ARRAYS OF MAGNETIC NANOSTRUCTURES: 
A DYNAMICAL AND STRUCTURAL STUDY BY MEANS OF X-RAY EXPERIMENTS

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

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By
Georg Heldt
School of Computer Science
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Abstract

The work in this PhD thesis covers two strands of x-ray experiments—firstly, the characterisation of large arrays of dense structures by means of x-ray scattering and secondly, the investigation of hybrid anisotropy square structures with x-ray microscopy.

The ability to accurately characterise large arrays of nanoscale magnetic structures is a key requirement for both scientific understanding and technological advance such as bit patterned recording media (BPM). In this work small angle x-ray scattering (SAXS) was investigated as a characterisation technique for large arrays of patterned structures. Dense arrays of magnetic nanostructures were prepared on x-ray transparent membranes and measured. The SAXS data was then modelled to obtain structure parameters such as the mean structure diameter, the diameter distribution and the mean position variance with statistical significance. Arrays (500 x 500 µm²) of nominally uniform nanostructures with centre-to-centre distances between 250 nm-50 nm were structurally characterised and compared to structure diameters obtained by optical scanning electron microscopy measurements. The mean structure diameter was found to be between 39 nm-15 nm and agree within the errors with the diameter obtained from SEM measurements. This work provides accurate data on the distribution (variance) of nanostructure sizes which is key for modelling these arrays for application in BPM.

In the second part of the work, the static and dynamic properties of patterned hybrid anisotropy square structures ([Co/Pd]-Py) were investigated by using time-resolved scanning transmission X-ray microscopy (STXM). In these patterned structures the magnetisation in the layers change both in magnitude and direction and gives rise to interesting new domain configurations. The reciprocal interaction between magnetic vortices in the Py layer and locally circular stripe domains in the Co/Pd was investigated and a mutual domain imprint between the layer was observed. In dynamic excitation experiments the precession of the vortex core is studied and showed good agreement with micromagnetic simulations made by Hrkac and Bryan. As demonstrated patterned hybrid anisotropy square structures have promising magnetic properties with potential applications in data storage (vortex switching) or spintronics (vortex oscillators).
Declaration

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List of Abbreviations

adj. rsquare - adjusted r²-value
AlN - aluminium nitride
BPM - bit patterned media
(c)SAXS - (coherent) small angle x-ray scattering
Co - Cobalt
DC - direct current (DC)
Fe - Iron
F.-v.d.M. - Frank-van der Merwe
FZP - fresnel zone plate
IPA - isopropanol
KOH - potassium hydroxide
LLG - Landau-Lifshitz-Gilbert
LHC - Large Hadron Collider
MIBK - methyl isobutyl ketone
N - Nitrogen
Ni - Nickel
O - Oxygen
OSA - order selecting aperture
Pd - Paladium
PMMA - polymethylmethacrylate
PSI - Paul Scherrer Institute
PVD - physical vapour deposition
Py - Permalloy (Ni₈₀Fe₂₀)
RF - radio frequency
rmse - root mean square error
SEM - scanning electron microscope
Si₃N₄ - silicon nitride
S.-K. - Stranski-Kastranov
SLS - Swiss Light Source
sse - sum of squared errors
STXM - scanning transmission x-ray microscopy
SW - Stoner-Wohlfarth
Ta - Tantalum
VSM - vibrating sample Vector magnetometer
V.W. - Volmer-Weber
XMCD - x-ray magnetic circular dichroism
List of Symbols

$A$ - exchange stiffness constant
$\vec{B}$ - magnetic flux density
$E_{aniso}$ - magnetocystalline energy
$E_{elast}$ - magnetoelastic
$E_{exch}$ - exchange energy
$E_{ext}$ - external field energy
$E_{Gibbs}$ - Gibbs free energy
$E_{stat}$ - magnetostatic
$E_{Uni}$ - uniaxial anisotropy energy
$F_{cyl}$ - cylinder form factor
$F_{||}$ - form factor contribution parallel to the cylinder axis
$F_{\perp}$ - form factor contribution perpendicular to the cylinder axis
$F(q,R)$ - form factor
$\vec{H}$ - magnetic field
$h_C$ - coercive field
$h_S$ - switching field
$H_a$ - anisotropy field
$H_C$ - coercive field
$\vec{H}_d$ - magnetic dipole field
$H_{hor}$ - horizontal component of magnetic field
$H_{vert}$ - vertical component of magnetic field
$G(q)$ - Debye-Waller factor
$K_{Uni}$ - uniaxial anisotropy constant
$\vec{M}$ - magnetisation
$M_R$ - remanent magnetisation
$M_S$ - saturation magnetisation
$T$ - temperature
$Z(E)$ - density of states

$Z(q)$ - structure factor

$\chi$ - magnetic susceptibility
Chapter 1

Introduction

At the beginning of 2013 the digital universe, an artificial term which comprises all the
digital data created by humans, was charted and estimated to be \( \approx 4-6 \) zetabytes \((10^{21}
bytes)\) \([47, 65]\). By 2020 it is expected to have increased 10 fold to \( \approx 40 \) zetabytes as
shown in figure 1.1. As a comparison, around the same time the LHC (Large Hadron
Collider) collaboration announced to have collected 100 petabytes of experimental
measurements over the past 20 years (75 petabytes were created in the past 3 years)
and the amount of data is still growing. To avoid data loss and to make the information
accessible to users all data recorded needs to be effectively archived on a long term
storage media. The leading technology for long term storage of vast amount of data is
magnetic recording.

<table>
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Figure 1.1: Estimated amount of generated data as a function of time. In 2013 the
amount of data generated world wide amounts to 4-7 zetabyte. By the year 2020 it will
have reached about 40 zetabyte. Data taken from an IDC report \([47]\).
To keep pace with the increasing demand of storage capacity, magnetic storage technology grew almost exponentially over the past 20 years following Kryder’s law, which describes the gain in hard disk drive (HDD) capacity over time and is similar to Moore’s law for magnetic recording.

In order to record data magnetically the information is digitalised and represented by fundamental binary states of 1’s and 0’s. An estimate of the magnetic stability (stability against magnetisation reversal) can be made by calculating the ratio of the thermal energy $E_{Th}$ ($E_{Th} = k_B T$, with $k_B$-Boltzmann constant, $T$-temperature) over the energy necessary to reverse the magnetisation direction $E_{Aniso}$ ($E_{Aniso} = K_{Uni1} V$, $K_{Uni1}$-uniaxial anisotropy constant, $V$-volume). This ratio is set to 40-60 which corresponds via the Néel-Arrhenius equation ($\tau = \tau_0 \exp(KV/(k_B T))$ with $\tau_0 \approx 10^{-9}$ being the attempt period and $K$ the dominating anisotropy) to a storage time $\tau$ of approximately 10 years. The switching time $\tau(T,K,V)$ is determined by the anisotropy of the magnetic material, the magnetic volume and the ambient temperature. However, in order to increase the areal storage density the indefinite reduction in size of magnetic bits is no practical solution due to ubiquitous thermal fluctuations which would make the magnetic bits unstable towards magnetisation reversal below a certain volume. Magnetic volumes below the threshold of $r_{super} \approx (k_B T/K)^{1/3}$ (derived from Néel-Arrhenius equation) are arbitrarily reversing their magnetisation direction (time scales depend on ambient temperature). This regime of statistical magnetisation reversal is called the superparamagnetic state. To avoid the arbitrary change of magnetisation direction in magnetic bits due to magnetic instability individual artificial three-dimensional magnetic structures (patterned media) can be fabricated each representing 1 bit of information- hence the name bit patterned media (BPM) as illustrated in figure 1.2. In BPM the transitions between individual bits are sharp due to the non-magnetic gaps between the magnetic structures which increase the signal-to-noise ratio (SNR) significantly. With current fabrication (ebeam lithographic) processes areal storage densities of 1-1.5 Tbit/in$^2$ are possible with an ultimate areal density of up to 3-4.5 Tbit/in$^2$ [144, 146].

In order to address individual magnetic structures for read/write purposes accurate positioning of the read/write head is necessary. The window in which a structure can be written is sketched in figure 1.3 a). However, deviations from the ideal lattice position of the structures (shown in b)) or fluctuations in the electron beam during exposure
Figure 1.2: In Bit Patterned Media (BPM) the magnetic grains form an artificial structure with the magnetisation pointing up/down (red arrows) which represents 1 bit. The grains are highly exchange coupled (see inset) thereby increasing the magnetic volume and making it more stable against thermal activation. In order to use bit patterned media as a future high density storage media the artificial structures have to be fabricated with small lateral distance.

which lead to a Gaussian distribution of structure diameters (shown in c)) or combinations of both (shown in d)) can occur during BPM fabrication. These fabrication errors were identified as sources of noise and have a detrimental effect on the SNR, therefore they are extensively studied \[2, 94\]. In order to develop reliable SNR models accurate input parameters of the patterned structures such as mean diameter, diameter distribution and position variance are necessary. To use BPM as a future storage media with several terabit/in\(^2\) recording capacity highly ordered arrays of uniform structures need to be fabricated. A fast and reliable investigation technique needs to be developed and explored which allows to investigate large numbers of nominally identical structures in order to draw statistically significant conclusions of the structural properties of the fabricated BPM. Previous techniques used to study BPM relied on Scanning Electron Microscopy (SEM) investigations of patterned media \[2\], or experiments with a Drag Tester \[79\]. Previous studies usually limited their sampling size to a few hundred individual structures \[2, 94\] - terabit recording, however, comprises \(10^{12}\) individual structures per in\(^2\) which requires a fast and accurate characterisation method. In this work a method is presented using Small Angle X-ray Scattering (SAXS) to determine structural parameters with statistical significance which are key to the recording
performance [2, 94, 112] of Bit Patterned Media such as position variations, diameter variations and the mean diameter.

SAXS is an ideal tool to characterise large ordered arrays of nominally identical nanostructures because the measured scattering pattern contains the collective structural information of a large number of individual structures. A theoretical model can then be fitted to the measured intensity distribution to obtain averaged structural parameters. Due to the simultaneous exposure of a large number of structures the data acquisition time is significantly reduced and measurements with high accuracy are possible.

Figure 1.3: Concept of reading/writing from/to BPM and possible sources of read/write errors. Reading/writing to/from BPM can only be done in narrow read/write window which relies on accurate positioning of the head with respect to the structure as shown in a). Fabrication errors, such as position variation (b)) or diameter variation (c)) or a combination of both (d)), can prevent the correct positioning of the head which leads to read/write errors and decreases the SNR in the medium.
In an effort to combine new magnetic materials and the potential of high areal data storage capacity provided by BPM patterned magnetic hybrid anisotropy samples were investigated. Hybrid magnetic bilayer films, where one layer has perpendicular anisotropy and the other has in-plane anisotropy, have an interface region where the competing anisotropies control the magnetic structure. A sketch of the sample is shown in figure 1.4. The combination of these two layers with orthogonal anisotropies leads to complex domain structure with interesting new properties that were investigated in this work. Existing experimental studies [12, 89] on continuous hybrid films have provided only indirect measurements of mutual domain interactions and concentrated mainly on the altered domain configuration in the layer with in-plane anisotropy. In a second strand of the work presented static and dynamic scanning transmission x-ray microscopy (STXM) experiments on hybrid anisotropy bilayer patterned structures were conducted. STXM with its ability to image magnetic contrast by exploiting x-ray magnetic circular dichroism (XMCD - see chapter 3.1.2), its high spatial resolution and its capability to tune to element specific absorption edges is an ideal research tool to investigate the interaction between the two layers. Furthermore, the experimental set-up allows for time resolved STXM experiments whilst applying a radio frequency (rf) magnetic field.

Figure 1.4: Sketch of patterned hybrid anisotropy bilayer structure. The top layer (Py) has in-plane anisotropy and couples via exchange and dipolar interaction to the bottom Co/Pd out-of-plane layer.
1.1 Aims and Objectives

The first objective of this work was to devise a fast and accurate measurement technique based on SAXS experiments in order to structurally characterize highly ordered arrays of nominally identical nanostructures. As a model system we choose BPM for which the structural characterization is essential in order to achieve the predicted high data recording densities beyond 1 Tbit/in. The structural parameters obtained can in return then be used to optimize the fabrication process or for noise simulations in BPM media.

In a second strand of this work the 3-dimensional domain structure in [Co/Pd]-Py hybrid anisotropy patterned nanostructures is explored through STXM measurements. Hybrid anisotropy systems, in which the magnetisation changes both in magnitude and direction in the layers exhibit magnetic phenomena not observed in individual layers. One of the most prominent features of the system is the ability to support new domain patterns and magnetic vortices. The controlled excitation and manipulation of the vortices is explored and could lead to magnetic vortex oscillators with a potential application as microwave transmitters with remarkable properties such as low power consumption and a narrow bandwidth as compared to conventional devices.
Chapter 2

Theoretical Background of Magnetism

2.1 On The Origin Of Magnetism

Although considered to be of different origin experiments in the 19th century revealed, that electricity and magnetism are indivisibly connected with each other. The theory of electromagnetism expresses this mutual dependence in four equations which are named after James Clark Maxwell who provided a unified theoretical framework to describe these dependencies [25, 96].

\[
\nabla \cdot \vec{E} = \frac{\rho}{\varepsilon} \quad (2.1) \quad \nabla \cdot \vec{B} = 0 \quad (2.2)
\]

\[
\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (2.3) \quad \nabla \times \vec{B} = \mu_0 \vec{J} + \mu_0 \varepsilon \frac{\partial \vec{E}}{\partial t} \quad (2.4)
\]
CHAPTER 2. THEORETICAL BACKGROUND OF MAGNETISM

These four differential equations describe the relation between the magnetic flux density \( \vec{B} \), the electric field \( \vec{E} \) and the current density \( \vec{J} \).

The magnetic flux density \( \vec{B} \) comprises two quantities - the magnetisation \( \vec{M} \) and the magnetic field \( \vec{H} \).

\[
\vec{B} = \mu_0 (\vec{H} + \vec{M})
\]

(2.5)

The proportionality factor relating \( \vec{B}, \vec{H} \) and \( \vec{M} \) is the vacuum permeability \( \mu_0 = 4\pi \times 10^{-7} \text{H/m} \).

The magnetisation describes the macroscopic magnetic dipole density in a magnetic material. Magnetic materials, subject to a magnetic field \( \vec{H} \), will experience changes in the magnetisation \( \vec{M} \), according to:

\[
\vec{M} = \chi(T,H) \vec{H}
\]

(2.6)

with \( \chi \) being the temperature dependent proportionality constant called the magnetic susceptibility. In general \( \chi \) is a function of temperature (T) and magnetic history of the sample. For ferromagnetic samples the susceptibility can be non-linear (due to hysteretic effects) and different definitions for the susceptibility are available e.g. the initial susceptibility \( \chi_0 = (\partial M/\partial H)|_{H=0} \) defined for the virgin curve only where a linear dependence between \( \vec{M} \) and \( \vec{H} \) is assumed.

Changes in \( \vec{M} \) can be attributed to magnetic ordering phenomena on the atomic level in the sample. As a consequence the relation 2.6 can be used to discriminate magnetic materials according to their response to an applied field as shown in figure 2.1.

A graphical representation of equation 2.5 for a ferromagnetic sample is shown in figure 2.2 and is called hysteresis loop. The graph of the magnitude \( \vec{M} \) as a function of applied field \( \vec{H} \) is shown for the magnetic easy axis (orange) and hard axis (blue).

These terms refer to the characteristic M-H loops which can be measured according to the orientation of the field with respect to the preferred axis of magnetisation. The magnetisation of a sample has a preferred axis of orientation in order to minimise the total magnetic energy. If a material parameter (e.g. magnetisation) experiences directional dependence it is said to have anisotropy. If the magnetisation has a preferred orientation along one axis only it is said to be of uniaxial anisotropy and is generally referred to as easy axis. The axis, that requires the highest field to reach the saturation magnetisation, is called the hard axis. The origin of the anisotropy arises from different physical properties (exchange, magnetostatic, magnetoelastic, magnetocrystalline) which will be explained in section 2.2.
2.1. BASIC EQUATIONS

- **Diamagnetism:** The applied magnetic field $\vec{H}$ induces magnetic moments that align antiparallel to the field due to Lenz’s Law.

- **Paramagnetism:** Pre-existing atomic magnetic moments realign in the direction of the field thereby minimizing the total energy. Thermal activation influences the alignment.

- **Ferromagnetism:** Spontaneous long range ordering aligns magnetic moments and creates magnetic domains. Thermal activation influences the ordering—the Curie Temperature ($T_C$) marks the point of vanishing preferential ordering.

Figure 2.1: a) shows the sample magnetisation $\vec{M}$ as a function of applied field $\vec{H}$. According to the sign of the slope ($\chi_0 = \partial M / \partial H$) materials are characterised as para ($\chi > 0$) - or diamagnetic ($\chi < 0$). In paramagnetic materials an increased magnetisation accounts for a higher degree of magnetic ordering as indicated by the alignment of the magnets. For a ferromagnet, magnetisation curves as a function of applied field and temperature are shown in b). Increased temperature causes thermal activation which destroys magnetic ordering (see inset in b)) and alters the M-H loops. Figures after [96].
CHAPTER 2. THEORETICAL BACKGROUND OF MAGNETISM

Figure 2.2: A plot of the magnetisation (\(\vec{M}\)) as a function of field (\(\vec{H}\)) is called a hysteresis loop (M-H loop). Shown are the idealised easy (red curve) and hard (blue curve) axis hysteresis loop. The main hysteresis loop parameter are: saturation magnetisation (\(M_S\)), coercive field (\(H_C\)), remanent magnetisation (\(M_R\)) and the anisotropy field (\(H_a\)). The insets show the energy landscape for the different magnetisation states. In the saturated state, a clear global minimum appears, whereas around \(H_C\) two minima appear separated by an energy barrier.

Pioneering work in the field of magnetism, ferromagnetic materials and M-H loops was conducted by A. Ewing [39].

If a magnetic field \(\vec{H}\) is applied along the easy axis of a completely demagnetised sample (\(\vec{B} = 0, \vec{M} = 0\)) an initial or virgin curve is measured (dashed orange line), whose slope is proportional to the sample’s initial permeability. Magnetic domains oriented along the direction of \(\vec{H}\) will increase in size due to domain wall motion. In an ideal defect-free sample the process of wall motion is reversible. However, if the domain wall passes defects and gets pinned hysteretic losses occur which result in a hysteresis loop. Domains magnetised perpendicular to the field direction have to rotate their magnetisation axis to minimise the Zeeman energy \(E_{\text{ext}} = M \cdot H \cdot \cos(\theta)\). In the fully aligned state the magnetisation reaches saturation (\(M_S\)), which is its maximum value at a given temperature. As the field decreases and becomes negative the reversal process takes place. The magnetisation retained by the sample at \(H=0\) is the remanent magnetisation (\(M_R\)). If the field reverses its direction (negative values) the same process occurs
but with the direction reversed. The field at which $M = 0$ is called the coercive field ($H_C$). In general, $H_C$ is a function of time since the magnetisation $\vec{M}(t)$ is a function of time. If a field is applied in the hard axis direction neither coercivity nor remanence are observed. Here, the magnetisation increases linearly as a function of applied field $H$ until a saturation value is reached. In materials with a single easy axis of magnetisation an important parameter to deduce from the hard axis loop is the anisotropy field $\vec{H}_a$. The anisotropy field can be determined geometrically as the point of intersection between the linear fit of the saturation magnetisation ($M_S$) and the slope of the hard axis loop (green lines). This method can be used to determine the uniaxial anisotropy constant ($K_{Uni1}$) if $M_S$ is known. A mathematical description of how to calculate the anisotropy field is given in subsection 2.2.2.

The first to describe a theoretical model of the underlying magnetic reversal mechanism were E.C. Stoner and E.P. Wohlfarth (SW-model) [123]. The SW-model is a zero temperature model assuming an ellipsoidal shaped single domain grain with a spatially uniform magnetisation. Furthermore, the magnetic body is required to have uniaxial anisotropy and the magnetisation to rotate coherently [126]. In its simplest form the free energy of the magnetic body is determined only by the Zeeman energy $E_{ext}$ (external field energy) and the uniaxial anisotropy energy $E_{Uni}$ (a single preferred axis of magnetisation approximated by a first-order series expansion):

$$E = E_{ext} + E_{Uni} = K_{Uni1} \sin^2(\theta) - H M_S \cos(\theta - \phi)$$

(2.7)

The parameters $\theta$ and $\phi$ refer to the angles between the direction of the easy axis and the magnetisation, and applied field respectively $K_{Uni1}$ is the uniaxial anisotropy constant. For reference a model outlining the parameters employed is sketched in figure 2.3 inset a). In order to find the energy minimum the value of $\theta$ for $\frac{\partial E}{\partial \theta} = 0$ and $\frac{\partial^2 E}{\partial \theta^2} > 0$ is computed. To normalise the results they are expressed in reduced units of $m = \frac{M}{M_S}$ and $h = \frac{H}{H_a}$. The initial two minima change with increasing field magnitude to one minimum after exceeding the switching field $h_C$ marked by a horizontal slope in the energy curve plot inset b). The red and blue curve in figure 2.3 show the two branches of the M-H loop. The field is applied at an angle of $45^\circ$. The arrows symbolise the point of switching. Here the magnetisation jumps from one energy minimum (solid curve) to the next and thereby reverses.

