. This stray field plays an important role in forming the magnetic domains. This will be discussed later.

Fig. 3.2 illustrates two cases of magnetization in an infinite thin film. In the

---

\(^6\)Since $\nabla \cdot \mathbf{B} = 0$, it gives: $\nabla \cdot \mathbf{H} = -\nabla \cdot \mathbf{M}$
case where magnetization is in-plane, shown in the left side of the figure, the surfaces which contain surface charge density are at an infinite distance away, so the resulting demagnetization field is negligible. On the contrary, for the out-of-plane magnetization, \( \mathbf{M} \), the demagnetization field is \( \mathbf{H}_d = -\mathbf{M} \), which means that all the tensor elements are zero except \( N_{zz} = 1 \). The magnetostatic energy per unit volume of the demagnetization field is given by

\[
E_d = -\frac{\mu_0}{2V} \int_V \mathbf{M} \cdot \mathbf{H}_d \, d^3r \tag{3.14}
\]

where \( \mu_0 \) is the vacuum permeability. For thin films, when the magnetization is parallel to the surface, the magnetostatic energy is the lowest, so the preferred direction of \( \mathbf{M} \) is in-plane rather than out-of-plane. In general, the anisotropy energy per unit volume of the thin film may be defined as

\[
E_d = -\frac{1}{2} \mu_0 M^2 \cos^2 \theta \tag{3.15}
\]

where \( \theta \) is the angle between \( \mathbf{M} \) and the film normal.

### 3.3.2 Magneto-crystalline anisotropy

Magneto-crystalline anisotropy which originates from the spin-orbit interaction firstly was proposed by Van Vleck [56]. The spin-orbit interaction within atoms has been discussed earlier. In a multi-electron system, spin-orbit interaction is given by the generalized form of Eq. 3.6

\[
H_{so} = \zeta \mathbf{L} \cdot \mathbf{S} \tag{3.16}
\]

where \( \mathbf{L} \) and \( \mathbf{S} \) are total angular- and total spin momentum. In solids the spin-orbit coupling is complicated by the existence of the bonding of the atoms, generally leading to the non-spherical shape of the orbitals. Thus, the orbitals lie in the preferred direction defined by the symmetry of the crystal. Because of the spin-orbit coupling the magnetization is preferably pointed to a direction called the easy direction. In the perfect crystal the magneto-crystalline anisotropy is proportional to the energy, \( \Delta E_{so} \), required to rotate the magnetization from the easy direction to the hard direction. By ignoring the magnetostatic effects, the magneto-crystalline anisotropy can be defined by the anisotropy of the spin-orbit energy [57]

\[
\Delta E_{so} = \zeta [\langle \mathbf{L} \cdot \mathbf{S} \rangle_{easy} - \langle \mathbf{L} \cdot \mathbf{S} \rangle_{hard}] \tag{3.17}
\]

Thus, the anisotropy energy depends on the lattice structure. In the perfect crystal the preferred directions of the magnetization are well defined and are the same in every point of the crystal, whereas in a polycrystalline sample the anisotropy energy differs from point to point. The preferred axes depend on the orientation of the crystallites and are influenced by the dislocations at the grain boundaries.
Any change in the lattice symmetry gives rise to a change in the magneto-
crystalline anisotropy. This can be obtained, for example, by imposing stress
on the sample or, in thin films, by epitaxial growth on a substrate. Both give
rise to magneto-elastic anisotropy [58]. The lattice mismatch between lay-
ered stacks in a multilayer structure also causes strain leading to induced
anisotropy [59, 60]. On the microscopic level, all these anisotropies fall in
the magneto-crystalline anisotropy category. In chapter 5 the anisotropy in
amorphous materials will be discussed.

3.4 Magnetic domains and domain walls
As mentioned in section 3.3.1, a homogeneously magnetized material pro-
duces a magnetic stray field, which is dependent on the shape of the material.
To minimize the energy of the stray field the magnetization \( M \) will break into
domains. Each domain has its own magnetization in a specific direction and
the transitions between these domains occur at regions called domain walls.
Because the domain walls also need energy to be formed, the formation of
domains is a balance between the energy cost of producing the stray field and
the cost of producing the domain walls. Domain walls can be simply classi-
fied into two groups: 180° and non-180° domain walls. In the first case the
magnetizations of the adjacent domains make an angle of 180° with respect to
each other which, for example, is shown in Fig. 3.3.

![Figure 3.3](image)

*Figure 3.3:* Kerr domain image taken of the 100 Å thick CoFeZr grown in the presence
of a magnetic field. There are two domains. Each domain is at 180° with respect
to the other. The image is taken at \( B = 0.35 \) mT. The imaged area of each scan is
\( 170 \times 130 \mu m \). From Paper II.

There are two prominent types of domain walls, each determined by how
the moments rotate; Bloch wall and Néel wall. In the first case, magnetic rota-
tion continuously happens, while the moments in the domain wall are pointed
parallel to the plane of the wall. In the second case, these moments are ori-
ented perpendicular to the plane of the wall. In the Bloch wall the energy
density increases with decreasing thickness of the thin film because the effec-
tive charges density is above and below the wall. Whereas in the Néel wall,
because the energy density is proportional to the area of the effective charge density inside the film, decreasing the film thickness causes a decrease in the energy wall [47]. Therefore, in order to minimize the magnetostatic energy associated with the effective charge density, a decrease in the film thickness gives rise to a decrease in the Bloch wall thickness, whereas the Néel wall thickness is increased. See Fig. 3.4.