The orientation of the applied field can be varied and various hysteresis loops can be calculated with the SW-model. Figure 2.4 shows the calculated loops for $\phi = 0^\circ, 30^\circ, 60^\circ, 90^\circ$. The case $\phi = 90^\circ$ corresponds to a hard axis hysteresis loop, in which
the curve is a linear function of the applied field until saturation is reached. To align with the field the magnetisation rotates coherently and reversibly. The coercive field \( h_C \), for which \( m=0 \), and the switching field \( h_S \), defined by \( \frac{\partial h}{\partial m} = 0 \), are calculated as follows:

\[
h_S = \left( \cos^2(\phi) + \sin^2(\phi) \right)^{-\frac{3}{2}}
\]

\[
h_C = \sin(\phi) \cos(\phi)
\]  

(2.8)  

(2.9)

The angular dependence of \( h_S \) and \( h_C \) are shown in figure 2.5. The minimum switching field (half the anisotropy field) is reached at an field angle of \( \phi = \pi/4 \). Above \( \phi = \pi/4 \) the magnetisation passes through zero (thereby defining \( h_C \)) before switching occurs as seen in figure in 2.4 (the blue hysteresis curve of \( 60^\circ \)). Below \( \phi = \pi/4 \) the magnetisation switches before passing through zero as seen in the green hysteresis curve (\( 30^\circ \)) in figure 2.4 and therefore no coercive field is defined below an applied field angle of \( \pi/4 \).
2.1. BASIC EQUATIONS

Figure 2.4: Calculated hysteresis loops using the Stoner-Wohlfarth model for various applied field angles (0°, 30°, 60°, 90°) as a function of normalised field magnitude $h$.

Figure 2.5: Normalised switching field $h_S$ and coercive field $h_C$ as a function of applied field angle $\phi$. Below an applied field angle of $\pi/4$ the magnetisation does not reduce to zero before switching occurs therefore $h_C$ is only defined above. Above an applied field angle of $\pi/4$ the magnetisation passes through zero before switching and $h_C$ is defined. At $\pi/4$ $h_S$ assumes its minimal value which is half the anisotropy field. The values for the easy and hard axis direction are at 0 and $\pi/2$. 
2.2 Magnetic Energy Terms

In its simplest implementation the Stoner-Wohlfarth model took only two magnetic energy terms into consideration (uniaxial anisotropy \( E_{\text{Un}} \) and Zeeman energy \( E_{\text{ext}} \)), but was thereby able to describe a wide variety of physical behaviour. However, in real material consisting of isolated randomly shaped particles, additional magnetic energy contributions need to be considered. The total magnetic energy (Gibbs Free Energy \( E_{\text{Gibbs}} \)) is a sum of four different energy terms:

\[
E_{\text{Gibbs}} = E_{\text{exch}} + E_{\text{aniso}} + E_{\text{stat}} + E_{\text{elast}}
\]  

The energy terms are the exchange \( E_{\text{exch}} \), the magnetocystalline \( E_{\text{aniso}} \), the magnetostatic \( E_{\text{stat}} \) and the magnetoelastic \( E_{\text{elast}} \) energy. Energy minimisation of the sum in equation 2.10 allows the magnitude and direction of the magnetisation of a sample to be deduced. In the following subsections the different energy terms will be explained briefly.

2.2.1 The Exchange Energy

The exchange interaction is a quantum mechanical phenomenon acting between neighbouring atoms with overlapping electron wave functions. The Pauli principle states, that two electrons cannot assume the same quantum mechanical state (be identical in all 4 quantum numbers \( n, l, m_l, s_z \)). For localised electrons in a molecule (e.g. \( \text{H}_2 \)) the total two electron wave function \( \psi \) can be split up into a spatial \( \phi \) and a spin \( \chi \) function:

\[
\psi(1,2) = \phi(r_1, r_2) \cdot \chi(s_1, s_2)
\]  

Since electrons are fermions, the total electron wave function has to be antisymmetric. Spatial and spin wave function, can be antisymmetric or symmetric, but in order to yield an antisymmetric total wave function only the following combinations are allowed:

\[
\psi_1 = \phi_s(r_1, r_2) \cdot \chi_a(s_1, s_2) \quad (2.12a)
\]
\[
\psi_2 = \phi_a(r_1, r_2) \cdot \chi_s(s_1, s_2) \quad (2.12b)
\]
2.2. MAGNETIC ENERGY TERMS

The subscripts denote the symmetric (s) or antisymmetric (a) functions. The total energy can be calculated as follows:

\[
E_{tot} = \int \phi_{s,a}^*(r_1, r_2) H(r_1, r_2) \phi_{s,a}(r_1, r_2) \, dr_1^3 \, dr_2^3 \tag{2.13}
\]

with \( H \) being the two electron Hamiltonian and \( \phi_{s,a} \) being the spatially symmetric (s) or antisymmetric (a) wave function.

The exchange energy (\( J \)) is calculated as follows:

\[
J_{ii} = \int \phi_i^*(1) \phi_j^*(2) \frac{e^2}{4 \pi \varepsilon_0 r_{12}} \phi_i(1) \phi_j(1) \, dr_i^3 \, dr_j^3 \tag{2.14}
\]

with \( \phi_i \) being the single electron wave functions and \( r_{12} \) the relative separation between the electrons. Dependent on the sign of the exchange energy the total energy is:

\[
E_{tot} = E_0 \pm J \tag{2.15}
\]

For the spatially symmetric solution the spin function must be antisymmetric which means anti-parallel alignment of spins (antiferromagnetism) and an exchange energy \( J < 0 \). Conversely, for the spatially antisymmetric solution the spin function must be
symmetric which means parallel alignment of spins (ferromagnetism) and an exchange energy $J > 0$. Both solutions of the wave function are illustrated in figure 2.6.

The antisymmetry of the wave function, as postulated by the Pauli exclusion principle, can be included in the Hamiltonian by adding an additional term which describes individual spin-spin interactions:

$$H = -2 \sum_{i>j} J_{ij} \vec{S}_i \cdot \vec{S}_j,$$  \hspace{1cm} (2.16)

with the dimensionless spin operators $S$ and the exchange integral $J$.

Equation 2.16 is known as Heisenberg Hamiltonian and can be simplified by taking only nearest neighbour interactions into account from a fixed atom which yields:

$$E_{exch}^i = -2JS_i \sum_j \vec{S}_j.$$  \hspace{1cm} (2.17)

Equation 2.16 can be simplified further by using $\vec{S}_i \cdot \vec{S}_j = S_i \cdot S_j \cdot \cos(\theta_{ij})$ and a subsequent Taylor-series expansion of the spin-angle yields $E_{exch} = JS^2 \sum_i \theta_{ij}^2$. A continuous solution can be derived by expressing the change of spin angle $\theta_{ij}$ between adjacent atoms as $\partial \theta / \partial x = \nabla \theta$. The change of spin direction is equivalent to the change of the normalised magnetisation $\nabla M$ which gives for the exchange energy:

$$E_{ex}^{ij} = VA \left( \frac{\partial \theta}{\partial x} \right)^2 = A \cdot V \left( \frac{\nabla M}{M} \right)^2$$  \hspace{1cm} (2.18)

Here $A = \frac{2JS^2}{a}c$ is the exchange stiffness constant ($a$ is the lattice parameter and $c$ the number of nearest neighbour atoms) and denotes the stiffness of coupling between adjacent spins, $V$ is the volume considered and $M$ the magnetisation. Typical values for $A$ in a ferromagnet are $1 - 2 \times 10^{-11} J/m$.

In 3d metals (e.g. Cobalt, Iron, Nickel) the discrete energy levels of electrons, which naturally arise from the Schrödinger equation, turn into a band structure as shown in figure 2.7 a). The 4s states get filled first completely because they have a lower energy state as seen in figure 2.7 a). In order to minimise the energy of the atomic lattice the exchange interaction can cause a preferential spin orientation in half filled bands. This is illustrated in figure 2.7 b). Exchange interaction causes a shift of the spin polarised density of state (Z(E)) between the spin up ($Z_\uparrow$) and spin down ($Z_\downarrow$) subbands. Thereby more states are available to one spin orientation which gives rise to
2.2. MAGNETIC ENERGY TERMS

Figure 2.7: Development of energy bands with decreasing interatomic distance (a) and, as a consequence of that, the energy shift of spin polarised density of states due to exchange coupling (b)). The 4s energy level is lower in energy compared to the 3d level and reaches farther out spatially. Therefore splitting of the 4s energy band occurs at larger interatomic distances. In 3d metals interatomic exchange interaction causes a spin polarisation and energy shift of the density of states (b)) which leads to a spin imbalance causing a net magnetic moment and ferromagnetic behaviour.

a net spin moment and to ferromagnetism. For instance in Nickel which has 10 valence electrons of which 0.6 electrons are nonlocalised ($4s^{0.6}$) and can be considered as free. The remaining electrons are distributed over the $3d^{9.4}$ state. The $3d^\uparrow$ (spin up) subband is filled completely with 5 electrons and the $3d^\downarrow$ (spin down) subband is filled with 4.4 electrons. This imbalance gives rise to the ferromagnetic behaviour encountered in Nickel [96].
2.2.2 The Magnetocrystalline Energy

The energy dependence of the orientation of magnetisation relative to the crystal axes is called magnetocrystalline anisotropy. The reason for anisotropic behaviour can be attributed partially to the interaction between the crystal field and the electron orbitals, which will lead via spin-orbit coupling to a preferred orientation of magnetisation. This interaction strongly reflects the underlying crystallographic symmetry. Figure 2.8 shows the crystal lattice and magnetisation curves as a function of crystallographic direction for two prominent ferromagnetic elements relevant to this work.

![Figure 2.8: The crystal lattice of Nickel (a)) and Cobalt (c)) with the hard (red) and easy axis (green) of magnetisation shown. The corresponding M-H loops measured along different crystallographic axes (b)) and (d)) show the dependence of the curves from the crystal lattice orientation. Data taken from [96]](image)

As can be seen in figure 2.8 b) and d) one direction of magnetisation saturates much faster and at lower fields compared to all other directions. This axis of magnetisation is called the magnetic easy axis (see section 2.1). For face centred single crystal Nickel it is the [111] direction and for hexagonal single crystal Cobalt the [0001] direction. Conversely, the direction which requires the highest magnetic field to saturate the sample is called the hard axis.
2.2. MAGNETIC ENERGY TERMS

The magnetocrystalline anisotropy energy can be expressed as a series expansion of orthonormal spherical harmonics [25, 96].

\[
E_a = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} k_l A_l^m Y_l^m(\alpha)
\]  

(2.19)

Here \(k_l\) defines the anisotropy constant, \(A_l^m\) is a coefficient to account for the crystal point group symmetry, \(Y_l^m\) are the spherical harmonic functions with the argument \(\alpha\) being the directional cosine. The invariance of energy terms under symmetry operations of the considered crystal lattice allow for the exclusion of energy terms which violate this rule. Since the magnetocrystalline energy has to be invariant against 180° rotation, the sum takes only even powers into account. Simplification of the sum 2.19 leads to expressions for hexagonal and cubic crystal lattices:

Hexagonal: \(E_{a}^{\text{hex}} = k_0 + k_2^0 \left( \alpha^2 - \frac{1}{3} \right) + k_4^0 \left( \alpha^4 - \frac{6}{7} \alpha^2 + \frac{3}{35} \right) + \ldots \)  

(2.20)

, assuming \(\alpha = \cos(\theta)\), with \(\theta\) being the polar angle in spherical coordinates.

Cubic: \(E_{a}^{\text{cub}} = k_0 + k_4^1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2 - \frac{1}{5}) + \) 

\[k_6^2(\alpha_1^2 \alpha_2^2 \alpha_3^2 - \frac{1}{11}(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2 - \frac{1}{5}) - \frac{1}{105}) + \ldots \)  

(2.21)

here \(\alpha = (\sin(\theta) \cdot \cos(\phi), \sin(\phi) \cdot \sin(\theta), \cos(\theta))\) with \(\theta = \pi/2\).

The uniaxial anisotropy energy density can be described in a power series expansion of the following form:

\[
E_{\text{uni}} = \sum_n K_{\text{Uni}n} \sin^{2n} \theta = K_{\text{Uni}0} + K_{\text{Uni}1} \sin^2(\theta) + \ldots
\]  

(2.22)

with \(\theta\) being the angle between the magnetisation direction and the easy axis. The zero order term is isotropic since no angular dependence is included. For most materials taking the expansion to the first order provides an accurate description of the effects of magnetocrystalline anisotropy. The following relations exist between the different anisotropy coefficients:

\[
k_2 = -K_{\text{Uni}1} - \frac{8}{7} K_{\text{Uni}2}
\]  

(2.23)

\[
k_4 = K_{\text{Uni}2}
\]  

(2.24)
with $K_{Unin}$ being the uniaxial anisotropy constants and $k_i$ being the anisotropy constant from the spherical harmonics series expansion. The calculated first-order anisotropy energy surfaces for fcc nickel and hcp cobalt (uniaxial anisotropy) with their hard and easy axis are shown in figure 2.9.

The calculated energy surface for fcc Nickel is a deformed prolate spheroid. The anisotropy constants were set to: $K_0 = 3$ and $K_1 = -4.5$.

The calculated energy surface for hcp Cobalt is an oblate spheroid. The anisotropy constants were set to: $K_{Uni0} = 2$ and $K_{Uni1} = 4.1$.

Figure 2.9: Calculated anisotropy energy surfaces for hcp Cobalt and fcc Nickel. No temperature effects have been taken into account and only first order terms from equation 2.21 and 2.20 have been considered. The energy minima/maxima indicated by a green/red line correspond to the crystallographic axes of high/low anisotropy and reflect the lattice symmetry.

The magnetic energy needed to saturate the sample in the direction of the hard axis is composed of the Zeeman energy and the uniaxial magnetocrystalline anisotropy (first-order approximation) and calculates as follows:

$$E = K_{Uni 1} \sin^2(\theta) - \mu_0 M_s H \sin(\theta)$$  \hspace{1cm} (2.25)$$

Taking $\frac{\partial E}{\partial \theta} = 0$ and setting $\theta = \frac{\pi}{2}$, for a fully saturated sample along the hard axis, yields:

$$H_a = \frac{2 K_{Uni 1}}{\mu_0 M_S}$$  \hspace{1cm} (2.26)$$

Here the anisotropy field $H_a$ has been derived mathematically as compared to the hysteresis loop in figure 2.2, in which the anisotropy field was found graphically as the point of intersection between the linear slope of the hard axis loop and the saturation magnetisation.

The values for the magnetic anisotropy constants $K_1$ and $K_2$ at room temperature (300 K) and 4.2 K for selected materials are shown in the table 2.1.
In order to explain the origin of magnetocrystalline anisotropy crystal field and spin-orbit interactions need to be taken into account. The interaction between the electric field, originating from neighbouring atoms (crystal field), in conjunction with the electron orbitals gives rise to the magnetocrystalline anisotropy. For ferromagnets such as Co and Ni the 3 d electrons determine the magnetic properties. However, for qualitative investigations and for simplification of the crystal field model we consider an atom with a p-orbital ($l=1$) in a uniaxial crystal electric field of two positively charged ions (below and above the atom) along the $z$ direction as visualised in figure 2.10.

Figure 2.10: Angular probability density functions ($|Y_l^m|^2$) of electrons with $l=1$ (p-orbitals) and $m_l=-1, 1, 0$ ($p_x, p_y, p_z$) as seen in a),b),c). The colour coding refers to the positive (red) or negative (blue) part of the axis on which the function $|Y_l^m|^2$ is plotted.

The $p_x$ and $p_y$ orbitals are less affected by the axially symmetric charge distribution since they are further away than the $p_z$ orbital. The symmetry of the charge distribution
CHAPTER 2. THEORETICAL BACKGROUND OF MAGNETISM

lifts the 3 fold degeneracy of the \( l=1 \) orbital lowering the energetic state of the \( p_z \) orbital but leaving the \( p_x \) and \( p_y \) orbitals in a higher, but still degenerate, energy state as sketched in figure 2.11.

![Figure 2.11: Degeneracy lifting of energy levels with \( l=1 \) and \( m_l = -1,0,1 \) due to an intrinsic crystal field.](image)

Due to the splitting of energy levels a directional preference for certain orbitals (\(-l \geq m_l \geq l\)) will occur. Since the orbital momentum couples to the spin via the spin-orbit coupling:

\[
E = \frac{\mu_0 Z e^2}{4 \pi m_e^2 r^3} \left( \vec{s} \cdot \vec{l} \right),
\]

the magnetic moment takes on a directional preferences.

A theoretical calculation from first principles regarding the anomalous perpendicular anisotropy found in Co layers on Au has been published by Újfalussy et al. [132]. Here, the perpendicular magnetic anisotropy can be attributed to changes in the sp-d hybridization at the Co-Au layer interface. The effect is strongest at a coverage of 1-2 atomic mono layers. Engel et al. used in situ Kerr measurements to investigate the perpendicular anisotropy energy in Co-X (X=Au, Pd, Cu) films and found the strongest perpendicular effect for coverages of around 1 atomic layer [37] which is in good agreement with theory.

### 2.2.3 The Magnetostatic Energy

For the magnetostatic case, with current density \( j=0 \), a scalar magnetic potential \(-\nabla \phi_m = \vec{H}\) can be defined similar to the electrical potential, which satisfies the Maxwell-Ampere equation \( \nabla \times \vec{B} = \mu_0 \nabla \times -\nabla \phi_m = 0 \). By using Maxwell equation 2.2 the divergence can be rewritten as \( \nabla \cdot \vec{B} = \mu_0 \nabla \cdot (\vec{H} + \vec{M}) = 0 \). Substituting the magnetic potential for the magnetic field \( \vec{H} \) yields:

\[
\nabla^2 \cdot \phi_m = -\nabla \cdot \vec{M}
\]

(2.28)
Equation 2.28 states, that the magnetisation at discontinuities of a magnetic material acts as a source for a magnetic dipole field ($\vec{H}_d$). This field is also referred to as demagnetisation or stray field and is oppositely orientated to $\vec{M}$ and $\vec{B}$. A three-dimensional model sketching the relationship between $\vec{H}_d$, $\vec{H}$ and the magnetic charges is shown in figure 2.12. As a consequence of $\vec{H}_d$ counteracting the applied field, the internal field, to which $\vec{M}$ responds will be weakened. The distribution of magnetic surface charges in the sample determines $\vec{H}_d$, therefore, it will be a function of magnetisation orientation and position within the sample.

Figure 2.12: Magnetic fields inside a magnetic body. The magnetic flux lines of the $\vec{B}$ field are closed due to Maxwell’s equation 2.2. The magnetic charges which act as sources of the demagnetisation field can be represented by blue/red spheres on top and bottom of the body. The demagnetisation field $\vec{H}_d$ is oppositely orientated to the $\vec{B}$ field.

The field inside the body can be calculated for an arbitrary direction using:

$$H_i = H_{appl} - NM \quad (2.29)$$

where the last term describes the contribution from the demagnetisation field. The proportionality constant $N$ is called demagnetisation factor. In general, $N$ will depend on the sample shape and magnetisation direction and will therefore be a demagnetisation tensor. Exact calculations of $N$ can only be done for samples shaped as an ellipsoid of revolution. In a ellipsoidal sample exposed to a uniform field, oriented with one of its principal axes along the field, $N$ will be diagonal and the magnetisation will be
antiparallel to $\vec{H}_d$ and uniform in the sample. For a sphere, an infinitely long cylinder or an infinite plane, with the magnetisation pointing along one of the major axis, exact demagnetisation factors can be calculated as given in table 2.13. For all other shapes an effective $N$ can be approximated.

<table>
<thead>
<tr>
<th>Shape</th>
<th>$\frac{1}{3}$</th>
<th>$0$</th>
<th>$\frac{1}{2}$</th>
<th>$1$</th>
<th>$0$</th>
</tr>
</thead>
</table>

Figure 2.13: Demagnetisation factors for a sphere, an infinite cylinder and an infinite plane. The arrows indicate the direction of magnetisation for which the corresponding demagnetisation factor is given above. In order to minimize the total energy some magnetisation directions are preferred compared to others. For the infinite cylinder and plane the magnetisation directions for which the demagnetisation factor becomes zero are preferred.

The creation of the demagnetisation field costs energy which can be calculated for a single-domain particle with known demagnetisation factor as follows:

$$E_{stat} = -\vec{M} \vec{H}_d V$$

(2.30)

As seen in figure 2.13 some magnetisation directions have little or no demagnetisation factors giving rise to a preferred orientation of magnetisation. This preference of the magnetisation axis on the basis of shape is called shape anisotropy. The field, is defined as the difference in demagnetisation factors for two perpendicular directions.

$$H_{shape} = M (N_1 - N_2)$$

(2.31)

As a consequence from the magnetic surface charges a magnetic stray field arises from a magnetic sample. In order to minimise the stray field energy the uniformly magnetised sample can break up into regions (domains) with antiparallel magnetisation.

### 2.2.4 The Magnetoelastic Energy

Ordering effects, present in magnetic samples such as exchange, dipolar or crystal field interactions, can lead to alterations in the sample dimensions, so called magnetostrictive effects. Also induced ordering due to an applied magnetic field can lead to changes
in the lattice dimensions as shown in figure 2.14 a) and b). The magnetostrictive strain in a sample can be calculated as follows:

\[ e = \frac{\Delta l}{l} = \frac{3}{2} \lambda_S \left( \cos^2(\theta) - \frac{1}{3} \right) \]  

(2.32)

The strain \( e \) is measured at an angle \( \theta \) with respect to the saturation magnetisation direction. The saturation magnetostriction coefficient \( \lambda_S \) describes the strain on changing the direction of magnetisation in the saturated state.

![Figure 2.14: Magnetoelastic contributions from an isotropic ferromagnetic sample (a)). b) and c): Field induced magnetic alignment which causes a sample deformation. d) and e): Stress induced magnetic anisotropy due to an alignment of elementary magnets resulting in a preferred net magnetisation direction.](image)

The inverse effect happens when stress is applied (\( \sigma \)) such as a lattice mismatch in a multilayer sample or physical compression/tension which in turn leads to a preferred magnetisation direction as illustrated in figure 2.14 d) and e). This effect is called stress induced magnetic anisotropy. The magnetoelastic energy density can be expressed as:

\[ E_{med} = -\lambda_S \sigma \frac{3}{2} \left( \cos^2(\theta) - \frac{1}{3} \right) \]  

(2.33)

with the uniaxial anisotropy constant being: \( K_u = \frac{3}{2} \lambda_S \sigma \).
2.3 Volume and Surface Anisotropy

In order to be able to predict the direction of magnetisation in a thin film sample a simple model can be devised. An effective anisotropy can be defined as the weighted average of the volume and the surface anisotropy [30, 63], regardless of their origin.

\[ K_{\text{eff}} = K_v + 2 \frac{K_S}{t} \]  

(2.34)

By convention, the term \( K_S/t \) (with \( t \) being the monolayer thickness) describes the difference in anisotropy between the interface and the bulk atoms. A plot of the effective anisotropy as a function of Cobalt layer thickness for a Co/Pd multilayer sample is shown in figure 2.15. A threshold value can be defined (\( t_\perp = -2 \frac{K_S}{K_v} \)) below which the effective anisotropy is perpendicular to the film plane. Above the threshold of \( t_\perp \) the effective anisotropy is orientated in-plane.

![Figure 2.15: Effective anisotropy \( K_{\text{eff}} \) of a \([\text{Co}(t \text{Å})/\text{Pd}(11\text{Å})]\) multilayer sample as a function of Co interlayer thickness. Below interlayer thicknesses of around 1.3 nm the anisotropy will be perpendicular to the film plane, above in-plane. Data taken from [30].](image)

Anisotropy values for [Co/Pd] and [Co/Pt] multilayers are shown in table 2.2. A review about the different anisotropy contributions on various single and multilayer films (growth directions, substrates and deposition techniques) can be found in [63, 134].
2.4 Magnetic Domain and Domain Walls

Macroscopic magnetic samples have been investigated with imaging techniques which revealed that the samples are non-uniformly magnetised and subdivided in areas with different magnetisation direction. A magnetic domain is a region of the magnetic sample where the magnetisation is uniform in direction and magnitude. In general domain sizes are in the order of 1-100 \( \mu m \) [4, 11, 96].

Figure 2.16 illustrates the evolution of magnetic domains. Here magnetic domains form as a consequence of minimising the magnetostatic energy in a finite, uniformly magnetised sample. In a) the uniformly magnetised sample has surface poles according to \( \vec{M} \cdot \vec{n} \). The magnetostatic energy density is given by: \( w = \frac{\mu_0}{2} \cdot M^2 \) [101]. The single domain from a) is subdivided into oppositely magnetised multidomains in b) and c). The magnetic field lines emanating from the ends of the sample form closed loops with adjacent domains due to oppositely magnetised ends. Given N being the number of domains, with each subdivision the magnetostatic energy in the saturated state is reduced by \( 1/N \) [70]. The process of domain formation continues until the creation of an additional domain costs more energy than can be gained by reducing the magnetostatic energy. In order to minimise the magnetostatic energy further in samples with negligible anisotropy or cubic anisotropy the magnetisation can form an in-plane flux closure domain (Landau pattern) as shown in d). In this domain configuration the magnetisation aligns parallel to the edges of the structure which allows for a stray-field free magnetisation pattern with negligible magnetostatic energy.

A special case of in-plane flux closure where the direction of magnetisation continuously rotates throughout the sample around an out-of-plane centre is the vortex state. In this configuration the magnetostatic energy contribution to the total energy can be

<table>
<thead>
<tr>
<th>Table 2.2: Surface and volume anisotropy values for selected multilayer compositions: Values taken from 1. Purcell et al. [104], 2. Draaisma et al. [33] and 3. Harzer et al. [56].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Layer</strong></td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>([Co/Pd]-wedge)</td>
</tr>
<tr>
<td>([Co/Pd(111)]_n)</td>
</tr>
<tr>
<td>([Co/Pt(111)]_n)</td>
</tr>
</tbody>
</table>
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Figure 2.16: The evolution of magnetic domains. As long as the reduction in magnetostatic energy outweighs the increase due to domain wall energy the uniformly magnetised sample will break up in magnetic domains as shown in a)-c). In d) the magnetic flux is confined within the sample and no magnetic charges exist at the sample surface. Figure after [96].

neglected because no magnetic stray-field is created due to parallel alignment of the magnetisation with respect to the edges of the structure - however the core with its strong out-of-plane component is highly energetic. A parameter often used to characterise magnetic domains is the quality factor $Q$ defined as the ratio between the dominant anisotropy term in the sample and the maximum energy density which is usually the stray field energy density $E_{stat}$ [60]. Figure 2.17 shows a simplified phase diagram of different magnetic domain pattern configurations as a function of the structure size. The diagram represents the results obtained from micromagnetic simulations [109] based on cubic particles with uniaxial anisotropy. In order to enable the formation of a vortex sample dimensions must be comparable or smaller than the width of a domain wall. This prevents the formation of a multidomain state since no domain wall can form. Conversely, to avoid a single domain state the sample dimensions have to be reasonably large to minimise the ordering effects of the demagnetisation field. The competing magnetisation processes in the formation of multidomain and single domain state allow the formation of a vortex only for a narrow size region as shown in figure 2.17. The solid lines in figure 2.17 separate the regions in which the preferred formation of a single, vortex and multidomain take place.

The boundary separating neighbouring domains is called a domain wall. In general, the width of a domain wall is between 10-100 nm [96] with an associated energy density of

47
approximately 1 $mJ/m^2$ [96]. Domain wall formation is a complex process, that seeks to minimise the energy necessary to change the orientation of magnetisation between domains. Due to the complicated nature of domain wall formation a large number of different domain wall types have been identified [60]. However, two idealised wall types can be identified (Bloch and Néel domain wall) which are essential to understand. In the following subsection these two types of domain wall are briefly highlighted.

### 2.4.1 Bloch Walls

A domain wall, in a uniaxial magnetic sample, which separates two antiparallel magnetised domains by a 180° domain wall is called a Bloch wall in recognition of Flex Bloch who first described this type of three-dimensional domain boundary [10]. Following Bloch’s initial work, Landau and Lifshitz contributed with theoretical considerations to the description of a Bloch domain wall [78].

An abrupt change of magnetisation across the wall (at the atomic lengthscale) would reduce the anisotropy energy ($E_{\text{aniso}}$) but at the expense of an increase in exchange energy ($E_{\text{exch}}$). In order to minimise contributions from both energy terms the angle of magnetisation rotates through the plane of the wall gradually until the magnetisation is reversed as seen in figure 2.18. To calculate the domain wall width and energy density,
the sum of the energy terms must be minimised:

\[ E_{Bloch} = E_{exch} + E_{aniso} \approx J S^2 \frac{\pi^2}{Na^2} + K_{Uni} Na \]  \hspace{1cm} (2.35)

Here N is the number of atomic sites (in the order of \(10^4 - 10^5\)) in the domain wall and a is the atomic spacing as illustrated in figure 2.18. The exchange term has been already explained in section 2.2.1. However, for simplicity the term \(\cos(\theta_{i,j})\) in the exchange energy, with \(\theta_{i,j}\) being the canting angle between adjacent spins, has been approximated by a first order Taylor series expansion. Assuming that the domain wall spreads out over N atomic sites and a fixed relative canting angle between neighbouring spins the angle \(\theta_{i,j}\) in equation 2.35 can be approximated be \(\pi/N\). Solving equation 2.35 for the domain wall width Na yields:

\[ \delta_{BW} = Na \approx \sqrt{\frac{JS^2 \pi^2}{K_u a}} = \pi \sqrt{A/K_u} \]  \hspace{1cm} (2.36)

which corresponds to the wall thickness. Substituting expression 2.36 in equation 2.35 gives the wall energy density of \(E_{Bloch} \approx 2\pi\sqrt{AK_{Uni}}\). A denotes the exchange stiffness constant and \(K_{Uni}\) the uniaxial anisotropy constant.

To calculate the orientation of magnetisation as a continuous function of position throughout the domain wall the variation of equation 2.35 is calculated. Minimising the variation is equivalent to solving the Euler equation:

\[ \frac{\partial f_a(\theta)}{\partial \theta} - 2A \frac{\partial^2 \theta}{\partial z^2} = 0 \]  \hspace{1cm} (2.37)

Here \(f_a(\theta)\) is the anisotropy energy, which can be simplified in the uniaxial case by substitution of: \(\frac{\partial}{\partial \theta} f_a(\theta) = K_{Uni} \sin^2(\theta)\), \(z\) being the Cartesian axis perpendicular to the domain wall and \(\theta\) the spin canting angle. This yields the following solution for the differential equation 2.37:

\[ \theta(z) = 2 \arctan \left( \exp \left( \frac{\pi z}{\delta_{BW}} \right) \right) \]  \hspace{1cm} (2.38)

with \(\delta_{BW}\) being the solution of equation 2.36. The solution 2.38 is plotted in figure 2.18 (red curve). The domain wall thickness (\(\delta_{BW}\), black horizontal arrow) can be defined by the intersection of the linear fits of equation 2.38 as shown by the dashed line representing the fits. The blue curve represents the change of magnetisation direction.
2.4. MAGNETIC DOMAIN AND DOMAIN WALLS

Figure 2.18: Simulation and visualisation of a 180° Bloch domain wall. The background plane shows the simulation of the relative magnetisation canting angle as a function of position (red) and its first derivative (blue). Equation 2.38 was used for the calculation for Cobalt with $A = 10^{-11} \text{J/m}$ and $K_{Uni} = 410 \times 10^3 \text{J/m}^3$. Mathematically, the wall thickness $\delta_{BW}$ is defined as the intersection of the linear fits (indicated dashed black lines). The spins (arrows) rotate with the canting angle $\theta_{ij} \approx \pi/N$ over the width $\approx N \cdot a$, with N being the total number of spins involved. For a Bloch wall the spins rotate through the plane of the wall as a guide for the eye the plane of rotation is indicated by a red solid circle.

as a function of position (first derivative of equation 2.38). The domain wall calculation was carried out for uniaxial Cobalt with an exchange constant of $A = 10^{-11} \text{J/m}$ and an anisotropy constant of $K_{Uni} = 410 \times 10^3 \text{J/m}^3$.

2.4.2 Néel Walls

In section 2.2.3 it was shown that the film thickness has a strong influence on the magnetostatic energy. In bulk material, where the surface poles originated due to Bloch wall formation, the magnetic charges are far enough apart to have only little effect on the total energy of the magnetic system. With shrinking dimensions, the surface poles get closer together and the magnetostatic energy contribution becomes more pronounced [114]. Beyond a critical thickness (see figure 2.20 a)) it is energetically more
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Figure 2.19: Section of a magnetic body with in-plane anisotropy. Visualisation of the evolution of spins across a 180° Néel domain wall. The single spins (arrows) rotate with the canting angle $\theta_{ij} \approx \pi/N$ over the wall width $\approx N \cdot a$, with $N$ being the total number of spins involved. The spins rotate in plane of the domain wall (symbolised by red solid circle) building up magnetic charges inside the magnetic body.

favourable for the magnetisation to rotate 90° in the plane of the sample and to form a Néel wall [59, 90]. The name refers to L. Néel in honour of his pioneering work in the field of magnetism. The planar rotation of spins causes magnetic volume poles to occur inside the film at the interface with neighbouring domains. The Néel wall energy density decreases with shrinking film thickness because the area density of surfaces charges is proportional to the interface area, whereas the energy density for the Bloch wall increases due to an increase in magnetostatic energy from the surface poles coming closer together (see figure 2.20 a)).

The wall width of Néel walls increases strongly with decreasing film thickness in order to separate the volume charges from another, whereas the Bloch wall width almost remains unchanged (see figure 2.20 b)).

To derive expressions for the wall thickness and the energy density the following energy terms have to be taken into account: $E_{\text{aniso}}$, $E_{\text{exch}}$, $E_{\text{stat}}$, yielding the following
2.4. MAGNETIC DOMAIN AND DOMAIN WALLS

energy density for a Néel:

\[
E_{Ne} = K_{Uni} \frac{\delta_{NW}}{2} + A \frac{\pi^2}{\delta_{NW}} + \left(2\mu_0 M^2\right) \frac{\delta_{NW}}{\pi} \arctan\left(\frac{t}{\delta_{NW}}\right) \tag{2.39}
\]

Minimising equation 2.39 with respect to \( \delta_{NW} \) and taken the thin film limit approximation (\( t/\delta_{NW} \approx 1 \)) into account with \( t \) being the film thickness, the Néel wall width \( \delta_{NW} \) and the Néel wall energy density are calculated as follows:

\[
E_{NW} \approx \pi t M_S^2 \quad (2.40) \\
\delta_{NW} \approx \pi \sqrt{\frac{2A}{K}} \quad (2.41)
\]

Theoretical calculations [69] and experimental Néel domain wall transmission electron microscope investigations in NiFe thin films [26] were consistent with theoretical predictions.

The different rotation of spins in Bloch and Néel walls represents the fundamental mechanisms to explain the change of magnetisation orientation between adjacent domains. The exclusive occurrence of these magnetisation transitions is usually limited to simple, idealized magnetic systems with a dominating anisotropy term. More often mixed transition states are found like Bloch or Néel lines. These stable topological defects arise between two adjacent Bloch (Néel) walls with opposite chirality [68] and may cause spin singularities such as magnetic vortices [71].

In perpendicular anisotropy [Co/Pd] multilayer films a stripe domain pattern forms
in order to minimize the magnetostatic energy contribution. The position of domain walls depends on local pinning centres fixing the Bloch domain walls [5]. Patterned elements of permalloy show a distinctive in-plane flux closure domain pattern. Due to the demagnetisation field and energy minimisation the direction of magnetisation will be in the plane of the sample.
Chapter 3

Theory of Vortex Dynamics and Small Angle X-ray Scattering

Having discussed in chapter 2 the origin of magnetic anisotropy and the formation of Néel and Bloch domain walls we now explore the theory of vortex formation/excitation in patterned structures and the theory of x-ray scattering on patterned nanostructures.

3.1 Vortex Dynamics

A magnetic vortex is a special type of magnetic domain configuration usually encountered in soft magnetic materials with neglectable anisotropy. The designation magnetic vortex refers to similarities with naturally occurring vortices such as in fluids or gases [61, 75].

The formation of a magnetic vortex is based on the minimisation of the total energy:

\[ E_{tot} = E_{ext} + E_{aniso} + E_{exch} + E_{stat}. \]

For the limiting case of a patterned elements of Permalloy (Py) with no applied external field \((E_{ext} = 0)\), exchange \((E_{exch})\) and magnetostatic energy \((E_{stat})\) dominate the total energy since Py is a soft magnetic material with almost vanishing magnetocrystalline anisotropy \((E_{aniso} \approx 0)\). The dimensions of structures supporting magnetic vortices is in the order of \(\mu m\) [19]. Assuming cylindrical symmetry the magnetic vortex structure can be described by the angle \(\theta(r)\) with \(\theta\) being the angle between the magnetisation direction and the \(z\)-axis and \(r\) the radius from the centre of the structure. The \(z\)-axis direction is perpendicular to the plane of the film. The total energy functional, calculated for the limiting case of infinitely thin
film thickness \((z \rightarrow 0)\) in cylindrical coordinates \((r, \varphi, z)\), equates to [41]:
\[
E_{tot} = 2\pi d \int_0^\infty (E_{exch}(\theta) + E_{stat}(\theta)) r \, dr
\]  
(3.1)

The associated Euler differential equation yields
\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \theta}{\partial r} \right) + \left( 1 - \frac{1}{r^2} \right) \cos(\theta) \sin(\theta) = 0
\]  
(3.2)

No closed analytical solution for \(\theta(r)\) can be derived, but different analytical approximations are available [61, 74].
\[
\theta(r) \approx \begin{cases} 
  c_1 r & r \rightarrow 0 \\
  \frac{\pi}{2} - \frac{c_2 e^{-r}}{r_0} & r \rightarrow \infty
\end{cases}
\]  
(3.3, 3.4)

with \(c_1, c_2\) and \(r_0\) being appropriate constants determined by boundary conditions. A possible continuous approximation is given by Feldtkeller et al. [41] using \(\beta = \sqrt{\frac{\mu_0 M_s^2}{8A}}\) as variational parameter:
\[
\theta(r) = \arccos(e^{\beta^2 r^2})
\]  
(3.5)

with \(A\) being the exchange stiffness constant. Figure 3.1 a) shows the asymptotic solutions to equation 3.3 (red), equation 3.4 (green) and equation 3.5 (continuous blue line), the inset shows the numerical solution (solid line) compared to the continuous approximation equation 3.5. The evaluation of the three-dimensional energy functional for extended films is a challenging computational problem due to the nonlocalised contribution of the magnetostatic energy to the magnetisation and the various energy minima the function assumes [18]. However, in most cases working with the approximations equation 3.3 and 3.4 is sufficient since only the limiting cases \(r \rightarrow 0\) and \(r \rightarrow \infty\) are of interest.

Close to the centre of the structure the in-plane flux closure domains develop a strong out of plane component (see figure 3.1). The inner region of the magnetic vortex structure has a strong out-of-plane magnetisation direction and is called vortex core [121]. The gradual change in magnetisation direction (out-of-plane \(\rightarrow\) in-plane) takes place on the scale of the exchange coupling length (see inset figure 3.1. The out-of plane vortex core together with the adjacent in-plane magnetisation forms the magnetic vortex. The core itself has a diameter about 1-3 exchange lengths \((l_{exp} \approx 5-6\text{ nm})\). Spin polarised scanning tunnelling microscopy measurements taken by Wachowiak et al. [136] showed a core diameter of around \(9 \pm 1\text{ nm}\) which is in reasonable agreement
3.1. VORTEX DYNAMICS

Figure 3.1: Calculated two-dimensional vortex profile. Angle between magnetisation direction and film normal ($\theta(r)$) as a function of radius ($r$) sketching a vortex profile. Red and green solid lines correspond to the asymptotic solutions equation 3.3 and 3.4 with $c_1 = 1.3$ and $c_2 = 1.7$. The blue line reflects the continuous solution equation 3.5. The inset shows the numerical solution (solid black line) taken from [41] in comparison to the approximation equation 3.5.

Figure 3.2: Calculated 2D-magnetisation profile of a vortex (a)) and an antivortex (b)). Approach 3.6 was used with the additive constant being $\phi_0 = \frac{\pi}{2}$. Corresponding in-plane and out-of plane magnetisation patterns of a (anti)vortex are sketched on the right.

with the theoretical predictions (thin film limit approximation) made by Feldtkeller et al. [41] of 6.4 nm. Magnetic vortices fall in the class of topological defects [18,93] and are alternatively known as localised topological solitons. They can be described by 2 topological invariants, namely the vorticity (winding number) $q$ and the polarity $p$ of the vortex. The vorticity is a measurement of magnetisation rotation on a closed path around the vortex core. It is usually measured in multiples of $2\pi$ [81]. The topological entity with $q = -1$ is designated as an antivortex [18, 50]. The other invariant - the polarity $p$ - is defined by the out-of plane magnetisation direction of the vortex core. As derived in equation 3.5, at $r = 0$, $\theta(r) = \arccos(1) = 0^\circ$ which means that the angle
between the magnetisation direction and the z-axis is 0°. Therefore, the magnetisation
direction can either be parallel or antiparallel to the z-axis which corresponds to p=+1
or p=-1 in equation 3.6. The parametrisation given in equation 3.6 was used in order
to visualise the two-dimensional magnetic vector field for a vortex and antivortex [74,
75, 99]. The parameter \( \phi_0 \) is a phase angle which determines the orientation of the
spin direction. The calculated two-dimensional magnetisation profile of a vortex and
an antivortex are shown in figure 3.2.

\[
\begin{align*}
x &= \sin(\theta) \cos(q(\phi + \phi_0)) \\
y &= \sin(\theta) \sin(q(\phi + \phi_0)) \\
z &= p \cos(\theta)
\end{align*}
\]  

As described, the competing energy contributions from the exchange and magneto-
static energy cause the formation of a vortex as the lowest energy state. In the vortex
case the rotating magnetisation prevents the building up of magnetic charges at the sites
of the structure therefore minimising the magnetostatic energy. Simultaneously, the
incremental rotation minimises the exchange energy enabling the energy functional to
assume a global minimum [18] with the vortex energy \( E_{vor} \approx 2\pi A d \log(R/\lambda) + E_{core} \).
For the antivortex the spins are better aligned within their domains resulting in minimal
exchange energy. However, the reduction comes at the expense of the magnetostatic
energy, because magnetic free poles are created at the edges of the domains/structure.
The antivortex energy, \( E_{anti} \approx \sigma d L + E_{cor} \), is therefore a higher energy state compared
to the vortex state and scales with the Néel wall length L [18].