*Figure 3.4:* In the Bloch wall the magnetic moments in the wall are oriented parallel to the wall. The effective charge density is on the external surface of the sample whereas, in the thinner film, the magnetic moments in the wall are oriented perpendicular to the wall (Néel wall), because of the sample’s effective internal surface charges. The left hand panel shows the rotation of magnetization in the Bloch wall the and Néel wall.
Magneto-optical effects were first studied by Michael Faraday in 1845. He showed that when polarized light passes through a piece of glass placed in a magnetic field the polarization plane of the outgoing light is rotated. This is called the Faraday effect. A similar phenomenon was found by John Kerr [61]. The Magneto-optical Kerr effect (MOKE) is the change in polarization of the light beam reflected by a ferromagnetic surface. MOKE can be employed as a probed technique for magnetic measurements.

At the microscopic level, both effects are related to the spin-orbit interaction. In fact the electrical field of the incoming light is coupled to the spin of the electron through the spin-orbit interaction. The general principle can be understood by taking a semi-classical view. Right-handed circular polarized (RCP) and left-handed circular polarized (LCP) light will drive the electrons in the material into opposite rotations with equal radii. By applying the external magnetic field parallel to the propagation of the incoming wave, the circling electrons are affected by the magnetic field. Therefore the radius of the LCP/RCP will be decreased/increased due to the action of Lorentz force on the electrons. The linear polarized light is a sum of LCP and RCP. If this light is incident on the magnetic material, the LCP and RCP will travel at different speeds in the material. As there is a phase shift between the LCP and RCP, the polarization plane of the total transmitted beam will be rotated.

X-ray Magnetic Circular Dichroism (XMCD) is also a magneto-optical effect based on X-ray absorption. XMCD is a technique used to measure a difference in absorption of RCP and LCP photons (X-rays) in a magnetic material.

This chapter will introduce the aforementioned techniques with the focus on MOKE.

### 4.1 MOKE

There are three different geometries for MOKE experiments; Longitudinal, Transverse and Polar geometries. They can be distinguished by the relative directions of the incoming wave and the magnetization vector. The different geometries are illustrated in Fig. 4.1.

In the Polar and Longitudinal geometry, the incoming linear polarized wave is reflected in an elliptical polarized wave and the polarization direction is rotated. The rotation of the polarization plane, $\theta_K$, and the change in the ellipticity, $\varepsilon_K$, are the two quantities which give the Kerr effect response. In the Transverse geometry the magnetization changes the intensity of the outgoing
Figure 4.1: Three different geometries of MOKE.

From a macroscopic point of view, the magneto-optical effect can be described by the analysis of the dielectric properties of a medium. The interaction of the magnetic sample and electromagnetic wave can be written as:

\[ D = \varepsilon E \]  (4.1)

where \( D, \varepsilon \) and \( E \) are respectively displacement vector, dielectric tensor and electric field of the incoming wave. The dependence of the dielectric tensor, \( \varepsilon \), on the magnetization, \( M \), is responsible for the Kerr response. By neglecting the higher order terms of the dielectric tensor for a cubic symmetry material, Eq. 4.1 can be represented by [63, 64, 65, 66]

\[
D = \begin{pmatrix}
\varepsilon & -iQM_3 & iQM_2 \\
iQM_3 & \varepsilon & -iQM_1 \\
-iQM_2 & iQM_1 & \varepsilon
\end{pmatrix} \cdot E = \varepsilon \cdot E + i\varepsilon Q \cdot M \times E \]  (4.2)

where \( Q \) is the Voigt constant [67] and \( M_i (i=1,2,3) \) is the component of the magnetization vector. For simplicity, it is assumed that the diagonal terms of the dielectric tensor are equal.

The off-diagonal elements of the dielectric tensor satisfies the Onsager relation, \( \varepsilon_{ij}(M) = \varepsilon_{ji}(-M) \) [68]. Thus, the Kerr effect exists as long as \( M \times E \) is not zero [63].
The general formula of the Kerr effect can be derived by solving Maxwell’s equations for the dielectric tensor [66]. The relation between incident and reflected beam can be given by the Fresnel reflection matrix [69]

\[
R = \begin{pmatrix}
    r_{pp} & r_{ps} \\
    r_{sp} & r_{ss}
\end{pmatrix}
\]  

(4.3)

The Fresnel coefficients in the matrix correlate the \( p \) and \( s \) polarized component of the incoming beam to the components of the outgoing beam. In the case of the Longitudinal Kerr effect, the complex Kerr response for the \( s \) and \( p \) polarization is defined by

\[
\Theta^{s(p)}_K = \frac{r_{ps(sp)}}{r_{ss(pp)}}
\]  

(4.4)

For the linear polarized incoming beam, the polarization of the outgoing beam will be elliptical. The Kerr response is a complex quantity, \( \Theta_K = \theta_K + i\varepsilon_K \) [70], with the real and imaginary parts respectively describing the rotation angle of the polarization plane and the ellipticity of the outgoing beam. [71]. Fig. 4.2 is a schematic view of the Kerr rotation and Kerr ellipticity.

![Figure 4.2: Schematic illustration of the Kerr rotation of the linear polarized incoming beam. The outgoing beam after reflection from a magnetized material is elliptically polarized. The main polarization plane is tilted over a small angle, \( \theta_K \), with respect to that of the incoming beam. The ellipticity of the reflected beam is \( \varepsilon_K \).](image)

From the derivation of the Kerr rotation for the MOKE geometries [69] the following points emerge:

- In the Longitudinal geometry, for normally \( p \)-and \( s \)-polarization incoming beams, \( \theta = 0 \), c.f. Fig. 4.1, the Kerr rotation is zero.
- In the Polar geometry, the maximum Kerr response occurs at \( \theta = 0 \).
- In the Transverse geometry, there is no Kerr response for both the \( s \)-polarized incoming beam at any incident angle, \( \theta \), and the normally \( p \)-polarized incoming beam; there is also a change in the intensity for the \( p \)-polarized outgoing beam.
- The Kerr rotation and ellipticity are less than 1° for most materials [70].
In this thesis Longitudinal MOKE geometry is used. A sketch of the setup is displayed in Fig. 4.3.

![MOKE setup diagram]

**Figure 4.3:** Schematic view of MOKE setup.

The linear polarized incoming beam at the incident angle, $\theta$, from a HeNe laser directs the sample. The sample is mounted on the rotatable sample holder positioned in the center of pole pieces of the electromagnet. The surface of the sample is parallel to the magnetic field. The magnetic field of the poles is detected by conventional Hall-probe and reaches a maximum of $H \approx 600$ mT. The reflected light passes a Faraday cell called a rotator, an analyzer which is set nearly to extinction position, and finally hits a photodiode. The Faraday cell consists of a glass rod surrounded by a coil which produces an axial field leading to a rotation of the polarization plane. The rotation is defined by Verdet’s law

$$\theta_F = VlH_{coil}$$

where $\theta_F$ is Faraday rotation, $H_{coil}$ is the magnetic field produced by the coil, and $V$ is the Verdet constant. By applying an AC current in the coil the reflected beam is modulated in such a way that the main polarization plane oscillates with the imposed frequency [72]. Magnetic measurements can be done by recording the hysteresis loop resulting from the Kerr rotation, see Fig. 4.4.

In order to map out the anisotropies in the sample, one can extract the remanence values from the recorded hysteresis loops. The remanence depends on the angle between the anisotropy axis and applied field. Fig. 4.5 shows the normalized remanence in terms of the rotation angle taken by MOKE in the range $0-360^\circ$ for a Co$_{68}$Fe$_{24}$Zr$_8$ amorphous layer. The results show uniaxial anisotropy.

The intensity of the beam inside the material varies as $I = I_0\exp(-\alpha t)$, where $t$ is the optical path length and $\alpha$ is the penetration coefficient. This intensity drops rapidly for the metals [73] because of their complex refraction index. Therefore the MOKE response, particularly from a magnetic layered stack, is...
Figure 4.4: The Kerr rotation of a magnetic amorphous sample consisting of [Co$_{68}$Fe$_{24}$Zr$_{8}$/Al$_2$O$_3$]$_{10}$.

influenced by the depth of the magnetic layers. The optical skin depth, $1/\alpha$, for the metals is in the range of 100-200 Å. Fig. 4.6 clearly illustrates the magnetic layer depth dependence of the MOKE response in double layers of magnetic amorphous CoFeZr; a nonmagnetic AlZr layer is situated between the CoFeZr layers. The in-plane uniaxial anisotropy direction of each magnetic layer is nearly perpendicular to the other.

4.2 XMCD

XMCD is a technique used for element specific measurement of spin and angular momentum. The origin of XMCD can be explained by the difference between transition probabilities from spin-orbit split initial $2p$-states to exchange-split $3d$ final states, c.f. Fig. 4.7 [52, 74].

In $3d$-element metals, the excitation of spin-polarized electrons arises from the interaction of incoming polarized light with the L-edges. The spin-polarization depends on both the edge and the polarization of incoming photons. For example, 25% spin-up and 75% spin-down electrons are excited by LCP photons at the L2 edge, whereas RCP photons do the opposite at the same edge. In the case of ferromagnetic metals the exchange-split of the $d$-level leads to a difference in population of unoccupied spin-up and spin-down electrons in the $3d$-level. This implies that the absorption of the LCP and RCP photons will be different.

The spin and orbital momentum, and also the ratio between them, can be extracted by applying the sum rules. For a more detailed description see Refs [75, 76, 52].
Figure 4.5: The remanence data of the amorphous Co$_{68}$ Fe$_{24}$Zr$_8$ single layer taken azimuthally by MOKE.