### 3.1.1 Magnetic Vortex Excitation

Various experimental methods have been developed to excite magnetic vortex do-
main structures such as continuous or single pulse magnetic pump probe experiments
[100, 105] , spin polarised current set-ups exploiting spin torque effects [102] and ro-
tating magnetic field exciting spin waves [66]. The excitation duration can, via fourier
transformation, be related back to the frequency domain and corresponds in the case
of single pulses to a broadband excitation and for a single, continuous frequency to a
single frequency excitation.

The time dependent change of magnetisation in the sample can be described by the
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Landau-Lifshitz-Gilbert (LLG) equation [9, 48, 77].

$$\frac{d}{dt} M = \frac{\gamma}{1 + \alpha^2} M \times H_{\text{eff}} \underbrace{\text{precession term}}_{\text{damping term}} + \frac{\alpha \gamma}{(1 + \alpha^2)M} (M \times (M \times H_{\text{eff}}))$$  \hspace{1cm} (3.7)

The first term describes the processional motion of the magnetisation around the direction of the effective field. The second term is a damping term, that aligns the magnetisation in the direction of $\vec{H}_{\text{eff}}$ by dissipating energy. The damping coefficient ($\alpha$) is a phenomenological construct introduced to ensure the alignment of magnetisation with the magnetic field $\vec{H}_{\text{eff}}$ for $t \to \infty$. Figure 3.3 shows a graphical representation of the terms contributing to the motion of magnetisation.

![Figure 3.3: Time dependent motion of the magnetisation $\vec{M}(t)$ according to their contributions in the LLG equation. The green circular trajectory (dashed) refers to the processional motion whereas the red spiral (dotted) reflects the damping term rotating the magnetisation eventually in the direction of the effective field.](image)

Using the LLG equation as a starting point A. A. Thiele [127] derived an expression for describing the motion of domains and spin systems such as 2D [58] or 3D vortices. In its simplest form, valid only for steady state motion and rigidly coupled vortex spins, it can be written as follows:

$$\dot{\vec{X}} \times \vec{G} = -\frac{\partial W}{\partial \vec{X}} = \vec{F}$$  \hspace{1cm} (3.8)

The vector $\vec{X} = (x, y, 0)$ describes the position of the vortex in the x-y-plane. The evolution over time of the position is given by $\dot{\vec{X}}$. $\vec{G}$ is the gyrocoupling vector which describes the net topological charge of the vortex and can be calculated as follows: $G = -2\pi pq \vec{e}_z$, with p and q being the topological invariants of the vortex [84, 133, 143].

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In materials with large in-plane magnetic anisotropy the magnetic vortex has no out-of-plane vortex component ($p=0$). As a consequence the gyrocoupling vector yields $\vec{G}=0$ thus indicating that the Thiele equation cannot be used in this case. Vortices in low anisotropy materials, such as permalloy, do possess an out-of-plane component in the core ($p = \pm 1$) which results in $\left| \vec{G} \right| \neq 0$. Excitations with non-vanishing gyrocoupling vector are called gyrotropic. The term $W(x,y)$ refers to the energy of the vortex as a function of position. The negative first derivative of the potential energy equals the gyrocoupling force which is equivalent to the Lorentz force [84]. An applied oscillating external magnetic in-plane field (e.g. from a stripline as described in section 3.1.4) exerts a torque on the out-of-plane vortex core. The displacement from the equilibrium position of the vortex due to the field can be described by Thiele’s equation. Requirements for the validity of the model are that the vortex stays rigid and undergoes a steady motion (circular motion around equilibrium point). Wysin et al. [143] incorporated an additional acceleration term in Thiele’s equation thereby bypassing the limitation of the rigid shape assumption.

In square magnetic elements of Permalloy, a Landau domain pattern will arise due to the magnetic energy minimisation. An applied in-plane field favours the formation of domains oriented collinear with the magnetic field vector (Zeeman energy). The parallel oriented magnetic domain will grow beyond the equilibrium point and the centre of the vortex shifts accordingly.

In a fast oscillating magnetic field (rf field) a vortex core displacement parallel to the field direction takes place due to domain growth. Furthermore, the domains oriented perpendicular to the magnetic field ($\vec{M} \perp \vec{H}$) experience a torque and start a precessional motion. The vortex core itself experiences a force perpendicular to the applied field [21, 23, 107] - the gyrocoupling force $\vec{F}$ (see equation 3.8). As a result of the torque affecting the magnetisation components perpendicular to the magnetic field ($\vec{M}_{\text{core}}, \vec{M} \perp \vec{H}$), a precessional motion of the vortex core around the equilibrium position (dotted circle) starts. The trajectory of the gyrotropic vortex motion depends on various parameters such as the local potential the vortex is moving in (intrinsic defects, imperfections), damping forces e.g. dipole interactions or a possible nonlinear contribution for the spin-torque force. [31, 54]. Figure 3.4 shows the the vortex gyration according to an applied rf magnetic field.

The sense of gyrotropic motion (clockwise: cw, counter clockwise: ccw) is independent of the chirality of the in-plane magnetisation of the vortex, but is strongly affected by the orientation of the out-of-plane magnetisation component $p$ of the vortex core.
3.1. VORTEX DYNAMICS

Figure 3.4: The dashed centre cross shows the equilibrium domain configuration in a Landau domain pattern. An AC current (rf excitation) flowing through the stripline creates an oscillating magnetic in-plane field (Oersted field $\vec{H}$) across the stripline. The initial domain growth (parallel to the applied field shown by solid black line) together with the torque on the domains perpendicular to the field and the torque on the vortex core result in a circular vortex core motion (dotted circle) with the gyration radius $R$. Figure after [19].

(+1 pointing up, -1 pointing down) [21]. Figure 3.5 shows a sketch of the sense of gyrotropic motion as a function of the polarisation direction ($p=+1$ and $p=-1$) and the applied field direction [106]. In case of the vortex core orientation pointing up ($p=+1$) the core gyrates clockwise regardless of the chirality (see figure 3.5 a) and b)), otherwise for $p=-1$ the core gyrates counter clockwise (see figure 3.5 c) and d)).
Figure 3.5: The sense of gyrotropic motion in an applied field depends on the vortex core polarity and is independent of the vorticity. For positive polarity (p=+1) the gyrotropic motion goes counter clockwise irrespectibly of the vorticity, as shown in the top row. For negative polarity (p=−1) the gyrotropic motion performs clockwise motion around the equilibrium position (bottom row). Figure after [19].
3.1. Imaging Magnetic Contrast

In order to observe domain structures in patterned magnetic structures Scanning Transmission X-ray Microscopy (STXM) was employed. The ability to tune the x-ray energy to element specific absorption edges allows imaging of individual layers. The experimental set-up in transmission geometry enables the investigation of buried layers which is essential in hybrid anisotropy samples in order to study the interactions between the layers.

X-rays penetrating the multilayer sample are absorbed according to Beer’s law \[108\]:

\[ I_{\text{trans}} = I_0 \exp(-\mu(P,E,Z)t(x,y)) \] .

The exponential decay depends on the local sample thickness \(t(x,y)\) and the absorption coefficient \(\mu\), which is a function of polarisation \(P\), energy \(E\) and atomic number \(Z\). The dependency of the x-ray absorption coefficient \((\mu)\) on the polarisation (left/right circular x-ray light) is used to measure an intensity contrast image which is correlated to the magnetic domain orientation. This effect is called X-ray Magnetic Circular Dichroism (XMCD) and was pioneered by Schütz et al. \[118\] and is widely employed in the investigation of magnetic samples \[116\].

X-rays impinging on the sample excite electrons in higher atomic states. For the experiments conducted the atomic transition \(p \to d\) was chosen \[122\]. The initial state of the p-orbital \((l=1)\) is split into a \(2p_{1/2}\) and \(2p_{3/2}\) level according to \(l \pm s\). Circularly polarised x-rays carry an angular momentum of \(\pm \hbar\) depending on the chirality, which can be transferred through absorption by electrons. Spin-orbit coupling allows for the partial transfer of the angular momentum to the spin. Oppositely handed polarisations transfer opposite momentum and result in the excitation of electrons with reversed spin. Since the bands in the d-shell are spin polarised and already partially filled the density of empty valence states differs for the two spin chiralities. The absorption of circularly polarised x-ray light is stronger the more empty states are available for excited electrons with matching spin. This polarisation dependent absorption can be turned into a magnetic contrast image by measuring the transmitted intensity separately for left and right-handed polarised x-rays and dividing both images. Figure 3.6 shows the absorption process in a simplified one-electron model \[122\].

The XMCD effect scales as \(\cos(\theta)\) with \(\theta\) being the angle between the photon spin \(s\) and the sample magnetisation direction \(M\). Maximal interaction can therefore be observed for (anti)parallel \((\theta = 0^\circ \text{ or } 180^\circ)\) alignment between magnetisation and photon spin as shown in figure 3.7. The sample was placed at an 90\(^\circ\) sample holder (film normal parallel to beam) in order to image the out-of-plane component of the sample.
Figure 3.6: Representation of the origin of magnetic dichroism using the one-electron model. The spin-orbit coupling causes the 2p level to split up into two sublevels. a) Oppositely circular polarised x-rays excite electrons with matching spin to empty valence band states. The density of states of the spin-split valence shell (spin up/spin down states) determines the intensity of absorption. Figure after [116]. b) By recording the transmission intensity for left and right circular x-rays a magnetic contrast image can be obtained by dividing both images. For the conducted experiments the L3 absorption edge was used due to higher signal-to-noise ratio.

magnetisation. However, to be able to simultaneously image both magnetisation components, the in-plane as well as the out-of-plane, the sample was placed at an angle of 30°. In this configuration the tilted in-plane magnetisation has an out-of-plane component of $M_{30°} = M \sin(30°) = M/2$, which can be imaged. Figure 3.7 visualises the decomposition of the tilted sample magnetisation into a parallel and a perpendicular component.
3.1. VORTEX DYNAMICS

Figure 3.7: Decomposition of the tilted in-plane magnetisation $\mathbf{M}$ in an parallel (green arrow $M_\parallel$), with $90^\circ$ to the x-ray beam, and a perpendicular (along the x-ray beam) component. This tilted sample set-up allows imaging in-plane and out-of-plane magnetic moments with STXM. The two different photon spin projections are shown on the left. Maximal interaction occurs for parallel or antiparallel alignment of the photon spin with the magnetisation direction.
3.1.3 Differential Imaging Technique

Imaging vortex dynamics is a challenging experimental task due to the low x-ray intensities, low signal-to-noise rate and small feature size ($\approx 10 \text{nm}$). In order to enable time resolved images a special differential imaging technique [22] is employed for dynamic measurements (see figure 3.8). Two consecutive magnetic contrast images with a $180^\circ$ phase shift (red arrows) are subtracted removing all static magnetic and non-magnetic contributions from the image (see figure 3.8 measurement 1). However, a second independent measurements was performed where the magnetic field amplitude was shifted by $180^\circ$ (measurement 2). Dynamic changes in the magnetisation should reverse contrast due the shift of the magnetic field amplitude.

Figure 3.8: Working principle of the differential imaging technique employed for time resolved vortex dynamic experiments. Two consecutive magnetic contrast images with a $180^\circ$ phase shift (red arrows) are subtracted in order to image the dynamic magnetisation changes. A $180^\circ$ phase shift of the excitation amplitude reverses the magnetic imaged contrast.
3.1.4 Magnetic Field Around The Stripline

In order to investigate the dynamic behaviour of magnetic vortices fast oscillating magnetic fields needs to be applied. This can be realised by a radio frequency (rf) current from a frequency generator passing through a micrometer sized conducting wire with a rectangular cross-sectional profile (stripline). The magnetic field $\vec{H}$ around the stripline can be calculated using Ampere’s law:

$$dH = \frac{j \, dx \, dy}{2\pi r}$$  \hspace{1cm} (3.9)

where $j$ is the current density and $r$ is the radius from the centre of the stripline. The current density can be expressed in terms of the current $I$ and the cross-sectional area of the stripline: $j = \frac{I}{\pi ab}$. Equation 3.9 can then be rewritten in Cartesian coordinates as:

$$dH(X,Y) = \frac{I}{8\pi ab \sqrt{(x-X)^2 + (y-Y)^2}} \, dx \, dy$$  \hspace{1cm} (3.10)

The lower case and upper case letters refer to the different coordinate systems used for the calculation as shown in figure 3.9. The lower letters refer to the integration variables and the uppercase letters refer to the point at which the magnetic field is calculated. The magnetic field components along the x and y-axis can be calculated by multiplying $\vec{H}$ with $\cos(\alpha)$ or $\sin(\alpha)$, with alpha being the angle between the vertical axis and the magnetisation direction. Expressing $\alpha$ in Cartesian coordinates yields the equation 3.11 which calculates the magnetic field distribution around a rectangular stripline with the dimension $a$ (width) and $b$ (height).

$$H_{\text{hor}}(X,Y) = \frac{I}{8\pi ab} \int_{-a}^{a} \int_{-b}^{b} \frac{(X-x)}{(x-X)^2 + (y-Y)^2} \, dx \, dy$$  \hspace{1cm} (3.11)

$$H_{\text{vert}}(X,Y) = \frac{I}{8\pi ab} \int_{-a}^{a} \int_{-b}^{b} \frac{(Y-y)}{(x-X)^2 + (y-Y)^2} \, dx \, dy$$  \hspace{1cm} (3.12)

The integrals in equation 3.11 and 3.12 can be evaluated either analytically or numerically [24, 62, 91]. For an input power of 15 dBm a current of around 0.025 A is assumed to pass through the stripline (50 Ohm terminated transmission line). With the current known the integrals in equation 3.11 and 3.12 can be numerically evaluated. A graphical visualisation of the vertical and horizontal field component of $\vec{H}$ are shown in figure 3.10. The magnetic field strengths were calculated for a point 20 nm from the...
bottom of the stripline with the dimension given in figure 3.9.

Figure 3.9: Sketch of the stripline dimensioning, the position of the patterned structures and the assumed magnetic field ($\vec{H}$). Alternating current passing through the stripline causes an oscillating magnetic field around the stripline suitable for excitation experiments on nanostructures. The nanostructures (assumed centre position at $\approx 20\,\text{nm}$) are overlaid by a the copper stripline providing the magnetic field.

The magnetic field around the stripline has an ellipsoidal shape (see figure 3.9) due to the different field strength of the components ($H_{\text{vert}}$, $H_{\text{hor}}$). According to calculations (figure 3.10) the magnetic field $\vec{H}$ above the stripline (approximately $-4\,\mu\text{m} \leq \text{horizontal distance} \leq 4\,\mu\text{m}$) is dominated by the horizontal component of the magnetic field. Further out, close to the edges of the stripline, the vertical component of the magnetic field supersedes the horizontal component. Around the edges of the stripline $H_{\text{vert}}$ reaches its maximum.
3.1. VORTEX DYNAMICS

Figure 3.10: Horizontal ($H_{\text{hor}}$, blue crosses) and vertical ($H_{\text{vert}}$, red circles) magnetic field components calculated for a point 20 nm from the bottom of the stripline. The horizontal field component stays almost constant ($\approx 1000$ A/m) over the full cross-sectional width (10 $\mu$m) of the stripline. The vertical field strength increases over distance from the centre of the stripline and peaks at the edge ($\pm 5\mu$m) of the stripline. For convenience the lateral stripline dimension is shown in form of a black rectangle (10 $\mu$m). The height of the rectangle does not correspond to the actual stripline height.
3.1.5 Change of Resistance in Platinum Temperature Sensors as a Function of Temperature

The application of radio frequency power to the stripline causes an increase in temperature of the sample. In order to estimate the temperature increase Platinum temperature sensors were fabricated close to the stripline. Platinum sensors were chosen due to their almost linear relationship between resistance and temperature which allows a reliable and accurate temperature estimate.

The temperature dependence of the Platinum sensor resistance can be modelled by the Callendar-Van Dusen equation \[27\], which simplifies for \(0^\circ C \leq T \leq \approx 800^\circ C\) to:

\[
R(T) = R_0(1 + AT + BT^2)
\]  

(3.13)

, with \(A \approx 3.9 \times 10^{-3} \text{ (}^\circ C\text{)}^{-1}\) and \(B \approx 5.7 \times 10^{-7} \text{ (}^\circ C\text{)}^{-1}\). The last term is four orders of magnitude smaller compared to the leading linear one, therefore equation 3.13 can be linearised. Experimental results are shown in chapter 6.3 and are plotted in figure 6.8.

The work reported here deals with the static and dynamic properties of magnetic vortices, the basic principles of x-ray imaging and the generation of the Oersted-excitation field in dynamic STXM experiments.

3.2 Small Angle X-Ray Scattering

The ability to accurately characterise large arrays of nominally identical nanoscale structures is a key problem in understanding and modifying their applicability, for instance as possible storage medium in Bit Patterned Media (BPM) [2, 94, 120]. X-ray scattering offers a fast and accurate method to characterise large scale nanostructure arrays with nanometer resolution.

3.2.1 Geometrical relations for small angle scattering experiments

Highly ordered arrays of cylindrical structures scatter the incident x-rays according to Bragg’s law.

\[
\Delta s = m \cdot \lambda = 2d \sin(\phi)
\]  

(3.14)

where \(\Delta s\) is the path difference of two rays, \(d\) is the centre-to-centre distance of the nanostructures, \(\lambda\) the wavelength of the incident x-rays, \(\phi\) the scattering angle and \(m\) the order of scattering. The coherently scattered waves interfere and yield an interference
3.2. SMALL ANGLE X-RAY SCATTERING

pattern on the detector with distinct Bragg-peaks. No energy transfer occurs during the scattering process so only isotropic, elastic scattering is considered. A constructive interference (Bragg peaks) is only possible, where the path difference ($\Delta s$) is an integer multiple of the wavelength $\lambda$. The principle scattering condition and the parameter used in equation 3.14 are shown in figure 3.11.

For the interpretation of the scattered intensity distributions a scattering vector $q$ is introduced, whose magnitude is given by:

$$ q = \frac{4\pi}{\lambda} \sin (\phi/2) \quad (3.15) $$

Here $\lambda$ is the wavelength of the incident x-rays and $\phi$ is the scattering angle. Inset c) in figure 3.11 describes the geometrical relations for the derivation of $q$ with $k_i$ and $k_s$ being the incident and scattered wave vectors.

### 3.2.2 Basic Scattering Model

In the following section a basic scattering model is introduced. A brief explanation and motivation for incorporating the different terms in the model is given. The following...
ansatz [15, 46, 76] is chosen in order to model the measured intensity distribution:

\[ I(q) = I_0 (b_1 - b_2)^2 \frac{N}{V} \left[ \langle F(q, R) \rangle_{R}^2 G(q) Z(q) \right] \]  

(3.16)

The first three terms (incident beam intensity \( I_0 \), scattering length difference \( b_1 - b_2 \) and the number density \( \frac{N}{V} \)) can be summarised in one parameter since these terms are independent of the scattering vector \( q \) and stay constant. The term \( \langle F(q, R) \rangle_{R}^2 \) is the radius weighted Fourier transform of the electron density for a polydisperse cylinder (see figure 3.12 b)). The expression \( F(q, R) \) contains geometrical information about the scattering structure and is therefore called the form factor [49, 53]. For a polydisperse cylinder whose diameter distribution follows a normalised Gaussian distribution, the form factor has to be weighted and integrated over all radii for each \( q \) value. \( G(q) \) is the Debye-Waller factor [29, 137], which describes the decay of the Bragg-peak intensity as a function of lateral displacement (see figure 3.12 c)). The final term \( Z(q) \) is used for scattering geometries in which a strong interparticle correlated scattering takes place, which allows deduction of the lattice structure. Due to the high ordering (square lattice) in the measured nanostructure arrays \( Z(q) = 1 \) for the SAXS experiments conducted.

Figure 3.12: Effects of polydispersity and lattice displacement on a square lattice array of cylindrical nanostructures. a) Uniform cylindrical structures arranged in a square lattice. b) Variations in the cylinder diameter cause a polydispersity (a distribution of diameter). c) Polydispersity and misplacements from the ideal square lattice positions cause the measured scattered intensity to decrease further.