Figure 4.6: The remanence values accompanied by the simulation data of a sample consisting of double layer magnetic amorphous 2×[Co$_{68}$ Fe$_{24}$Zr$_8$/Al$_{70}$Zr$_{30}$]. The different intensity between points A and C, and B and D show the different contribution in MOKE response from the top and bottom layers in the stack. The data is taken from Paper II.
Figure 4.7: A sketch of spin-dependent transitions from 2p-levels to 3d-levels.
5. Magnetic anisotropy in amorphous thin films

In general, *amorphous* materials are materials which have no structural long-range ordering. These materials are produced by some kind of nonequilibrium process like solidification from the melting state [77, 78]. In principle, rapid solidification impedes the formation of the topological long-range ordering in the alloy. This feature gives rise to amorphous materials which have no microstructural discontinuities like grain boundaries. In the case of magnetic amorphous materials, the macroscopic magnetocrystalline anisotropy is also absent.

Magnetic amorphous materials can be based on either 3d-transition- or rare-earth metals. In the first case, the alloy may contain glass forming elements such as: boron, phosphor, carbon or silicon, or the alloys can be built up with early transition metals such as: zirconium or niobium. Examples include CoZr, FeZr or CoFeZr (which is investigated in Paper II, II & IV). For the CoFeZr alloy, at least 10% Zr is needed to make an amorphous state at room temperature [79].

In this thesis Co$_{68}$Fe$_{24}$Zr$_{8}$ was grown by using the sputtering technique at room temperature. The main advantage of this technique is to maintain the stoichiometry of the metallic compound target.

The use of amorphous materials as a building block of layered thin films has a large potential for tailoring magnetic properties, for example, the magnetic anisotropy. These properties are of great technological importance, for example, when using the magnetoresistance effect. This chapter deals with random anisotropy and induced anisotropy in magnetic amorphous materials.

5.1 Random anisotropy

Although long-range crystallinity is clearly absent in amorphous materials, resulting in no magnetocrystalline anisotropy, on the scale of a few nanometers, the spin orbit coupling gives rise to local anisotropy [80, 81]. The random anisotropy in the amorphous material arises from the variation of strength and direction of anisotropies; the local energy density of uniaxial anisotropy can be defined by $K_{loc}$. The direction of the local easy axis fluctuates with a correlation length, $R_a$, which is in the order of a few nanometers in amorphous alloys. The local magnetic moments interact with each other by exchange interaction of the stiffness, $A$, which can be defined by Eq. 3.4. The contribution
of exchange energy and random uniaxial anisotropy in the free energy, $F$, per unit volume of the system is given by the following simple model [82]

$$\frac{F}{V} = A[\nabla \mathbf{m}(\mathbf{r})]^2 - K_{loc} \left[ \mathbf{m}(\mathbf{r})^2 - \frac{1}{3} \right]$$  \hspace{1cm} (5.1)

where $\mathbf{m}(\mathbf{r}) = \frac{M}{M_s}$. The exchange interaction implies the orientational correlation length, $R_f$, of the local magnetic moments. In principle, there is a competition between exchange energy and local spin interaction. The first term on the right side favors the long-range correlation in the magnetic direction and is in the order of $A/R_f^2$. Whereas the second term favors the short-range fluctuations in the magnetic moment direction. By taking a random collection of random anisotropies and using random walk theory [83], the macroscopic anisotropy $K_{mac}$ scales as [84]

$$K_{mac} = K_{loc} \left( \frac{R_a}{R_f} \right)^{3/2}$$  \hspace{1cm} (5.2)

By minimizing $F/V$ with respect to $R_f$, we have [47]

$$R_f = \frac{16A^2}{9K_{loc}^2R_a^3}$$  \hspace{1cm} (5.3)

The estimated values of orientational correlation length are listed in Table 5.1. For amorphous material it is assumed $A \approx 10^{-11} \text{J/m}^3$ and $R_a \approx 2 \text{ nm}$.

<table>
<thead>
<tr>
<th>Amorphous material</th>
<th>$K_{loc}$</th>
<th>$R_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3$d$-elements</td>
<td>$\approx 10^5 \text{ J/m}^3$</td>
<td>$\approx 20 \mu \text{m}$</td>
</tr>
<tr>
<td>4$f$-elements</td>
<td>$\approx 10^6 \text{ J/m}^3$</td>
<td>$\approx 20 \text{ nm}$</td>
</tr>
</tbody>
</table>

Table 5.1: A comparison between exchange correlation lengths of 3$d$-elements and 4$f$-elements amorphous material. Data taken from [47].

Fig. 5.1 is a schematic representation of the variation of local magnetization with respect to distance, for both strong and weak local anisotropy.

One must consider that the exchange interaction, tending to keep atomic moments parallel to each other, acts from atom to atom, and possibly affects a few nearest neighbors. It is the overall stiffness of this exchange coupled system, governed by the strength as well as the range of the exchange interaction, that figures in determining $R_f$. The value of $R_f$ is the result of a competition between the exchange interaction and the coupling of each atomic moment to the local anisotropy direction, which in this model changes over a distance, $R_a$. If the anisotropy is uniform over the length, $R_f$, then the moments will all point in the same easy anisotropy direction. But if there is a small defect that changes the anisotropy at the site of only one atom, then it is unlikely that it
will follow the local anisotropy, but rather stay parallel to the easy axis of its neighbors to which it is exchange coupled.

In 3d-elements amorphous material, $R_f \gg R_a$, leading to a small macroscopic anisotropy. Fig. 5.2 shows the evidence of random anisotropy in Co$_{68}$Fe$_{24}$Zr$_8$. The size of areas with the same grey color are approximately in the order of 20\,$\mu$m, which is expected for the 3d-elements amorphous alloys.

5.2 Induced anisotropy

One way to tailor the magnetic properties of magnetic amorphous materials is to induce anisotropy and it can generally be achieved by field annealing [85, 86, 87, 88, 89], stress annealing [90, 91, 92], and also growth in the presence of a magnetic field [93, 94, 95]. The actual mechanism of the induction of the macroscopic magnetic anisotropies in the magnetic amorphous material has not been well understood until now. Some authors have followed the directional pair ordering model [96, 97, 98, 47]:

The pair ordering model has been successfully applied to describe field annealing induced anisotropy in crystalline alloys [99]. Since a similar magnetic effect is observed in amorphous alloys, the same model applies for field annealing in amorphous materials [89]. In the annealing process the mobility of the atoms is increased so that they are able to change
Figure 5.2: Kerr domain images taken of the 100 Å thick Co$_{68}$Fe$_{24}$Zr$_{8}$. The imaged area of each scan is 170 × 130 μm. The non-uniformity in the magnetization within the pattern is a sign of random anisotropy in the sample at demagnetization state (B=0 mT). There are some areas which are not aligned to the field even above B=4.5 mT. From Paper II.

their position$^1$. This may result in the local structures moving towards a more stable structure. When a magnetic field is applied some atom pairs orient themselves relative to the magnetization direction so that the magnetic anisotropy energy is minimized. Once the material is cooled the mobility of the atoms decreases and thus the significant diffusion of atoms is stopped. By removing the magnetic field, the atomic pair directional ordering due to the new arrangement of the atoms may still have a dominant anisotropy to maintain the magnetization in the direction which it had during annealing. The mechanism behind this anisotropy may be the same as in magnetocrystalline anisotropy. The spin-orbit interaction in this model is a coupling between the magnetization direction and the bond direction between the atoms. The magnetization direction and bond direction are related to $\mathbf{S}$ and $\mathbf{L}$ respectively. This microscopic coupling can give rise to bond directional anisotropy. The bond directional order is affected by displacements of the atoms. These displacements can be obtained by imposing some stress on the system or can arise from the magnetoelastic

---

$^1$It should be noted that during the process the annealing temperature must be lower than the Curie temperature.
The coupling between strain and directional bond order can be defined by [100, 47]

\[ E_{\text{strain}} = \varepsilon \lambda_s \sum_{i=1}^{Z} N_i \left( \cos^2 \theta - \frac{1}{3} \right) \]  

(5.4)

where the sum is taken over the \( Z \) nearest-neighbors directions, \( \varepsilon \) is the local magnetoelastic parameter, \( \lambda_s \) is the saturation magnetostriction coefficient, \( N_i \) is the number of bonds in the \( i \)th direction, and \( \theta \) is the angle between \( \mathbf{M} \) and the strain.

The imposing strain changes the number of bonds in the \( i \)th direction and this results in a change in the internal energy of the magnetic system.

The same model can be used in the case of growth in the presence of a magnetic field. When the sample is grown the macroscopic magnetization is not developed until the critical thickness is reached.\(^2\) By continuing the growth of the film, the magnetostriction effect is obtained as a source of strain.

In the macroscopic view, the strain energy depends on the induced field direction during annealing or growing of the film. This leads to induced anisotropy. The same result can also be achieved by clamping the substrate while materials are growing. By releasing the film, the presence of the magnetoelastic effect gives rise to induced anisotropy [103].

Fig. 5.3 illustrates the induced uniaxial anisotropy in the 100 Å layer thick of Co\(_{68}\)Fe\(_{24}\)Zr\(_{8}\) deposited on the Si(111) substrate. The film was grown in the presence of a magnetic field. By comparing Fig. 5.2 and Fig. 5.3 one can conclude that the random local anisotropies move towards more stable positions so that each local uniaxial anisotropy is aligned parallel to the magnetization direction, which in this case is the magnetic field direction. This gives rise to macroscopic uniaxial anisotropy in the material.

\(^2\)The ordering temperature depends on the magnetic layer thickness and can be phenomenologically described as \( T_C(t) = T_C(\infty)[1 - bt^{-\lambda}] \) where \( t \) is the thickness of the magnetic layer; \( b \) and \( \lambda \) are constants [101, 102].