The form factor for cylindrical structures can be factorised into two terms - one along the cylinder axis \( (F_{||}) \) and one perpendicular to it \( F_{\perp} \) (see figure 3.13).

\[ F_{\text{cyl}}(q) = F_{||}(q) F_{\perp}(q) \]  

(3.17)
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with

\[ F_{\parallel}(q) = \frac{1}{L} \int_{-L/2}^{L/2} \exp(-i q \cos(\theta) z) dz = \left[ \frac{\exp(-i q \cos(\theta) z)}{-i q \cos(\theta)} \right]_{-L/2}^{L/2} = \frac{\sin(q \cos(\theta) (L/2))}{q \cos(\theta) L/2} \]

and

\[ F_\perp = \frac{1}{\pi R^2} \int_0^R d\rho \int_0^{2\pi} d\phi \exp(-i q \sin(\theta) \cos(\phi) \rho) = \frac{2J_1(q R \sin(\theta))}{q R \sin(\theta)} \]

For a cylinder the form factor therefore yields:

\[ F_{cyl}(q) = F_\perp(q) \cdot F_{\parallel}(q) = \left( \frac{\sin(q \cos(\theta) (L/2))}{q \cos(\theta) L/2} \cdot \frac{2J_1(q R \sin(\theta))}{q R \sin(\theta)} \right) \]

The angle \( \theta \) refers to the tilting angle of the cylinders with respect to the z-axis. The parameter \( L \) is the length of the cylinder and \( R \) the radius. \( J_1 \) is the Bessel-function of the first kind. For the conducted experiment \( \theta = 90^\circ \) i.e., the first term in equation 3.20 equals unity, because for \( x \to 0 \) the term \( \frac{\sin(x)}{x} = 1 \). Therefore, under normal x-ray incidence parallel to the cylinder axis, the form factor in equation 3.20 simplifies to [97, 111]:

\[ F_{cyl}(q) = \frac{2J_1(q R)}{q R} \quad \text{for} \quad \theta = \pi/2 \]

For reference, the corresponding angles \( (\theta, \phi) \) and parameter \( (L,R) \) are shown in figure 3.13. Both scattering contributions \( (F_{\parallel} \text{ and } F_\perp) \) of equation 3.17 are shown in figure 3.13 a) and c). In order to calculate the scattered intensity pattern a cylinder diameter of 20 nm was assumed and for \( F_{\parallel} \) equation 3.18 was used with \( \theta = 0 \) and accordingly for \( F_\perp \) equation 3.19 with \( \theta = 90^\circ \).

In order to account for the polydispersity the form factor has to be weighted with a suitable distribution [15, 111]. The polydispersity arises from the inherent properties of the electron beam lithography process. In section 4.1.1 it is shown that a Gaussian distribution can describe the statistical broadening of the diameter of the nanostructure. Therefore a Gaussian distribution is used as a weighting function for the form factor calculation 3.20 giving:

\[ I_{poly}(q) = \left( \int_0^{R_{disk}} \frac{\sin(q \cos(\theta) (L/2))}{q \cos(\theta) L/2} \cdot \frac{2J_1(q R \sin(\theta))}{q R \sin(\theta)} \right)^2 \times \left( \frac{1}{\sigma \sqrt{2\pi}} \exp\left( -\frac{1}{2} \left( \frac{x-\mu}{\sigma} \right)^2 \right) \right) \]

\[ dR \]

\[ (3.22) \]

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Figure 3.13: The form factor for cylindrical structures can be separated into contributions along the cylinder axis (a)) and perpendicular (c)) to it. The scattered intensity distribution has been calculated according to equation 3.20 with $\theta = 0$ for a) and $\pi/2$ for c). The frame of reference and the parameters characterising the cylindrical structures are shown in b) and d).

The variance or standard deviation is therefore a measurement of uniformity of the nanostructures (regarding the structure radius) whereas the mean of the distribution allows the deduction of an averaged nanostructure radius in the system. Figure 3.14 shows the calculated scattering intensity as a function of $q$ and various standard deviations. The mean nanostructure diameter was assumed as 20 nm with a standard deviation of 0.1, 0.5, 1, 1.5, 3, 5, 20 nm. The pronounced minima and maxima in the scattering curve at small polydispersity (0.1 nm) arise due to interference effects (compare to figure 3.11) in the scattered beam. In less uniform samples (increasing standard deviations) the fringes decay until the intensity curve assumes a featureless, monotone decrease in intensity. The inset in figure 3.14 shows the corresponding probability
functions for different polydispersity standard deviations (0.5, 1.5 nm). Variations in the position of the nanostructures in the square lattice reduce the scattered intensity. To account for this displacement an exponentially decaying term, similar to the Debye-Waller factor, is added to the total scattered intensity [46, 111]. As a result, the total scattered intensity calculates as follows:

\[
I_{tot}(q) = \left( \int_0^{R_{disk}} \frac{\sin(q \cos(\theta)(L/2))}{q \cos(\theta)L/2} \cdot \frac{2J_1(qR \sin(\theta))}{qR \sin(\theta)} \right)^2 \times \left( \frac{1}{\sigma \sqrt{2\pi}} \exp \left( -\frac{1}{2} \left( \frac{x-\mu}{\sigma} \right)^2 \right) \exp(-q^2 \sigma_{pos}^2) \right)^2
\]

(3.23)

Figure 3.15 shows the different contributions described in equations 3.20, 3.22 and 3.23: the single particle cylinder form factor (blue), the form factor extended by a
Gaussian radius distribution (red) and the form factor extended by a Gaussian radius distribution and an exponentially decaying term (black). The decreased intensity at larger q values is a result of the Debye-Waller term and accounts for the placement disorder. For the calculation, the cylinder diameter was assumed to be 20 nm, the radius standard deviation was set to $\sigma = 1 \text{ nm}$ and the positional standard deviation $\sigma = 2 \text{ nm}$. These values are in line with values reported in previous studies [51, 87].

![Figure 3.15: The equations 3.20, 3.22, 3.23 are plotted for comparison demonstrating the different contributions to the total scattering intensity. blue) single particle form factor; red) form factor extended by a Gaussian radius distribution; black) the form factor extended by a Gaussian radius distribution and the Debye-Waller factor.](image)

The work reported here deals with x-ray scattering patterns obtained from large arrays of nominally identical nanoscale structures. A model was devised to describe the measured scattering pattern and to deduce structural array parameter such as mean structure size, structure variation, position variation.
Chapter 4

Sample Fabrication and Experimental Methods

In this chapter, first the sample fabrication methodology is described followed by a description of the techniques used for characterisation. A key requirement for this work was the creation of uniform arrays of nanometer scale magnetic structures. The fabrication of large sample areas (in the order of a few mm$^2$) of nanostructures pushes current fabrication methods towards its limits.

In principle, two different approaches to the fabrication of magnetic nanostructures can be used. Top-down methods employ established microfabrication techniques e.g. lithographic methods from the semiconductor industry, to fabricate devices/structures with small dimensions. In contrast, bottom-up methods try to assemble structures from elementary building blocks e.g. by self assembly.

The resolution of conventional photolithography techniques scales with the utilised wavelength [55]. Photolithographic light sources have wavelengths in the order between 190 nm (excimer laser) and 440 nm (Hg-vapour lamps) giving rise to structure sizes in the same order. However, ultimately higher resolution can be achieved by switching to smaller wavelengths. In electron beam lithography high energy electrons are used providing wavelengths of the order of a few picometer ($\lambda \approx 3.87$ pm at 100 keV) and thereby in conjunction with high resolution e-beam resists allow the creation of features smaller than 10 nm [145]. In this work a top-down approach was taken using e-beam lithography to fabricated the nanostructured samples.


4.1 Sample Fabrication

This thesis reports research on magnetic nanostructures using x-ray transmission (STXM) and scattering experiments (SAXS). This requires that nanostructures are fabricated on x-ray transparent substrates. Commercially available $Si_3N_4$-membranes are chemically inert, and thin enough to allow for the transmission of x-rays. This extremely fragile membrane is transparent to x-rays and allows STXM and SAXS experiments to be conducted. The 200 nm thick $Si_3N_4$-membranes come in a 4x4 array on a chip which can be processed further. The membranes, as delivered, are backside supported with bulk Si (several $\mu$m in thickness) in order to make them more resilient to mechanical deformation such as ultrasonic agitation, rinsing, spin coating and shock which occur naturally during the nanofabrication process. After finishing the fabrication process the Si is removed and the membranes become transparent to x-rays. Figure 4.1 shows a schematic of the substrate employed.

Figure 4.1: $Si_3N_4$-membrane used as substrate for nanostructure fabrication. The as purchased substrate is backside supported with Si in order to allow nanostructuring. For the experiments the Si backside support is removed thus making the substrate x-ray transparent.

The different fabrication steps are shown schematically in figure 4.2 and listed in the order of processing.

1. Spin Coating

Polymethylmethacrylate (PMMA) with a molecular weight of 50 000 g/mol (50 K) diluted to solid content of 2 % in ethyllactate was spin coated on the substrate with a speed of 4500 rpm for a time of 45 sec and subsequently baked out at 175° for 5 min. This gives an approximately 30 nm thick 50 k PMMA layer on the substrate. In a next step, 950 000 g/mol (950 K) PMMA with a solid content of 1 % in ethyllactate was used with the same spinning and baking conditions to create an additional 20 nm thick top PMMA layer (see figure b).
Figure 4.2: Multistage sample fabrication process illustrating the main process steps a)-e). STXM samples undergo additional e-beam lithography steps f) to provide a copper transmission stripline and platinum meander temperature sensors. The final step is a potassium hydroxide etch bath to remove the silicon backside support. The final sample design is shown in g) and h).
CHAPTER 4. SAMPLE FABRICATION AND EXPERIMENTAL METHODS

The resist thicknesses as a function of spinning velocity were experimentally measured and interpolated as shown in figure 4.3.

2. **E-beam Lithography And Development**

In this double resist layer process the bottom low molecular weight PMMA layer on top of the Si substrate is 20\% more sensitive [83] to electron exposure than the 950 K PMMA [32], which means that we create a negative sidewall profile (undercut) due to the electron exposure as illustrated in the close-up in figure 4.2 c). This undercut profile is essential for lift-off techniques since it facilitates the later stripping of the PMMA layers and unwanted material after thin film deposition. After e-beam exposure the sample is developed in a solution of Methyl isobutyl ketone (MIBK) and Isopropyl alcohol (IPA) at a ratio of 1:3 for 75 secs in an ultrasonic bath (figure 4.2 c)). Afterwards the sample is rinsed for 30 sec in IPA and again in distilled water to stop the development. A negative pattern of the desired structure has been transferred into the resist by dissolving the exposed resist areas.

3. **Sputter deposition**

In the following film deposition step the top PMMA layer serves as a mask thereby defining the structure diameter (figure 4.2 d)). The magnetic thin film is deposited by sputtering as described in section 4.1.2. To help the lift-off the film height should not exceed half the bottom PMMA layer thickness.

4. **Lift-Off**

After film deposition, unwanted resist covered with magnetic material is removed with acetone in an ultrasonic bath leaving the nanostructures on the substrate. The structures are sonicated for 30 sec afterwards rinsed in acetone and pure water and finally blow dried with nitrogen.

In a final process step the silicon backside support is removed in a potassium hydroxide (KOH) solution for samples intended for SAXS experiments. In order to protect the nanostructures during this process step the patterned frontside and sidewalls of the sample were (spin) coated with an alkaline protective resist (ProTEK B3®). Samples intended for STXM experiments undergo two more e-beam exposures creating a 200 \(\mu\)m long, 10 \(\mu\)m wide and 200 nm high copper stripline and Platinum meander sensors used as temperature sensors (see figure 4.2 f)). The copper for the stripline was deposited by thermal evaporation and the platinum for the temperature sensors in a self-manufactured sputter system which is described in section 4.1.2.
4.1. SAMPLE FABRICATION

Figure 4.3: PMMA resist thickness as a function of spinning speed. To minimise statistical errors resist thicknesses have been measured several times using a Dektak profilometer. An exponential decay of the form $y = A \exp\left(-\frac{x}{B}\right) + y_0$ fits the data points very well with $r^2 > 0.93$.

In figure 4.4 microscopy images of the fabricated STXM (a)) and the SAXS sample (b)) are shown prior to removal the Si backside support of the membrane window in a KOH etch bath.
CHAPTER 4. SAMPLE FABRICATION AND EXPERIMENTAL METHODS

Figure 4.4: Microscopy images of the final STXM and SAXS sample. a) shows an optical microscope image of a STXM sample with the evaporated Cu-stripline in the centre, the sputtered Pt heat sensors and the $[Co/Pd]_8 + Py$ nanostructures. In b) a close-up of a scanning electron microscopy image of nanoislands on the $Si_3N_4$-membrane is shown. The image section is part of a 500x500μm² array of nanostructures for small angle x-ray scattering experiments.
4.1. SAMPLE FABRICATION

4.1.1 Electron Beam Lithography

For the creation of structures with dimensions in the nanometer regime an optimised high resolution lithographic process was used. Electron beam lithography (e-beam) provides the resolution and positional accuracy necessary to fabricate dense arrays of nanometer structures. The patterning was done with a state-of-the-art e-beam system (Vistech EBPG 5000+) which, in conjunction with a high resolution e-beam resist, allowed for the fast and reproducible exposure of samples.

To enable high resolution e-beam writing accurate position control is essential. Therefore the e-beam writer is equipped with a sophisticated position and deflection system as illustrated in figure 4.5 a). The position of the sample holder is controlled by a closed loop two axis laser interferometer with 0.5 nm accuracy. Areas to be written are subdivided into main fields and these are further subdivided into subfields as shown in figure 4.5 b). The main field size is in the order of several $\approx 100 \, \mu m$ giving a large deflection but at slow speed. Each main field consists of several subfields on the order of a few $\mu m$ which can be written at a fast speed (with a frequency of up to 50 Mhz) due to the small deflection involved. Single e-beam shots can expose a coherent area due to the proximity effect (broadening of exposed region beyond the point-like electron beam) or beam overlap. By adjusting the beam step size and beam diameter a coherent exposure can be avoided and nanoscale structures can be written with variable period and diameter. In order to explore the exposure limits electron scattering and electron-resist interaction need to be taken into consideration.

PMMA is an electron sensitive, positive tone resist, which forms long polymer chains.
connecting the molecules. High energy electrons can break up the intermolecular connections and scission the polymer chain as shown in figure 4.6. This main chain scission leads to chemical changes and a degradation of PMMA [1, 20]. Scissioned polymer chains have a reduced molecular weight and are more likely to dissolve in a development solution [57]. Various development parameter such as temperature (cold development) [28, 95] and development solution (MIBK and IPA) [73, 119, 140] have been shown to have an effect on the quality of the developed structures.

![Figure 4.6: Main chain scission mechanism in PMMA polymer chains due to high energy electron-resist interaction according to [20].](image)

The impinging electron beam experiences two energy dependent scattering mechanisms. The incoming point-like beam spreads out due to small angle forward scattering in the resist. This scattering is mainly due to electron-electron scattering and increases the beam divergence as shown in figure 4.7 a). As the electrons penetrate further through the sample they eventually enter the substrate. There exists a certain probability for the electrons to be back scattered into the resist and cause further exposure in the surrounding resist. The effect of resist exposure due to backscattering is known as the proximity effect [98, 113, 141] and can reach out up to several microns, as seen in figure 4.7 b) (red trajectories). Both effects can be modelled using Monte Carlo simulations [131]. In order to model the two effects (forward scattering and backscattering) for a PMMA/Silicon sample, the program CASINO [35] was used and 2000 electron trajectories were calculated, as shown in figure 4.7 a) and b). Both scattering events are highly dependent on the initial electron energy as sketched in figure 4.8 a) for 30 keV and for 100 keV in b). At high incident electron energies the forward scattering is significantly reduced allowing very small and narrow features to be written. Backscattering, however, is vastly dependent on the substrate/material used and its thickness. The interplay between forward scattering and backscattering as a function of energy and resist height gives rise to a negative sidewall profile or undercut which is necessary for a successful lift-off process. Mathematically, the beam divergence distribution due to scattering (also point spread effect) can be described by a sum of Gaussian functions [17, 98, 113, 141, 141].
4.1. SAMPLE FABRICATION

\[ f(r) = \frac{1}{\alpha^2 \pi (1 + \eta)} \left[ e^{-r^2/\alpha^2} + \frac{\eta \alpha^2}{\beta^2} e^{-r^2/\beta^2} \right] \]  

(4.1)

The first Gaussian term refers to the initial beam distribution and its broadening through forward scattering. The second term accounts for the backscattering of electrons with the parameter \( \eta \) denoting the exposure ratio of backward to forward scattering. Experimental evidence acquired by electron microscopy experiments by Fisker et al. [42] showed, that artificially created particles follow closely a Gaussian/Lognormal island size distribution depending on the fabrication method.

Figure 4.7: Monte Carlo simulation for 2000 100 keV electron trajectories penetrating a 60 nm layer of PMMA (a)) and entering the silicon substrate (b)). The red trajectories in b) show the back scattered electrons that contribute to the proximity effect. Figure a) shows a close-up (black square in b)) of the electron paths down to 200 nm penetration depths demonstrating the very narrow forward scattering at high energies (100 keV).

Figure 4.8: Comparison of electron scattering angles between an electron beam with 30 keV in a) and 100 keV in b). For low incident energies the beam divergence will increase (scattering angle \( \alpha \)) due to forward scattering but the proximity effect (scattering angle \( \beta \)) is low. At high incident electron energies almost no forward scattering takes place (small scattering angle \( \alpha \)) but the backscattering of electrons can be significantly higher (large scattering angle \( \beta \)) causing a broadening of the expected structure dimensions.
4.1.2 Sputter Deposition of Magnetic Thin Films

Once the pattern masks were written in the resist with the e-beam and developed they have to be coated with magnetic material in order to create the nanostructures. Sputtering [7, 124, 125], a physical vapour deposition (PVD) technique, was used to create multilayer thin film structures with component layer thicknesses in the order of 1-3 monolayers. Sputtering is a widely used process in industry and laboratories to create homogeneous coatings of large areas quickly. The term sputtering (originally cathodic disintegration) refers to an experiment first described by R. Grove et al. [52]. The complex process of sputtering occurs when a (sputter)target is subject to particle irradiation striking the surface and transferring, due to a (multi) recoil collision processes, sufficient energy to overcome binding forces to adjacent atoms thereby causing the release of surface atoms. A variety of different sputter systems are available (either self-made or purchased) - most common are Direct Current (DC), Radio Frequency (RF) and dc magnetron sputtering systems. The DC sputter system uses a high negative voltage between the target and the ionised gas for sputtering. In DC magnetron systems, magnets behind the targets facilitate the sputter process and make sputtering more efficient. These two systems operate only with conductive sputter targets, a circumstance the RF systems overcomes by using a radio frequency current for sputtering. A schematic sketch of the dc magnetron sputter system used in this work with the main components outlined is shown in figure 4.9.

The sample is placed on a horizontally moveable holder and by adjusting the sample holder’s velocity the film thickness can be controlled (see table 4.1). The sputter yield, which is the ratio between released atoms and the incident particles, can vary between 0 and 10^3. Various factors influence the yield e.g. the impact energy, the particle mass, the angle of incidence and the target material. In general, the sputter yield increases with heavier incident particles. The sputter system was operated with argon as sputter gas due to the relatively high mass, easy availability, cost-efficiency and its inert properties towards sputter target materials.

The sputter chamber was baked out for 3h during evacuation to reduce the base pressure. After 6 h the base pressure was in the range of 0.7-2 x 10^{-6} mbar, the sputter pressure (with argon flow on) was set to approx. 3 x 10^{-3} mbar. The targets have been sputtered with powers between 50-200 W. A list with the main sputter parameters and values is given in table 4.1.
Figure 4.9: Main components of the sputter system used for thin film coating. Three individual sputter targets can be simultaneously placed inside the vacuum chamber allowing for the consecutive sputtering of three different films. Reactive sputtering is possible due to an artificial gas inlet ($N_2$). The square sputter aperture, which defines the area to be sputtered and influences the film homogeneity, is adjustable but was kept at 80 mm. The velocity of the sample holder, which moves under the sputter targets on a conveyor belt, defines the thickness of the sputtered film. Prior to each film deposition the heating tape was set to 100°C for several hours to improve the base pressure (0.7-2 x $10^{-6}$ mbar). The heating tape was switched off and the vacuum chamber was left to cool down to room temperature for the deposition. The sputter targets are water cooled to avoid overheating during sputtering.
CHAPTER 4. SAMPLE FABRICATION AND EXPERIMENTAL METHODS

For the dc magnetron process used in this work a negative voltage is applied at the sputter targets which causes $Ar^+$-ions from the ionised argon gas to accelerate towards the targets. Due to the magnetic field from the magnets behind the target the electrons move in helical trajectories around the magnetic field lines forming a dense plasma ring adjacent to the target surface and thereby ionising further argon atoms, as shown in figure 4.10 a). If the argon pressure is too low not enough $Ar^+$ can be generated and a self-sustaining plasma can not be established. Therefore, the argon flow rate is a critical value influencing the sputter yield. The $Ar^+$-ions are accelerated towards the negatively charged target, as see in figure 4.10 b). A minimum energy threshold exists between 15-40 eV below which no sputtering can occur [7, 124].