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Figure 5.3: Kerr domain images taken of the 100 Å thick Co$_{68}$Fe$_{24}$Zr$_{8}$ sample at the easy axis. The film was grown in the presence of a magnetic field. The imaged area of each scan is 170 × 130 μm. The single domain is seen (a) at B=0 mT (demagnetization state) and (b) at B=0.35 mT. The domain wall movements at the intermediate state (B=0.35 mT) occur rapidly. (c) After imposing B= 0.35 mT, the domain wall moves across the field of sight within 20 s, resulting in a single domain state within the observed region. From Paper II.
6. Summary of papers

6.1 Coherence structure in multilayers (Paper I)

In Paper I the influence of the growth temperature on the chemical modulation and crystallinity of Fe/MgO multilayers was investigated. A series of such multilayers was grown at 120, 165, 220 and 290 °C. Fig. 6.1 illustrates the XRR measurements. The sample grown at 165° shows a well-defined layered structure and sharp interfaces between Fe and MgO in comparison to the other samples. The TEM results corresponding to the layered structure, depicted in Fig. 6.2, also confirm the continuous layers with small variation for the aforementioned sample. However, as the growth temperature increases the thickness variations of the layers are increased.

The high resolution TEM micrograph of the sample grown at 165 °C (as seen in Fig. 6.3) shows that the Fe(002) and MgO(002) lattice planes are in registry to each other. The observed Fe (110) and MgO(100) lattice planes are also in registry.

However the XRD measurements did not reveal any superlattice diffraction peaks that are seemingly in contradiction to the observation as explored by TEM. This was explained by considering the large lattice mismatch in height between Fe and MgO lattices, which imposes the presence of the step height of MgO and Fe terraces at the interfaces. Such steps cause the coherency of

Figure 6.1: XRR spectra of the [Fe/MgO]₁₅ multilayer thin films at different growth temperatures. From paper I.
Figure 6.2: TEM images of $[\text{Fe/MgO}]_{15}$ multilayers grown at a) 165 °C and b) 290 °C. From Paper I.

Figure 6.3: High resolution phase contrast TEM micrograph of the Fe/MgO multilayer grown at 165 °C. From Paper I.
the total structure to be destroyed. Therefore, the diffraction data only shows the strained Fe(002) peak and well-defined Laue fringes arising from the Fe layers.

### 6.2 Imprinting magnetic anisotropies in magnetic amorphous layers (Paper II)

The imprinting of specific anisotropy in laminated amorphous multilayers was addressed in this paper and we used laminated Co$_{68}$Fe$_{24}$Zr$_{8}$/Al$_{70}$Zr$_{30}$ as a soft magnetic stack. TEM results clearly show the absence of crystallinity as well as well-defined layering in both mono-layer and double-layer Co$_{68}$Fe$_{24}$Zr$_{8}$, as seen in Fig. 6.4.

![Image](image.png)

**Figure 6.4:** High-resolution phase contrast micrograph of the mono-layer Co$_{68}$Fe$_{24}$Zr$_{8}$ (upper) and double-layer Co$_{68}$Fe$_{24}$Zr$_{8}$ (lower) in cross-section view. From Paper II.

A two-fold in-plane anisotropy in mono-layer Co$_{68}$Fe$_{24}$Zr$_{8}$ was imprinted by applying a magnetic field during growth. MOKE measurements, shown in Fig. 6.5, illustrate easy and hard axes in such a sample. This was also observed by MOKE microscopy.

Revolving the sample holder made it possible to imprint anisotropy in the next Co$_{68}$Fe$_{24}$Zr$_{8}$ layer in the magnetic amorphous multilayers. In the case of revolving the sample holder by 90° for double-layer Co$_{68}$Fe$_{24}$Zr$_{8}$, the induced
Figure 6.5: (a) Schematic illustration of uniaxial anisotropy in the mono-layer Co$_{68}$Fe$_{24}$Zr$_8$ sample. The MOKE measurements reveal such uniaxial anisotropy as (b) easy and (c) hard axes. From Paper II.
anisotropy axes extracted by MOKE measurements of two Co$_{68}$Fe$_{24}$Zr$_{8}$ layers were not perpendicular, see Fig. 6.6.

![Figure 6.6](image)

**Figure 6.6:** a) Schematic illustration of the magnetic state in the double-layer Co$_{68}$Fe$_{24}$Zr$_{8}$ sample. b) Magnetization vs applied field for such a sample at different angles with respect to the growth field direction of the bottom layer. From Paper II.

This can be understood by considering that the applied field during the deposition is not completely parallel to the sample edge. Because the intensity of laser light decays exponentially with the depth in the sample, this resulted in the top layer contributing more to the MOKE signal than the bottom layer. Thus there was a difference between the extracted remanence at different directions with respect to the edge of the sample.
6.3 Spin and orbital moments in amorphous Co$_{68}$Fe$_{24}$Zr$_{8}$ (Paper III)

The anisotropy in spin-orbit coupling is the essence of magneto-crystalline anisotropy in a crystal lattice. The absence of crystalline order in amorphous material seemingly does not lead to the removal of the orbital contribution to the total moment. In Paper II induced anisotropy was observed when Co rich amorphous material was grown in the presence of the magnetic field. This type of anisotropy cannot arise from long-range structural anisotropy; the origin of induced anisotropy, as discussed in Paper III, can therefore be understood by the properties of the local structure which can have local structural anisotropy.