<table>
<thead>
<tr>
<th></th>
<th>Ta (15 Å)</th>
<th>Co (3 Å)</th>
<th>Pd (9 Å)</th>
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<tr>
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<td>50</td>
</tr>
<tr>
<td>velocity (m/min)</td>
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<td>3.58</td>
<td>2.7</td>
</tr>
<tr>
<td>argon flow (sccm)</td>
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<td>6/4</td>
<td>6/4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Py(20 nm)</th>
<th>Al(5 nm)</th>
<th>AlN(150 nm)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5</td>
<td>142</td>
</tr>
<tr>
<td>power (W)</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>velocity (m/min)</td>
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<td>5.4</td>
<td>1</td>
</tr>
<tr>
<td>argon flow (sccm)</td>
<td>6/4</td>
<td>6/4</td>
<td>5(Ar)&amp;5($N_2$)</td>
</tr>
</tbody>
</table>

Table 4.1: Sputter parameter for the fabricated magnetic thin films. The film thicknesses are denoted in top line in brackets behind the material. The velocity parameter refers to the speed of the movable sample holder on which the sample is fixed. Before each deposition a 120 second pre-sputtering sequence was executed to ensure clean sputter target surfaces. The first digit in the argon flow rate is the pre-sputter flow, the second is the rate during sputtering. All sputter parameters are assumed to scale linearly for altered layer thicknesses.

Depending on the $Ar^+$-ion energy 4 different sputter regimes can be distinguished.

1. **Low Energy** \((0 < E < 50 \text{ eV})\)
   In this regime hardly any sputtering takes place.

2. **Single-Knockon** \((50 \text{ eV} < E < 1 \text{ keV})\)
   The incident particle undergoes a small number of collisions with surface atoms transferring energy and momentum to surrounding atoms. Eventually, a surface atom receives a (recoil) momentum transfer directing it away from the surface and enough energy is transferred to overcome binding forces and to release the atom from the surface. This event is shown in figure 4.10 c).
Figure 4.10: Illustration of the basic physical sputter mechanism taking place at the sputter target surface for the DC magnetron process used here. a) shows the formation of the plasma ring in close proximity of the sputter target. Electrons move preferentially in helical trajectories within the magnetic field confining the plasma into a doughnut shape. b) The positively charged $\text{Ar}^+$-ions are accelerated towards the negatively biased target. The incident ions penetrate the target and displace adjacent atoms on their way (b)). Eventually, in c) momentum and energy transfer enable atoms close to the surface to be ejected and to move towards the substrate to form a thin film layer. Usually the angular emission profile is assumed to be cosine-like, however changes in the sputter ion’s energy can lead to different angular emission profiles as shown on the right hand side in d).
3. **Linear Cascade** (1 keV < E < 50 keV)

The incident particle undergoes a large number of collisions while penetrating into the target. The energy and momentum transfer releases secondary cascades of excited atoms scattering statistically through the sample. Statistically, some surface atoms receive a (recoil) momentum transfer directing it away from the surface with enough energy to overcome binding forces and to emerge from the surface.

4. **Ion Implantation** (E > 50 keV)

The incident particle energy is so high, that it penetrates deep into the sample and little surface atoms receive sufficient energy and momentum transfer to be sputtered.

In general, the emission profile, as shown in figure 4.10 d), of sputtered atoms follows a cosine angular distribution [82] (black circle). The arrows represent the relative sputter yield in the corresponding directions. However, sputter target crystallinity [139] and the angle of particle impact have a strong influence on the emission distribution. The incident particle’s energy also changes the distribution - low energy particle bombardment broadens the distribution into an under-cosine shape (red circle), whereas high energy particle impact makes the distribution more directional bringing it into an over-cosine shape (blue circle).

A second effect during sputtering is that impinging Ar-ions release secondary electrons from the sputter target. These secondary electrons are driven by the electrical field into the plasma. Here they support the ionisation of further Ar atoms and thereby helping to sustain the plasma at even lower pressures. Low sputter pressure reduces the probability of collisions between Ar-gas atoms and sputtered atoms ensuring a homogeneous sample coverage. After the atoms were knocked-out of the target they move ballistically towards the substrate to which they adhere. The process of sputtering involves no direct heat sources and the plasma ring around the targets is spatially separated from the sample (5-10 cm) therefore the average sample temperature during deposition remains low (slightly above room temperature). The high sputter rate at a low substrate temperature in combination with the increased average energy of sputtered atoms and the angular sputter distribution (facilitated by scattering processes due to the Ar-sputtergas atmosphere) result in smooth interfaces between adjacent layers and reduced strain between the different layers as well as the substrate and film [16,64,142]. This, in return, leads to almost defect free, high quality thin multilayer films with expected magnetic
properties. Insufficient adhesion can cause film cracks, embrittlement and eventually the delamination of films or nanostructures. With the build-up of subsequent sputtered atoms a three dimensional thin film structure can evolve determined by the surface energy and surface mobility of the adhered atoms (adatoms). The atomic ordering follows the principle of energy minimisation allowing the differentiation of three main growth modes [3, 6, 138] which will be introduced briefly in the following.

- **Frank-van der Merwe**
  In this growth mode the formation of one atomic layer is completed first before an additional one starts on top of it [44] (see figure 4.11). This mode appears often for materials which are sputtered on a substrate of the same material.

- **Stranski-Kastranov**
  Firstly, a single or multi atomic layer forms after that the growth changes and continues into three dimensional island formation, as seen in figure 4.11.

- **Volmer-Weber**
  Here a three dimensional island formation starts right from the beginning on eventually leading to a continuous film as shown in figure 4.11.

![Figure 4.11: Possible growth modes of sputtered atoms on a substrate. Front: Frank-van der Merwe (F.-v.d.M.); middle: Stranski-Kastranov (S.-K.) and back: Volmer-Weber (V.W.). Shown are snapshots of different monolayer coverages (0.5, 1, 1.5, 2 monolayer). Figure after [86].](image)

Besides these three main models Argile et al. [3] reported on the occurrence of two additional, but less common, growth modes namely the simultaneous multilayer (SM)
growth and the monolayer plus simultaneous multilayer (MSM) growth. In the SM model adatoms are considered to have no surface mobility. Layers form as atoms assemble randomly on the surface. As further atoms stack up three dimensional film growth takes place. If the adatoms are mobile on the substrate surface but stick to their own kind SMS growth takes place forming a continuous layer first with subsequent island growth following the SM growth mechanism.

The actual growth mode is governed by the surface energy \[ \gamma \] and in order to determine the mode the following energy contributions need to be taken into account - \( \gamma_A \) the surface energy of the adsorbate, \( \gamma_S \) the surface energy of the substrate and \( \gamma_{AS} \) the interface surface energy. Depending on the sign of the total energy, \( \Delta \gamma_{\infty} = (\gamma_A + \gamma_{AS}) - \gamma_S \), film growth will take place according to the Frank-van der Merve model (for \( \Delta \gamma_{\infty} < 0 \)) or for \( \Delta \gamma_{\infty} > 0 \) according to the Volmer-Weber or Stranski-Kastranov model. At finite temperatures a thin adsorption layer always forms on top of the substrate, therefore the Volmer-Weber case is a idealised model of the Stranski-Kastranov case [3].

As discussed previously sputter parameter such as Argon pressure, energy distribution of sputtered atoms or the substrate temperature can have a large impact on the film formation. Increased working gas pressure leads to multiple collisions of sputtered atoms changing their angular distribution. The utilisation of a working gas with a higher atomic mass improves the energy transfer for sputtering while maintaining a low working gas pressure [8,16]. A first model to describe the microstructure of evaporated films was developed by Movchan et al. [88]. A refined model for sputtered films taking thermal activation and sputter pressure into account was proposed by Thornton et al. [129, 130]. Messier et al. [85] extended Thornton’s model by incorporating the influence of ion bombardment on the film structure.

Figure 4.12 shows the microstructure zone model as given by Thornton as a function of normalised temperature and argon pressure. Four different film textures can be identified in which the morphology of the film differs considerably.

- **zone 1**
  
  In this zone sputtering takes places at oblique angles, due to the high argon pressure, leading to porous columnar structures with high surface roughness. Atomic Shadowing effects during growth lead to voids in the film which may incorporate gaseous impurities.

- **zone 2**
  
  This zone is regarded as a transition state between zone 1 and 3 with minimal surface roughness and fibrous small crystallites.
4.1. SAMPLE FABRICATION

Figure 4.12: Microstructure zone model according to Thornton [129, 130] for sputtered metal films as a function of argon pressure and normalised substrate temperature ($T_M$ - material melting temperature). Four different growth regimes can be identified: zone 1) columnar growth but voids due to shadowing effects, zone 2) transition zone with fibrous grains little roughness, zone 3) columnar grains with boundaries, zone 4) equiaxed grains.

- **zone 3**
  The grain structure is columnar with defined grain boundaries. Surface diffusion of adatoms plays an important role during formation of this zone.

- **zone 4**
  Due to the high temperatures bulk diffusion takes place forming a dense structure of equiaxed grains. Sporadic recrystallisation can take place.

Although grain size predictions are material dependent, in general, the grain size increases with increasing temperatures as shown in the Thornton diagram on the temperature axis. Keeping the interface roughness low is important for the fabrication of multilayer samples with out-of-plane anisotropy such as in Co/Pd-multilayer.
4.2 Sample Characterisation Methods

4.2.1 Vibrating Sample Magnetometry

Vibrating sample magnetometry provides an easy method to determine the magnetic properties of thin film samples. A wide range of measurements are possible from the basic magnetic characterisation by M-H loops (hysteresis loop) to more advanced measurements such as remanance curves or time dependent sweep rate. In this work M-H loops were used to determine the basic magnetic properties of the samples as a function of time. The Microsense Vibrating Sample Vector Magnetometer (VSM) model 10 allows for the control of environmental variables over a wide range, e.g. the maximum applied magnetic field (up to 2 Tesla) and the field angle (in-plane, out-of-plane, $0 - 360^\circ \pm 0.05^\circ$). Figure 4.13 shows a sketch of the VSM and illustrates its main components and working principal.

Magnetic samples subject to elevated temperatures can alter their magnetic properties e.g. ferromagnetic samples lose their magnetisation when heated beyond the Curie temperature. To allow magnetic measurements as a function of temperature the temperature of the sample environment can be varied between $150 K < T < 1000 K$. This allows to investigate the influence of elevated temperatures, which occur during rf power application in STXM experiments (see chapter 6.3), on the magnetic properties of mixed anisotropy samples. The result of a VSM-measurement is a hysteresis loop, which measures the magnetic moment with respect to the angle of applied magnetic field (see chapter 2.1). The interpretation of the curve allows for the derivation of magnetic properties (such as $K_{uni}$, $M_S$) of the sample. Faraday’s Law (see equation 2.40) forms the basis on which the VSM acquires an electrical readout signal from a magnetic sample.

Integrating Faraday’s Law, with respect to Stokes theorem, yields $V = -\frac{\partial \Phi}{\partial t}$, which allows the measurement of a voltage if the magnetic flux changes with time. The change in magnetic flux is captured by 8 detection coils (4 pairs of Mallison coils). They are arranged in pairs of 2 and placed at an angle of $90^\circ$ with respect to each other as shown in inset in figure 4.13. An actuator sets the quartz sample holder rod in oscillatory motion with around 75 Hz. The circular sample (8 mm diameter) is fixed with pristine Teflon or, for temperature measurements, with Kapton tape to the holder. A sophisticated joining (Mallison arrangement) of the coils cancels out most of the background noise such as field fluctuations, background fields and coil vibrations. The intrinsic noise of the system (e.g. Johnson electronic noise) can be reduced by using lock-in
amplifiers for the measurement.

Figure 4.13: Sketch of the main components of the ADE Vibrating Sample Magnetometer model 10. The VSM is decoupled from the ground (air cushion) and stabilised (iron foundation) to prevent the transfer of vibrations. The angle of the applied field can be adjusted with the help of a rotatable platform on which the magnets are mounted. The bottle with the detection coils can be heated and cooled to investigated the influence of temperature on the magnetic properties. A close-up of the pickup coils from the bottle, which measure the change in magnetic flux, is shown in inset a). Here only a set of two pairs of Mallison coils are shown. The ADE VSM has 4 pairs positioned along orthogonal directions. The air gap between the pole shoes is adjustable.

4.3 X-ray Experimental Methods

In order to investigate the structural and magnetic properties of the fabricated samples the unique properties of x-ray radiation were used. An x-ray microscope was used to image magnetic domains in patterned samples and the coherence of x-ray was used to obtain a two-dimensional scattering image of a nanostructured array.

The Scanning Transmission Microscope experiments (STXM) and the Small Angle X-ray experiments (SAXS) were conducted at the Swiss Light Source (SLS) at the Paul Scherrer Institute (PSI). The SLS is a 3rd generation electron synchrotron that provides electromagnetic radiation from the infrared (≈1 eV) to the soft x-ray (in the order
of 100 eV) up to the hard x-ray (in the order of 10 keV) region. A synchrotron is a circular particle accelerator (usually electrons are used) in which the particle energy and the magnetic fields, which keep the particle in orbit, are ramped up synchronously till they reach a predefined final energy. Electrons deflected by magnetic fields experience a Lorentz force, \( \mathbf{F} = q(\mathbf{v} \times \mathbf{B}) \), and emit energy in form of radiation called synchrotron radiation or light. Synchrotron light has some unique features which makes it valuable for material science, biological investigations, crystallographic and chemical experiments. The emitted light is highly polarized (linearly in the plane of the synchrotron) and has a distinct pulsed time structure (allowing for time-resolved experiments). The SLS is a very brilliant (> \(10^{18}\) photons/(s \cdot mm^2 \cdot mrad \cdot 0.1 \cdot %bw)) x-ray source and the insertion devices are tunable over a wide wavelength spectrum. The SLS has a circumference of 288 m and operates at a electron energy of 2.4 GeV. It can be subdivided into 3 main operational segments as shown in figure 4.14:

- **The electron gun and the linear accelerator (linac)**

  The electrons are extracted from a heated cathode with the help of an applied high voltage (90 kV). In order to minimise the mutual repulsion of electrons they have to be accelerated rapidly close to the speed of light, which is done in the subsequent linac. Here rf-cavities apply a steady microwave field at around 3 GHz in order to accelerate the electrons. At the end of the acceleration segment the electrons have an energy of around 100 MeV and a velocity of > 0.999c. The electron beam is transferred to the booster ring via a fast switching (kicker) magnet.

- **The booster ring**

  Basically, the booster ring is a separate synchrotron designed to accelerated the electrons to their final beam energy of 2.4 GeV. In case of the SLS the booster ring has the same circumference as the storage ring and is in the same tunnel. The booster’s ring primary duty is to constantly provide electrons and refill the storage ring with electrons. A side-effect of the accelerating technique is the bunching of electrons, which is the formation of distinct electron clouds (packets) as opposed to a continuous electron distribution along the ring. The electron beam changes rings via a transfer tunnel.
• The storage ring

The electron current in the storage ring is about 400 mA and lasts for several hours but is constantly topped-up (top-up mode of operation) by the booster ring to maintain beam current and intensity. The ring resembles more a polygon with several straight line segments which contain insertion devices. These devices (undulator, wiggler) magnetically deflect the electron trajectories and cause the emission of extremely intense synchrotron light, which is several order higher in magnitude compared to what is obtainable from bending dipole magnets. The light is than guided to the endstation(s) of the beamlines attached to the insertion devices.

The following figure 4.14 shows a schematic of a synchrotron. For the SLS the booster and storage ring have the same diameter and are located in the same tunnel.

Figure 4.14: Sketch of an electron synchrotron with the main components outlined. Electrons are emitted from the gun and accelerated to almost the speed of light in the linac. The booster ring increases the electron energy to the desired final beam energy, which for the SLS is 2.4 GeV. For the SLS booster and storage ring have the same diameter and are located in the same tunnel. In the storage ring the electron bunches are stored for several hours. Each time the electron trajectory is bend to hold the bunches in orbit (dipole bending magnets) radiation is emitted (synchrotron radiation). Special insertion devices (Wiggler/Undulator) cause deliberately an oscillatory electron trajectory and guide the emitted radiation through beamlines to the endstations and where it is made available for experiments.
4.3.1 Coherent Small Angle X-Ray Scattering (cSAXS) Beamline

Small Angle X-ray Scattering (SAXS) offers the possibility in a single measurement to simultaneously average over a large number of nanoscale structures. SAXS measurements are typically sensitive to structure dimensions between 5 - 100 nm. The exposure during the experiment takes only a few seconds and the measured scattering patterns can be modelled and analysed using conventional scattering theory and image processing algorithms. The SAXS experiments were conducted at the cSAXS (X12SA) beamline at the Swiss Light Source, which is located at the Paul Scherrer Institute. This beamline gets its light from an undulator and operates in a hard x-ray energy regime between 4-19 keV with an energy resolution $\Delta E/E < 0.02\%$ and a photon flux at the sample position of about $10^{12}$ photons/sec. The beamline layout is shown in figure 4.15.

Figure 4.15: Sketch of the cSAXS (X12A) beamline and its main components. Synchrotron radiation created in the undulator is guided through the beam optics to the sample. The nanostructures on the $Si_3N_4$-membrane scatter the incident radiation according to Bragg’s law. The scattered beams interfere and create an interference pattern which can be recorded by the Pilatus 2D detector. The evacuated drift tube reduces unwanted scattering by air.

The use of an undulator increases the spectral brightness, reduces the divergence of the beam (smaller spot sizes possible) and allows photons to partially maintain a fixed phase relationship (coherence) compared to other insertion devices. From the polychromatic beam a single x-ray energy is selected and directed onto the sample. The spot size on the sample is variable with dimensions (horiz. x vert.) between $1.5 \times 0.8 mm^2$ and $20 \times 5 \mu m^2$. The beam is scattered by the nanostructures, following Bragg’s law, and leaves a discrete series of peaks on the 2D detector array. Scattered beams travel through an evacuated drift tube on their way to the detector in order to reduce undesired additional scattering from air which would increase noise levels in the measurement. In order to increase the accessible q-space drift tubes of 2.158 m (measurements up to $q \approx 3 nm^{-1}$) and 7.0885 m (measurements up to $q \approx 0.96 nm^{-1}$)
4.3. X-RAY EXPERIMENTAL METHODS

are available. A schematic for the calculation (equation 3.15) of the available q-space is given in figure 4.16.

Figure 4.16: Geometric relations between the experimental parameter in order to calculate the q-space coordinates of the Bragg-peaks. The sample-detector distance is determined by the employed drift-tube. Two drift tubes with dimension of 7088.5 and 2158 mm were available to address different q-space regimes. The detector pixel dimensions are fixed at 172 $\mu$m. The centre of the beam was found at pixel coordinates $x=953.5$, $y=762.5$ and stays fixed for all images.

Figure 4.17: Photographs of the cSAXS endstation showing the movable sample holder with samples attached (yellow frame). X-rays come from the right (red arrow), penetrate the membrane and are scattered. The scattered beam enters the drift tube (left side), which is an evacuated hollow cylinder, to propagate undisturbed by by air. Image b) shows a close-up of the $Si_3N_4$-membrane windows mounted in a) (yellow frame) a.
The Pilatus x-ray 2D detector is a PSI-development and is capable of single-photon counting without introducing read-out noise. The active area is 1475 x 1679 pixels with single pixel dimension of $172 \times 172 \mu m^2$. The sample holder is movable in the horizontal and vertical direction in order to measure different samples. The nanostructures are on $Si_3N_4$-membrane windows which are transparent to x-ray radiation and are arranged in a 4x4 array on a Si-chip as shown in figure 4.17 b). The two transparent rectangular samples in the middle row are glassy carbon calibration samples. Sample exposure time and exposure frequency are adjusted to achieve sufficient signal-to-noise ratio without saturating the detector.

### 4.3.2 Scanning Transmission X-ray Microscopy at the PolLux Beamline

In samples composed of different magnetic materials a three-dimensional complex domain structure can develop which is governed by the interface properties and mutual interactions between the layers. In order to investigate these effects an imaging technique is required with sufficient resolution (in the order of ten’s of nm), depth resolution (because layers are buried) and element specificity.

Figure 4.18: Polychromatic x-ray light is emitted from the dipole bending magnet of the synchrotron ring, focused through a toroidal mirror and made monochromatic by a dispersive grating (300 or 600 lines/mm). The x-rays are focused by a fresnel zone plate (FZP) with the order selecting aperture (OSA) blocking higher diffraction orders. X-rays penetrating the sample on the $Si_3N_4$-membrane are detected with a photodiode.
4.3. X-RAY EXPERIMENTAL METHODS

Scanning Transmission X-ray Microscopy (STXM), is a non-destructive, readily applicable imaging technique combining high spatial resolution (around 20 nm) and sampling depths, since it uses transmission, with element sensitivity. The spectral energy resolution is greater than \( E/\Delta E > 3000 \) [43, 108]. The STXM is installed at the Swiss Light Source at the PolLux beamline (X07DA) and operates in the soft x-ray energy range between 250-1600 eV with x-ray polarisation either linear or circular. The accessible x-ray energy range makes it ideal for the investigation of 3d transition metals such as Co and Py (Ni\(_{80}\)Fe\(_{20}\)), whose L3 absorption edges are at 778 eV (for Co) and 852 eV (for Ni) [128]. In 3d transition metals the magnetic properties arise due to an incompletely filled d shell with valence electrons [38]. Tuning to the element specific absorption edge allows imaging of an individual Co or Py layer.

The sample is imaged point by point (raster scanned) for left and right circular polarised light for a given duration. The dimension of the scanned pixel matrix depends on the resolution wanted (usually 100x80) with a exposure time of around 30 ms. Image stability restricts the parameter values accessible due to thermal load, stepper motor accuracy, resolution and microscope stability. Subsequently the left and right hand circular recorded images are divided by another to obtain magnetic contrast as described in chapter 3.1.2.

In general, the synchrotron radiation is polarised in the plane of the ring as shown in figure 4.19. Above and below the plane of the ring the synchrotron light is left/right circularly polarised. In order to access that light the circulating electron bunches are vertically deflected out of the orbit by \( \approx \pm 300 \mu\text{rad} \). This shifts the circular polarised light to the plane of the ring and makes it usable for the experiments. The deflection is compensated via fast orbit feedback quadrupole magnets making the deflection invisible to other beamlines.

Soft x-ray radiation gets easily absorbed in air, therefore STXM measurements have to take place in an evacuated vacuum chamber (\( \approx 10^{-6} \) mbar) or in a protective gas atmosphere (nitrogen, helium). The focus length (\( f \)) of the fixed mounted zone plate is energy (E) dependent (\( f(E) = d_{\text{FZP}} \frac{\Delta r}{c^2} E \), with \( c \) being the speed of light and \( h \) Planck’s constant) and can be simplified to \( f(E) \approx 7 \frac{\mu\text{m}}{\text{eV}} E \) [108] for typical zone plate parameters e.g. outer diameter \( d_{\text{FZP}} = 240 \mu\text{m} \), the outermost transparent ring \( \Delta r = 35 \text{nm} \). This leaves a gap of 5.5-6 mm between FZP and sample at the L3 energies for Co and Py with a typical OSA-sample distance of \( \approx 0.8 \text{mm} \). Figure 4.20 a) shows the endstation (STXM) of the the PolLux beamline. A close-up of the optical components (zone plate, OSA and sample mounting) is shown in figure 4.20 b).
CHAPTER 4. SAMPLE FABRICATION AND EXPERIMENTAL METHODS

Figure 4.19: The different polarisation states of synchrotron light emitted from a bending magnet. In order to access the circularly polarised light the electron bunches are deflected vertically (up or down) which shifts the cone of emission (shifted grey part) and allows the desired polarisation to pass through the aperture. Figure after [108].

Focusing on to the sample must be carried out carefully so as not to destroy the fragile membrane due to the close proximity of order selecting aperture (OSA). For the same reason the sample should have no protruding solder points or wires. The sample mounting and wire connections are shown in figure 4.21.

The nanostructures are fabricated on a \( \text{Si}_3\text{N}_4 \)-membrane which is supported by a silicon 0.5x0.5 cm\(^2\) frame. The sample is glued to a ready-made printed circuit board (PCB). Gold printed connectors on the PCB board allow for the transmission of the rf signal to the sample as shown in figure 4.21 (red arrows). Additional gold connector lines are available on the PCB which are used for the 4 point temperature sensor as shown in the close-up. The connections from the board to the sample were made with an \( \approx 3 \mu m \) thin aluminium wire, as seen in the close-up on the right. An ultrasonic wedge wire bonder was used to make the connections. To minimise the chances of a ruptured connection two aluminium wire connections were made. The PCB holder is fixed with 2 screws.
4.3. X-RAY EXPERIMENTAL METHODS

Figure 4.20: Series of photographs of the PolLux beamline with STXM endstation. a) shows an overview of the endstation, the rack on the right contains the control electronics for the dynamic measurements. A close-up of the optical elements (FZP, OSA and the sample) can be seen in b). The copper coloured cylinder contains the fresnel zone plate (FZP). The metal pole between sample and FZP holds the order selecting aperture (OSA), which is a small pinhole to exclude the passing of higher diffraction orders from the FZP. The sample itself is tilted by $30^\circ$, with all connections attached (blue/red wires). To avoid drift problems during sample acquisition the wires have to be released of any strain. The red spot on the sample is a reflected laser beam from the positioning interferometer.

to a trapezoidal metal sheet with circular holes under the $Si_3N_4$-membrane to allow x-rays to pass through.

For the experiments conducted in this work STXM is the ideal tool because it is a non-destructive, readily applicable imaging technique which allows magnetic domain configuration images to be taken with high spatial resolution (around 20 nm), sampling depths and element sensitivity. The defined time structures of x-ray pulses from the synchrotron enables time resolved experiments of magnetic phenomena such as vortex oscillation or domain movement.
Figure 4.21: Photograph of a STXM sample and sample holder. Temperature sensor wires are soldered directly onto the PCB holder. To avoid interferences and impedance mismatches coax connectors were soldered onto the PCB holder for transmitting rf-excitation signals. The close-up on the right shows the different bond pads and aluminium threads connecting them to the PCB gold connector lines.
Chapter 5

Characterisation of Large Arrays of Magnetic Nanostructures with Small Angle X-Ray Scattering

5.1 X-ray Intensity Distribution for Nanostructure Arrays

As discussed in chapter 1 a potential application of large arrays of nominally identical magnetic structures is in magnetic recording as bit patterned media (BPM). The ability to accurately characterise large arrays of nanoscale magnetic structures is a key requirement for both scientific understanding (e.g. input parameter for read/write error modelling of BPM) and technological advance (feasibility of BPM with state-of-the-art fabrication techniques). In order to investigate the structural properties of lithographically created nanostructure arrays, SAXS measurements were performed on large area two-dimensional arrays. The square arrays have a length of 500 $\mu$m in both lateral dimensions. A series of samples were fabricated where the centre-to-centre spacing varied for each array (between 40 nm and 250 nm) in order to investigate the effects on the structural parameter (mean radius, radius standard deviation, positional mismatch) and to explore the limits of SAXS measurements. Table 5.1 gives an overview of the lithographically created arrays, the array periods, the number of nanostructures and possible data density (assuming each discrete structure represents one binary state). Two identical sets of samples were produced using the methodology described in chapter 4.1 which were sputter coated with a magnetic $[Co(3\,\text{Å})/Pd(9\,\text{Å})]_8$ multilayer with
perpendicular anisotropy. The samples were designated as sample Co/Pd (I) and sample Co/Pd (II). Measurements revealed that no nanostructures were present below the 40 nm period array due to possible lithographic fabrication limits. In order to check for manufacturing defects, array and island uniformity, scanning electron microscopy (SEM) images of the islands were taken for all fabricated arrays. Figure 5.1 shows an example of an 50 nm period array of cylindrical nanostructures.

Before taking SAXS measurements position calibrations were made in order to ensure that the Si$_3$N$_4$ membrane is exposed to the x-ray beam. To provide high quality statistical data a matrix of 9 different measurement positions was predefined for each array to be measured in an automated script. Each position was exposed 6 times for 2 seconds.
5.1. X-RAY INTENSITY DISTRIBUTION FOR NANOSTRUCTURE ARRAYS

Figure 5.2: Sketch of the measurement positions on the nanostructured sample and different post-processing methods. For the subsequent data processing the images obtained can either be evaluated individually according to their position or all summed up together to yield the maximum signal-to-noise ratio.

(see figure 5.2). The short image acquisition time (seconds) reduces the thermal load on the sample and minimises the blurring of the scattering pattern (which is caused by vibration and thermal expansion). By mapping various positions across the array this measurement procedure provides an average measurement of the structural properties of the array.
A set of 6 x-ray energies was pre-set at which the samples were to be measured: 6.89, 7.4, 7.667, 7.694, 7.701, 7.71 keV. These energies were selected to sweep across the K absorption edge of cobalt which is at 7.709 keV [128]. Figure 5.3 shows the positions of the energies relative to the k-absorption edge. To increase the signal-to-noise ratio the measurements started with an incident x-ray energy of 6.89 keV in order to minimise the absorption and allowing for a higher transmitted intensity. Subsequently the remaining energies were measured.

Figure 5.3: X-ray absorption coefficient ($\mu$) for a thin Cobalt foil as a function of energy. Sharp increases (edges) occur when the energy corresponds with an electron orbital (K,L,M .. shell), which represent the minimum energy necessary to create free vacancies. The green arrow represents the energy range covered by the experiment. In the inset the change of the absorption coefficient is shown with a strong peak corresponding to the Co K absorption edge at 7709 eV. Data taken from [110].

An example of a recorded x-ray intensity pattern is shown in figure 5.4 a). The Pilatus x-ray detector (see chapter 4.3.1) is subdivided into active regions separated by inactive trenches carrying read-out electronics and connectors. The intense direct beam superimposes the Bragg-peak intensity as shown in b) which makes a direct analysis difficult. The detector images are captured as a function of pixel position. The relation to calculate the scattering angle $\theta$ is given in chapter 3.2 and the geometrical relations necessary to calculate $q$ are shown in chapter 4.3.1. The two-dimensional pixel position intensity distribution is converted into a function of the scattering vector $q_x$ and $q_y$ by using equation 3.15. The centre of the direct beam was found to be at pixel coordinates x=953.5, y=762.5 (compare with figure 5.4 a)) and stays constant for
5.1. X-RAY INTENSITY DISTRIBUTION FOR NANOSTRUCTURE ARRAYS

Figure 5.4: In a) a measured x-ray intensity pattern of a nanostructured array with a 250 nm period is shown. The measurements were taken at an x-ray energy of 6.89 keV. The rectangular structures are detector arrays which are separated by inactive regions bearing read-out electronics and connectors. The very intense direct beam is cut out by a rectangular aperture in order to avoid damaging the detector. The Bragg-peaks are aligned in a square lattice reflecting the underlying periodic ordering of the nanostructure array. Figure b) shows the same data set but from a cross-sectional perspective. The discrete Bragg-peaks are clearly visible.

In figure 5.4 b) a cross-sectional intensity distribution image of the two-dimensional scattering pattern in a) is shown. The broad peak in the centre in 5.4 b) is caused by the intense direct beam. Towards the edges the beam intensity decays causing the background intensity to become constant. The discrete spikes on top of the solid curve represent the individual Bragg-peaks whose scattered intensity is greater than the background.

In order to accurately determine the structural parameters of the array, the background intensity must be subtracted from the Bragg-peak intensity. A Matlab program was devised to identify and separate the peaks from the background intensity. Figure 5.5 shows the decomposition of the initially recorded x-ray intensity distribution (top) into one dataset which contains the Bragg-peak intensity (bottom left) and one which contains the background intensity (bottom right).
CHAPTER 5. SMALL ANGLE X-RAY SCATTERING

The initial two-dimensional data set is the same as that shown in figure 5.4 a). In the background image all the pixels identified to form a peak are removed and stored separately in a matrix. Pixels falsely identified as peaks are removed in the subsequent data processing by a moving averaging fit (see section 5.3).

The relation between real space dimensions and the reciprocal space dimensions is described by the following equation:

\[ q = \frac{2\pi}{d} \]

with \( q \) being the reciprocal space vector and \( d \) the real space length.

To map out and fit the intensity oscillations arising from the form factor (structure factor assumed to be unity) of the nanostructures properly, the total number of Bragg-peaks needs to be high with a dense spacing in order to capture the local minima accurately. However, because of the inverse proportionality between real space dimensions and q-space vector (see equation 5.1) the number of Bragg-peaks decreases for the very dense arrays as seen in figure 5.6. Naturally, less measured data points in reciprocal space make the subsequent fitting more challenging and the quality of the fit \( r^2 \)-value reduces. Low intensity Bragg-peaks which appear as secondary peaks next to regular Bragg-peaks are called satellite peaks. For dense arrays satellite peaks appear in the scattering pattern. However, the satellite peaks are easily identifiable in the scattering pattern because their intensity is several orders of magnitude lower. For the modelling of the structural parameter of the array only the major Bragg-peaks were taken into account and the satellite peaks were neglected. A discussion of the possible origin of the satellite peaks follows at the end of this chapter.
5.1. X-RAY INTENSITY DISTRIBUTION FOR NANOSTRUCTURE ARRAYS

Figure 5.5: In order to analyse the Bragg-peak intensity the initial x-ray distribution image is decomposed into two data sets. The bottom left image shows the data set which contains the individual Bragg-peak intensities only, the bottom right image shows the data set with the background intensity only. Pixels, defining a Bragg-peak, were excluded from the background intensity data set and set to zero intensity leaving a dark spot.

Figure 5.6: Three-dimensional visualisation of the x-ray intensity distribution for the 250 nm (a)) and 40 nm (b)) array period. In a) the dense Bragg-peak intensities form a distinct circular ring structure reflecting the underlying form factor of the nanostructures. As the period decreases the number of Bragg-peaks decreases as seen in b) and the oscillations are less obvious.
CHAPTER 5. SMALL ANGLE X-RAY SCATTERING

Three-dimensional representations of a Bragg-peak plot of the recorded intensity distribution of the 250 and 40 nm period are shown in figure 5.6. The scattered intensity can be factorised into contributions from the form factor ($F(q)$) and the structure factor ($Z(q)$) as given in equation 3.16. Due to the strict square lattice arrangement of nanostructures the structure factor can be assumed to be unity. Therefore, any intensity variations can be directly related to the form factor of the structures allowing the deduction of structural array parameter (mean island diameter and distribution, island lateral misplacement). With a dense distribution of Bragg-peaks a mapping of the form factor oscillations is possible. These form factor oscillations can be seen in figure 5.6 showing a pronounced radial intensity variation.

5.2 Background Subtraction Methods

Although the intensity variations can readily be seen in the plots the Bragg-peak intensity in the data is still superimposed by the direct beam and background intensity. In order to provide accurate Bragg-peak intensities for subsequent fitting of the model, precise background intensity subtraction must be carried out on the recorded scattering intensity distribution. Figure 5.7 shows an illustration of three different approaches of background subtraction that were utilized in order to correct the Bragg-peak intensity for direct beam and background intensity.

The peak intensity is composed of the Bragg-peak intensity (illustrated as pyramidal spikes) and the direct beam/background intensity (illustrated as pillars below), which needs to be subtracted in order to obtain the corrected Bragg-peak intensity.
5.2. BACKGROUND SUBTRACTION METHODS

Figure 5.7: Background subtraction methods for the determination of the corrected Bragg-peak intensity. In panel a) (patch approach) the Bragg-peaks are excluded from the scattered intensity distribution and the pixel vacancies are patched by gradient adjusted planes in order to create a smooth intensity distribution. By subtracting both data sets the corrected Bragg-peak intensity is obtained. In panel b) (analytical approach) the background intensity distribution is approximated by a analytical function and subtracted to give the corrected Bragg-peak intensity. The direct Gaussian fitting approach in c) employs no intermediate data processing steps and fits Gaussian distributions directly to each measured Bragg-peaks.
5.2.1 The Patch Approach

As part of the analysis process the measured x-ray intensity distribution is decomposed into a Bragg-peak intensity and a background intensity data set (see chapter 5.1). However, the obtained background intensity data set has pixel vacancies (pixel previously defining a Bragg-peak and after decomposition set to zero intensity) were the Bragg-peaks were beforehand. In order to get a smooth background function, necessary for the subsequent subtraction, the pixel vacancies in the background intensity data set were filled with gradient adjusted planes (patches) (see figure 5.8). The planes are described by the following equation: \( m \cdot x + n \cdot y + p \), where the fit parameter \( m_x, n_y \) (gradients along the axes) and the intensity \( p \) are determined from a fit of the pixels surrounding the vacancy. After the subtraction of the patched background from the initial scattering distribution only the corrected Bragg-peak intensities remain.

![Initial x-ray intensity distribution and patched background intensity](image)

Figure 5.8: Patching of the background intensity distribution. A section of the original x-ray intensity distribution of a 250 nm period array is shown in a). The pixels defining a Bragg-peak were identified and removed. In order to obtain a continuous background for the subtraction the vacancies were filled with gradient adjusted patches as shown in b).
5.2.2 The Analytical Function Approach

The second approach to determine the corrected Bragg-peak intensity is to fit an analytical function to the background intensity. To increase the statistical significance and to improve the signal-to-noise ratio, the background intensity was averaged and plotted as a function of radius as shown in figure 5.9. The background/direct beam intensity decay is expected to follow one of the two functions: 1.) an exponentially decaying function of the type \( a \cdot \exp(-b \cdot x) + c \cdot x + d \) or 2.) a power law function \( a \cdot (x - e)^{-b} + c \cdot x + d \), where a, b, c, d and e are fit parameters. In order to determine the function type and the corresponding parameter values both functions were fitted to the background pixel data. As an example the background data set (green circles) for a 250 nm period array is shown in the figure 5.9 as well as the fit for the power law (red trace) and exponential decay (blue trace). The divergence of the power law fit at large radii (red trace in inset b)) is a non-physical solution as the background (green circles) clearly approaches zero. Therefore the power law is disregarded in the further discussion.

![Figure 5.9](image-url)  
Figure 5.9: Radially averaged plot of the background intensity with two analytical background functions. The background x-ray intensity is represented by green dots, the red curve corresponds to the power law fit and the blue to the exponential fit. The insets show the background intensity and the fits at different radial positions. Inset a) shows a close-up at the base of the background intensity and inset b) at large radial position where the background intensity remains almost constant. The power law (red trace) fits the background better in a) but diverges at larger radii as shown in b), which is non-physical. The exponential fit approximates the intensity distribution on average better, especially at large radii as seen in inset b).

The total amount of measured pixels comprises \( \approx 2.5 \times 10^6 \) - in order to computationally
efficiently fit the background data only a subset of equally spaced background pixel was used for the subsequent fitting with the exponential function. This subset (approx. 150 000 or 6% of the totally measured background pixels) accelerates subsequent data processing (fitting) significantly. In order to ensure the independence of the fit parameter from the number of data points in the subset, a fit with approximately twice the amount of data points (approx. 280 000 or 11% of the totally measured background pixels) and one half of the amount of data points (approx. 100 000 or 4% of the totally measured background pixels) was made for comparison.

Non-physical background data points, which arise due to an incorrect decomposition of the measured x-ray distribution into Bragg-peaks data and background data, were disregarded. For example, inset a) in figure 5.9 shows the base of background intensity distribution curve (green circles) superimposed with data points at zero intensity. The data points at zero intensity are erroneous data points (falsely identified pixel from the central aperture and included into the background data set) which were disregarded.

The fit parameter for the three different reduced data sets are shown in table 5.2.

<table>
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<th>subset</th>
<th>x 10^4 data points</th>
<th>a [x 10^2]</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>adj. r^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>5.41±0.02</td>
<td>0.1685±0.0003</td>
<td>-0.05</td>
<td>57±1</td>
<td>0.930</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>4.81±0.01</td>
<td>0.1642±0.0002</td>
<td>-0.05</td>
<td>59</td>
<td>0.964</td>
</tr>
<tr>
<td>3</td>
<td>280</td>
<td>4.83±0.01</td>
<td>0.1632±0.0002</td>
<td>-0.05</td>
<td>57±0.4</td>
<td>0.933</td>
</tr>
</tbody>
</table>

Table 5.2: Fit parameter for the exponential background function obtained from subsets with 100 000, 150 000, 280 000 data points. Parameters with no error values were fixed during the fitting in order to avoid non-physical negative intensities.

To avoid non-physical negative intensities the boundary conditions for certain parameters (linear term and the intensity-offset) were constrained during the fit whereas the other parameters were free to vary between negative infinity and positive infinity. In case where the parameter was limited by the constraints the error could not be computed. Constraining the parameter boundaries changes the quality of the fit (r^2-value) only minimally (≈ 0.001).

The r^2-value is a measurement of the goodness of the fitted model compared to the measured data and is defined as \( r^2 = 1 - \frac{SS_{res}}{SS_{var}} \). The numerator describes the sum of squares of the residuals \( SS_{res} = \sum_i (y_i - f_i(x_i)) \), with \( y_i \) being the individual data points and \( f_i \) are the predicted data points by the model. The denominator, \( SS_{var} = \sum_i (y_i - \bar{y}) \), scales proportionally to the variance of the data set with the mean \( \bar{y} = 1/n \sum_i^n y_i \). The r^2-value takes on values between 1, equivalent to a perfect match between model and measured data, and 0 meaning no convergence.
Naturally, for the larger data set the individual sums will increase since they depend on the number of data points but the ratio should stay fixed for the three data sets. The data set 2 shows a slightly increased $r^2$-value compared to data sets 1 and 3. This can be attributed to the fact that the three data sets take different subsets of pixels for the fitting into account which results in a slightly better fit for this particular data set compared to the other two. The coefficients for the first subset are slightly increased, however, the coefficients for the 2nd and 3rd subset agree almost within the errors (except $\Delta b$ which has a difference of $6 \times 10^{-4}$). This demonstrates that sampling the background intensity is a valid approach and leads to an analytical function that provides a good approximation of the background.