In Paper III the $m_{\text{orbit}}/m_{\text{spin}}$ of both Fe and Co in amorphous Co$_{68}$Fe$_{24}$Zr$_{8}$ was determined by using the XMCD technique. The idea behind these measurements was to explore the origin of anisotropy in magnetic amorphous materials. A series of amorphous Co$_{68}$Fe$_{24}$Zr$_{8}$/Al$_{70}$Zr$_{30}$ multilayers and a thick Co$_{68}$Fe$_{24}$Zr$_{8}$ layer were grown by using magnetron sputtering. Structural studies revealed the amorphous structure and the layer quality in the Co$_{68}$Fe$_{24}$Zr$_{8}$ layers. In both the multilayers and the thick samples the XMCD measurements showed that the orbital contribution to the total moment was decreased for both Co and Fe compared to their bulk values. This can be attributed to the random positions of the atoms giving no long-range crystalline order in amorphous material. However the orbital moment of Fe was more quenched than that of Co. It was also seen that the $m_{\text{orbit}}/m_{\text{spin}}$ for Co in the multilayers was more suppressed than in the case of the thick Co$_{68}$Fe$_{24}$Zr$_{8}$ layer, which showed the interface effect on the $m_{\text{orbit}}/m_{\text{spin}}$.

The hysteresis loops taken from the reflection in both Fe and Co were identical, resulting in the Co and Fe being strongly coupled. Addition of Fe in a Co rich amorphous material decreases the coercivity leading to softening of magnetic properties. Therefore the local anisotropy can be tailored by changing the Co and Fe ratio leading to a change of the effective $m_{\text{orbit}}/m_{\text{spin}}$ on the material.

6.4 Structural and magnetic properties of Co$_{68}$Fe$_{24}$Zr$_{8}$/Al$_{2}$O$_{3}$ multilayers (Paper IV)

In Paper I a crystalline metal/insulator system was discussed. However, the thickness variations and imperfection at the interface caused by the atomic steps are not desirable for surface sensitive systems like TMR structures. By using amorphous building blocks this problem can be overcome. The structural stability and magnetic properties of amorphous Co$_{68}$Fe$_{24}$Zr$_{8}$/Al$_{2}$O$_{3}$ multilayers as a metal/insulator system were investigated in Paper IV. Two series of such multilayers were grown, one with the presence of a magnetic field and the other without. The thickness of Co$_{68}$Fe$_{24}$Zr$_{8}$ layers varied from 10 to 30 Å in each series. In the thinnest sample the Co$_{68}$Fe$_{24}$Zr$_{8}$ layers formed amorphous islands surrounded by the oxide layers; this can be understood by
considering that at the initial stage of the growth there were not too many atoms causing the local chemical composition to change. However, for the thickest Co$_{68}$Fe$_{24}$Zr$_8$ multilayer, continuous amorphous and nano-crystalline layers were observed due to the difference in the surface diffusion rates of the Fe, Co and Zr atoms on the oxide layers.

The magnetic characterizations also supported the structural results. The low values of the remanences, together with no striking differences in the loops can be attributed to the superparamagnetic behavior of the isolated islands. Fig. 6.7 illustrates the ferromagnetic response as a hysteresis loop of the thickest multilayer grown without the field. A variation of the remanences at different points on the sample can be attributed to random anisotropy in the sample (not shown here).

![Figure 6.7: The hysteresis loop for the Co$_{68}$Fe$_{24}$Zr$_8$(30Å)/Al$_2$O$_3$ multilayers measured in an arbitrary direction. The sample was not grown in the field. The measurements were performed at room temperature. From Paper IV.](image)

The clear easy and hard axes observed for the samples grown in the field with the continuous layers of Co$_{68}$Fe$_{24}$Zr$_8$ are reported on in Paper II. These layers were seen as a combination of both amorphous and polycrystalline material.

6.5 Diffusion barriers (Paper V & VI)

The hydrogen absorption and release rate of material in the presence of amorphous Al$_2$O$_3$ as a diffusion barrier was investigated in Paper V. The rate of hydrogen uptake strongly depends on the Al$_2$O$_3$ layer covering the V layer. However the hydrogen uptake rate increases by decreasing the Al$_2$O$_3$ thickness. This can be attributed to the reduction of the hole density caused by
decreasing the Al₂O₃ layer thickness since the defects in the oxide layer provide catalytically active sites. The diffusion rate in the samples capped with Pd was enhanced by about two orders of magnitude since Pd acts as a non-thermal activated material.

Apart from the role of Pd as a catalyst for hydrogen dissociation in Paper V, a Pd layer as a capping layer can prevent the underlying structure from oxidation [104]. Furthermore, due to the high paramagnetic and polarizability of Pd, the magnetization behavior of the sample can be affected by the induced moments in Pd [4].

A study of the effect of coating thin Al₂O₃ with Ti and V on the hydrogen uptake is described in Paper VI. Two series of samples (Ti and V series) were fabricated. In the first series, Ti either covered Al₂O₃ or was doped in the Al₂O₃, whereas in the second series V covered and was doped in the Al₂O₃. There were not considerable changes in the hydrogen transport rate when the Al₂O₃ was covered by Ti or V. Thus the oxide layers of Ti and V as capping layers did not increase hydrogen uptake. In the case where the Ti was doped in the Al₂O₃, the transport rate improved compared to the covered case but was still lower than the reference sample. For the sample in which V was doped, the hydrogen uptake rate did not change in comparison with the V covered sample. The random distribution of Ti and V also did not seem to improve the transport rate in the Al₂O₃. The results showed that the dissociation and effective diffusion cannot be the reason of catalysis in Alanates by Ti.
Svensk Sammanfattning

På senare år har anmärkningsvärda förbättringar uppnåtts både i tillverkn- ing och experimentell karakteriseringsteknik för att utforska de spännande fysikaliska egenskaperna hos nanostrukturmaterial. Låg dimensionellitet och låg symmetri är de drag hos dessa material som leder till unika fysiska egenskaper som inte finns i bulkmaterial, och av den orsaken är mycket intres- santa för både grundforskning och nanoteknik. På den tekniska sidan kan man tänka på det stora inflytandet av informationsteknik (IT) i det dagliga livet med hjälp nanostrukturer med den andra industriella revolutionen. När ferromagnetiska material bildar småskaliga strukturer som tunna filmer eller multilager uppvisar de magnetiska egenskaper och transportegenskaper (t ex elektrisk ledningsförmåga) som inte observeras i bulkskikt. Den gigantiska magnetoresistansen (giant magnetoresistance, GMR) som upptäcktes av A. Fert och P. Grunberg [1, 2] och gav grunden för ultratåt magnetisk datalagring är ett ex- empel på påverkan av materialets dimensionalitet.

Materialegenskaper i låg dimension kanske undersökas i tunna filmer och mul- tilager. De fysiska egenskaperna hos dessa system beror på lagrens perfektion, tjockleksvariationer, kristallstruktur och skillnad i atomavstånd mellan de in- gående materialen. Tillväxt av metall-isolator-system är av intresse för använ- dning i magnetiska tunnelövergångsenheter. De strukturella egenskaperna hos ett sådant system kan påverkas av ökande temperatur och fallet met- all/oxid, Fe/MgO-multilager som ett metall-isolator-system, diskuteras i ar- tikel I. Där har det visat sig att samordningen av den totala strukturen påverkas starkt av trappstegsformade kanter i gränsytorna. Användning av amorfa ma- terial är ett sätt att ta bort dessa atomsteg på gränsytor i multilager, vilket har visats i artiklarna II, III och IV.

I tillämpningar av tunnelmagnetoresistans (TMR) är möjligheten att välja den magnetiska anisotropins riktning av intresse eftersom den så kallade ut- byteslåsningseffekten (exchange bias effect) är kopplad till anisotropin. En enaxlig anisotropi i samma plan som filmens yta kan inpräntas genom att provet utsätts för ett yttre magnetfält under tillväxten. Detta ger en möjlighet att skapa en lätt magnetiseringsriktning i amorfa magnetiska material, vilka sedan kan använda som ett fastläsningslager i TMR-material. I amorfa mag- netiska material kan både sammansättning och utsträckning skräddarsy de magnetiska egenskaperna. I artikel II diskuterades särskilt en möjlighet för in- präntning av anisotropier i amorfa CoFeZr-multilager. Spinn- och banmoment i CoFeZr-skikt samt lagerperfektion i Co_{68}Fe_{24}Zr_{8}/Al_{70}Zr_{30}-multilager har undersökts i artikel III.
Beräkning av kvoten mellan ban- och spinnmoment hos Co och Fe från XMCD-mätningar (magnetisk cirkulär dikroism med röntgenstrålning - x-ray magnetic circular dichroism) visade att bannmomentets bidrag till det totala magnetiska momentet minskade både i Co och Fe jämfört med bulkvärdena. Detta kan bero på den slumpmässiga placeringen av atomer i det amorfa materialet som ju saknar kristallin ordning över större längdskalor. Den inducerade anisotropi som observerats i artikel II uppkommer inte ur magnetokristallin anisotropi, men den lokala strukturella anisotropin kan vara roten till lokal magnetisk anisotropi samt inducerad isotropi. Detta kan härledas ur spinnbankopplingen i sådana material.

En studie av både tillväxt och magnetiska egenskaper hos Co$_{68}$Fe$_{24}$Zr$_{8}$/Al$_2$O$_3$- multilager har presenterats i artikel IV. Det har visat sig att skiktens perfektion i multilagen, vilket i sin tur påverkar de magnetiska egenskaperna, beror starkt av tjockleken hos beståndsdelarna. När det gäller CoFeZr-skikt formas huvudsakligen amorfa öar på oxidytan på grund av avvätning. Dessa prover visade också superparamagnetiskt beteende på grund av de isolerade magnetiska öarna som låg inbäddade i Al$_2$O$_3$. I de tunnaste lagren observerades istället ett kontinuerligt skikt på grund av skillnaden i diffusionshastighet mellan Fe, Co och Zr. Den slumpmässiga magnetiska anisotropin i detta prov härrör från fluktuationer i den lätta axelns riktning. Om provet tillverkas i närvaro av ett yttre magnetfält erhålls en inducerad anisotropi liknande den som redovisas i artikel II.


Anisotropin i sådana material är av särskilt stort intresse och förklaras i kapitel 5. En översikt av artiklarna presenteras slutligen i kapitel 6.
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