At large radii, the power law fit deviates significantly from the background intensity at an increasing rate as shown in inset b) in figure 5.9 (red trace). The relative error after subtraction of the analytical background fit function on the Bragg-peak intensities is significantly higher at large radii where the Bragg-peak intensity is low (around 20-50 counts) compared to small radii at the base of the background intensity where the intensities reach 1 000-10 000 counts. Since the exponential function fits the background better at large radii whereas the power law function diverges, the exponential function is chosen to approximate the x-ray intensity background with the fit coefficients obtained from the largest data subset.

The three-dimensional exponential analytical background function used for subtraction to obtain the corrected Bragg-peak intensity is shown in figure 5.10 a). Figure 5.10 b) shows a cross-sectional superposition of the measured x-ray intensity distribution (red) and the plotted analytical background function (blue). As shown in inset a) in figure 5.9 the exponential background function underestimates the x-ray intensity at the base of the direct beam intensity (indicated by black ellipse) but at the same time enables the determination of the Bragg-peak intensity at the outer regions of the detector (large radii) with higher accuracy.
5.2.3 The Direct Gaussian Approach

In the third approach to determine the corrected Bragg-peak intensity, each peak is directly fitted with a two-dimensional Gaussian distribution. For the fitting, the following equation was used $a \cdot \exp(-((\sqrt{(x - centre_x)^2 + (y - centre_y)^2})/d)^2) + m \cdot x + n \cdot y + p$, where $a$, $x$, $y$, and $d$ are fit parameters defining the Gaussian curve (Bragg-peak), $m$ and $n$ describe the gradient adjusted background plane, and $p$ is the background intensity offset. In order to get the corrected peak intensity, the background offset must be subtracted from the fit. Figure 5.11 a) shows a close-up of a Bragg-peak intensity distribution (red circles) close to the centre of the scattering pattern. For the fitting a 9 by 9 pixel matrix of measured intensities (red circles) was used with the maximum pixel intensity being the centre of the matrix. The discrete intensity distribution defining the peak is overlaid with a fitted continuous Gaussian distribution with an $r^2$-value $\geq 0.999$. Figure 5.11 b) shows a fitted section of a 250 nm period array.

For comparison, the x-ray intensities obtained after background subtraction by the three different approaches are shown in figure 5.12. For the 250 nm period array around 2000 single Bragg-peaks were identified (dependent on the approach used) and mapped out as a function of radius as shown by the blue data points in figure 5.12. In order to increase the signal-to-noise ratio the x-ray intensity distribution (blue data points) was radially averaged (red data points) with a bin size of $\pm 2$ pixel. The intensity oscillations caused by the form factor are revealed in all three plots but differences
5.2. BACKGROUND SUBTRACTION METHODS

Figure 5.11: Fitting of the recorded Bragg-peaks with a Gaussian distribution taking into account the background intensity offset and the background gradient; a) shows a measured pixel intensity distribution of a single Bragg-peak (red circles). The intensity distribution was fitted with a Gaussian distribution (coloured peak). For better visibility of the defining data points the fit is transparent. b) shows a fitted section of a 250 nm period Co/Pd array. Each spike corresponds to a fitted Bragg-peak in the intensity distribution arise due to the quality of the three different background subtraction methods.

Due to the finite detector pixel size the Bragg-peak maximum is not extremely well resolved as seen in the few pixels defining the Bragg-peak in figure 5.11. Especially for sharp peaks (defined by a few pixels only) with large intensity increases over few pixels the highest measured pixel intensity does not necessarily coincide with the maximum of the intensity distribution. In order to compensate for the mismatch between the measured maximum intensity (limited by finite resolution) and the maximum of the continuous intensity distribution all measured Bragg-peak intensities were additionally fitted with a Gaussian distribution (except for the direct Gaussian fitting approach since it is done here inherently). For example, the measured maximum intensity of the Bragg-peak shown in figure 5.11 a) is located at pixel position: (x:955, y:821) - the fit, however, determines the maximum intensity at pixel position: (x:955.4, y:820.9) resulting in an radius discrepancy of 0.2 pixel. The fitting causes a slight mismatch of the fitted maximum peak intensity positions ($\leq 1$ pixel) between Bragg-peaks of the same radial distance from the centre. In order to radially average the intensity distribution the fitted intensities were averaged with a bin size of $\pm 2$ pixel. Fitting the subtracted background intensities reproduces the previously seen form factor oscillations but noticeable deviations are visible between the different approaches. For comparison and
Figure 5.12: Corrected Bragg-peak intensities from a 250 nm Co/Pd nanostructure array following the patch (a), analytical function (b) and direct Gaussian fitting (c) background subtraction approach. Shown are the logarithmic Bragg-peak intensities mapped on a radial axis after application of the different background subtraction methods (blue circles). Subsequently the intensities were averaged with a bin size of ±2 pixel (red circles). All three methods reveal the form factor oscillations qualitatively (four intensity dips), however the distribution of intensities (blue) around the averaged values (red) shows significant differences in the three plots.

to highlight these differences the maximum measured pixel intensities (green points) are plotted along with the fitted intensities (black points) as shown in figure 5.13, 5.14 and 5.15.
5.2. BACKGROUND SUBTRACTION METHODS

Figure 5.13: Comparison between measured maximum pixel intensity (green circles) and radially averaged and Gaussian fitted maximum peak intensity (black circles) for a 250 nm period nanostructure array following the patch approach. Both data sets show similar intensity oscillations arising from the form factor of the scattering object.

Figure 5.14: Comparison between measured maximum pixel intensity (green circles) and radially averaged and Gaussian fitted maximum peak intensity (black circles) for a 250 nm period nanostructure array following the analytical function approach. At intermediate radii both data sets start to coincide due to improved background subtraction. However, compared to the other two approaches the oscillations are rather poorly resolved.
Figure 5.15: Comparison between measured maximum pixel intensity (green circles) and radially averaged and Gaussian fitted maximum peak intensity (black circles) for a 250 nm period nanostructure array following the direct Gaussian fitting approach. Both data sets show similar intensity oscillations arising from the form factor of the scattering object. At larger radii, where the relative Bragg-peak intensity drops the background noise makes fitting increasingly more difficult, which reflects in larger intensity variations (compare the spreading of black points (fitted maximum) at the 4th oscillation with figure 5.13).
In general, 5 intensity maxima and 4 minima (for a 250 nm period array) can be seen in figures 5.13, 5.14 and 5.15. In the analytical function approach (see figure 5.14) the Gaussian fitted Bragg-peak intensity (black circles) and the maximum measured pixel intensity (green circles) of the Bragg-peaks begin to coincide starting from intermediate radii. The analytical function underestimates the measured x-ray intensity distribution up to radii of \( \approx 200 \) pixel and overestimates the background for the remaining radii. Underestimation of the background causes a broadening of the Bragg-peaks after subtraction because background pixels are added to the pixel matrix defining a peak. The peak broadening results in a lower fitted intensity compared to the maximum measured intensity (black circles below green circles). Conversely, an overestimation reduces the number of pixels defining a Bragg-peak which helps fitting the peaks (because less data points need to be fitted) and results in similar intensities. Figure 5.12 b) shows a large spread of the radially mapped intensity distribution after background subtraction (for radii above 600 pixels) compared to the other two methods. This is an indication that noise becomes dominant in this intensity regime and the analytical background subtraction fails to approximate the measured background.

Based on a comparison of the plots in figure 5.12 a) and c), the background subtraction works equally well for the patch and direct Gaussian fitting approach. However, looking at the fitted intensities in figure 5.13 and 5.15 the patch approach seems to work better at intensities at large radii (5th oscillation). This is important in order to capture as many form factor oscillations as possible to facilitate subsequent fitting and to enhance the accuracy of the parameters obtained. The direct fitting approach shows a large variance in the last oscillation in figure 5.15. At large radii the Bragg-peak intensity decreases to 10's of counts but the background noise remains almost constant (\( \approx \leq 5 \) counts) which increases the fitted intensity variance. This effect does not occur for the patch approach since after the subtraction all background noise should have cancelled out.

Therefore the patch approach was chosen as the background subtraction method to calculate the Bragg-peak intensity from which the structural array parameters will be deduced with the help of model 3.23.

## 5.3 Intensity Distribution Smoothing

After radial averaging, outliers and erroneous data points were excluded from the data set by performing a moving average smoothing. For every 7 consecutive data points
a linear fit was calculated along with the standard deviation of the data points. Data points whose deviation from the fit is larger than 1.8x standard deviations (92% confidence interval) are excluded. This procedure is repeated three times in order to capture most of the outliers. Figure 5.16 shows the data set of a 250 nm period array. The initial data (after the background subtraction) in figure 5.16 a) shows many outliers - b), c) and d) show the data set after (single, twofold, threefold) application of the exclusion procedure.

Figure 5.16: Exclusion of erroneous data points by moving average. After the first exclusion almost all erroneous data points are removed. The second and third exclusion remove data points which were not captured before. Cut-off threshold for the exclusion is the 1.8σ bound obtained by the linear fit of 7 consecutive data points. Data points within the confidence interval are unaffected from the exclusion.

The smoothed data set in figure 5.16 d) still contains outliers at low radii which could not be removed. The algorithm to detect Bragg-peaks most likely identified the sharp
5.3. INTENSITY DISTRIBUTION SMOOTHING

intensity gradient at the central aperture falsely as peaks. The high intensity of these data points increases the sum of squared errors (SSE) which influences subsequent fitting because the minimum of the SSE represents the best fit of the model to the data set. The sum of squared errors can be calculated as follows: \( SSE = \sum_{i=1}^{n} (f(x_i) - y_i)^2 \). In order to reduce the influence of these erroneous points the first three data points were omitted from the form factor fit.

The model 3.23 can now be applied to the smoothed data set. A nonlinear least square fit of the model to the data set determines the model parameters. The following parameters are varied during the fit: initial intensity, the nanostructure radius (mean of the Gaussian distributed radius), the radius standard deviation (standard deviation of the Gaussian distributed radius) and the positional deviation (exponential decay of the Debye-Waller factor). The fitting terminates and is assumed to have converged when the difference of two consecutively varied coefficients or function values falls below the threshold of \( 10^{-6} \).
5.4 Modelling the Scattering Intensity Distribution of Large Area Co/Pd Nanostructure Arrays

After the exclusion of erroneous data points the data sets can now be fitted with the model 3.23. In figure 5.17 selected fits of different array periods are shown. The plots in figure 5.17 demonstrate that with decreasing array period the total number of Bragg-peaks decreases, therefore the exclusion of erroneous data points becomes essential, especially for dense arrays, in order to obtain accurate fitting results.

Two identical samples (Co/Pd (I), Co/Pd (II)), comprising arrays with periods of 250 nm, 100 nm, 80 nm, 70 nm, 60 nm, 50 nm were fabricated and measured. Tables 5.3- 5.8 show the model parameters obtained from the fitting of the measured x-ray scattering pattern. The nine entries refer to the nine different positions each period was measured (see figure 5.2). The last line gives the weighted average values of the three fitting parameters of interest (mean radius, standard deviation of the radius and the position deviation) of all nine positions measured. The quality of the fit can be assessed by the degrees of freedom corrected \( \textit{r}^2 \)-value (adj. \( \textit{r}^2 \)) and the root mean square error (rmse). The rmse value, also known as standard deviation, is calculated according to:

\[
\text{rmse} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (f(x_i) - y_i)^2}
\]

with \( y_i \) being the measured intensities and \( f(x_i) \) the intensities predicted by the model. The adjusted \( r^2 \) value is calculated as follows:

\[
\text{adj.} \ r^2 = 1 - \left(1 - r^2\right) \frac{n-1}{n-p-1},
\]

where \( p \) is the number of independent fit parameters and \( n \) the sample size. Each individual data set is fitted separately, producing an independent set of parameters. The quality of the fit is reflected in the error interval of the fit parameters. In order to obtain averaged structural parameters for the array the quality of each of the fits (and thereby the quality of the fitted parameters) were taken into account. Each fit parameter was weighted (with its error) during averaging, according to equation:

\[
\overline{x}_{\text{mean}} = \frac{\sum_i w_i x_i}{\sum_i w_i},
\]

with the weight \( w_i = \frac{1}{\sigma_i^2} \) and the parameter value \( x_i \). The standard error of the weighted average calculates as follows:

\[
\sigma_{\overline{x}} = \sqrt{\frac{1}{\sum_i w_i}}.
\]

Fit parameters, for which the standard error could not be calculated (Not a Number-NaN) due to vanishing coefficient (\( \approx 0 \)), were set to the value \( 1 \cdot 10^{16} \). This ensures that the corresponding coefficient has the weight \( 1 \cdot 10^{-16} \) (\( \approx 0 \)) and therefore does not influence the averaging.
Figure 5.17: Section of measured intensity distributions (blue circles) and model fits (red crosses) for different nanostructure array periods (250 nm, 100 nm, 80 nm, 70 nm, 60 nm, 50 nm). Error bars are given for the measured intensity but become visible only at low intensities. As guidance for the eye the calculated intensities are connected with straight line segments. The model intensities are calculated at the exact same q-space values as the measured intensities followed by a nonlinear least square fit to determine the fit parameter (structural parameter) of the model. Goodness of fit values and model fit parameter for the different periods are given in table 5.3-5.8.
### Table 5.3: Fitted model parameter of the 250 nm period array for nine different array areas. Weighted average values are in the last line.

<table>
<thead>
<tr>
<th>sample Co/Pd (I) 250</th>
<th>fitted model parameter</th>
<th>goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intensity</td>
<td>mean radius[nm]</td>
</tr>
<tr>
<td>Co/Pd (I) 250</td>
<td>104100</td>
<td>19.130</td>
</tr>
<tr>
<td></td>
<td>110827</td>
<td>19.9</td>
</tr>
<tr>
<td></td>
<td>62774</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>28174</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td>115555</td>
<td>19.8</td>
</tr>
<tr>
<td></td>
<td>102422</td>
<td>19.3</td>
</tr>
<tr>
<td></td>
<td>28832</td>
<td>19.1</td>
</tr>
<tr>
<td></td>
<td>32628</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>27661</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>11503</td>
<td>19.4</td>
</tr>
<tr>
<td>weighted average:</td>
<td>19.57±0.02</td>
<td>1.08±0.02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>sample Co/Pd (II) 250</th>
<th>fitted model parameter</th>
<th>goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intensity</td>
<td>mean radius[nm]</td>
</tr>
<tr>
<td>Co/Pd (II) 250</td>
<td>104100</td>
<td>19.130</td>
</tr>
<tr>
<td></td>
<td>116342</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>112656</td>
<td>19.8</td>
</tr>
<tr>
<td></td>
<td>97205</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>101548</td>
<td>19.2</td>
</tr>
<tr>
<td></td>
<td>90914</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>23801</td>
<td>19.0</td>
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<tr>
<td></td>
<td>11104</td>
<td>20.9</td>
</tr>
<tr>
<td></td>
<td>13800</td>
<td>19.6</td>
</tr>
<tr>
<td>weighted average:</td>
<td>19.41±0.04</td>
<td>0.92±0.03</td>
</tr>
</tbody>
</table>
### Table 5.4: Fitted model parameter of the 100 nm period array for nine different array areas. Weighted average values are in the last line.

<table>
<thead>
<tr>
<th>sample Co/Pd (I) 100</th>
<th>fitted model parameter</th>
<th>goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intensity</td>
<td>mean radius [nm]</td>
</tr>
<tr>
<td>376110</td>
<td>12.556</td>
<td>0.996</td>
</tr>
<tr>
<td>134334</td>
<td>11.7</td>
<td>1.3</td>
</tr>
<tr>
<td>278300</td>
<td>11.6</td>
<td>0.9</td>
</tr>
<tr>
<td>302462</td>
<td>14.1</td>
<td>1.7</td>
</tr>
<tr>
<td>141776</td>
<td>11.4</td>
<td>0.9</td>
</tr>
<tr>
<td>79522</td>
<td>11.2</td>
<td>1.0</td>
</tr>
<tr>
<td>188807</td>
<td>13.8</td>
<td>0.9</td>
</tr>
<tr>
<td>83282</td>
<td>11.4</td>
<td>0.5</td>
</tr>
<tr>
<td>3374</td>
<td>10.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

**weighted average:** 11.65 ± 0.06 1.0 ± 0.05 1.6 ± 0.04

<table>
<thead>
<tr>
<th>sample Co/Pd (II) 100</th>
<th>fitted model parameter</th>
<th>goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intensity</td>
<td>mean radius [nm]</td>
</tr>
<tr>
<td>106675</td>
<td>10.413</td>
<td>0.536</td>
</tr>
<tr>
<td>95132</td>
<td>10.3</td>
<td>0.6</td>
</tr>
<tr>
<td>114313</td>
<td>10.5</td>
<td>0.4</td>
</tr>
<tr>
<td>141155</td>
<td>10.5</td>
<td>0.4</td>
</tr>
<tr>
<td>91785</td>
<td>10.3</td>
<td>0.5</td>
</tr>
<tr>
<td>147070</td>
<td>10.4</td>
<td>0.4</td>
</tr>
<tr>
<td>9780</td>
<td>10.4</td>
<td>0.6</td>
</tr>
<tr>
<td>17929</td>
<td>9.9</td>
<td>0.5</td>
</tr>
<tr>
<td>16724</td>
<td>10.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**weighted average:** 10.4 ± 0.03 0.5 ± 0.03 1.72 ± 0.04
### Table 5.5: Fitted model parameter of the 80 nm period array for nine different array areas. Weighted average values are in the last line.

<table>
<thead>
<tr>
<th>Sample Co/Pd (I)</th>
<th>Intensity</th>
<th>Fitted model parameter</th>
<th>Goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mean radius [nm]</td>
<td>standard deviation [nm]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.108</td>
<td>0.671</td>
</tr>
<tr>
<td></td>
<td>272475</td>
<td>9.9</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>237607</td>
<td>9.7</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>237449</td>
<td>10.1</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>218610</td>
<td>10.0</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>389037</td>
<td>9.8</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>172762</td>
<td>10.6</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>125537</td>
<td>9.6</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>65504</td>
<td>9.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Weighted average:</td>
<td>9.94±0.04</td>
<td>0.68±0.03</td>
<td>1.94±0.02</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Co/Pd (II)</th>
<th>Intensity</th>
<th>Fitted model parameter</th>
<th>Goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mean radius [nm]</td>
<td>standard deviation [nm]</td>
</tr>
<tr>
<td></td>
<td>107874</td>
<td>9.436</td>
<td>0.478</td>
</tr>
<tr>
<td></td>
<td>170299</td>
<td>9.3</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>94895</td>
<td>9.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>89177</td>
<td>9.6</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>41697</td>
<td>9.3</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>137645</td>
<td>9.4</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>3582</td>
<td>9.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>18959</td>
<td>9.3</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>23133</td>
<td>9.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Weighted average:</td>
<td>9.44±0.05</td>
<td>0.52±0.05</td>
<td>1.87±0.05</td>
</tr>
</tbody>
</table>
### 5.4. MODELLING OF A LARGE AREA CO/PD NANOSTRUCTURE ARRAYS

#### Table 5.6: Fitted model parameter of the 70 nm period array for nine different array areas. Weighted average values are in the last line.

<table>
<thead>
<tr>
<th>Sample Co/Pd (I) 70</th>
<th>Fitted model parameter</th>
<th>Goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Co/Pd (I) 70</td>
<td>214630</td>
<td>8.950</td>
</tr>
<tr>
<td>Sample Co/Pd (I) 70</td>
<td>216287</td>
<td>8.8</td>
</tr>
<tr>
<td>Sample Co/Pd (I) 70</td>
<td>221093</td>
<td>8.8</td>
</tr>
<tr>
<td>Sample Co/Pd (I) 70</td>
<td>253946</td>
<td>8.9</td>
</tr>
<tr>
<td>Sample Co/Pd (I) 70</td>
<td>211686</td>
<td>8.6</td>
</tr>
<tr>
<td>Sample Co/Pd (I) 70</td>
<td>182267</td>
<td>8.6</td>
</tr>
<tr>
<td>Sample Co/Pd (I) 70</td>
<td>140428</td>
<td>9.4</td>
</tr>
<tr>
<td>Sample Co/Pd (I) 70</td>
<td>131274</td>
<td>9.4</td>
</tr>
<tr>
<td>Sample Co/Pd (I) 70</td>
<td>111484</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Weighted average: 8.86 ± 0.03, 0.61 ± 0.03, 1.87 ± 0.04

<table>
<thead>
<tr>
<th>Sample Co/Pd (II) 70</th>
<th>Fitted model parameter</th>
<th>Goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Co/Pd (II) 70</td>
<td>143977</td>
<td>8.876</td>
</tr>
<tr>
<td>Sample Co/Pd (II) 70</td>
<td>280640</td>
<td>9.0</td>
</tr>
<tr>
<td>Sample Co/Pd (II) 70</td>
<td>184449</td>
<td>8.8</td>
</tr>
<tr>
<td>Sample Co/Pd (II) 70</td>
<td>86020</td>
<td>9.1</td>
</tr>
<tr>
<td>Sample Co/Pd (II) 70</td>
<td>230761</td>
<td>8.8</td>
</tr>
<tr>
<td>Sample Co/Pd (II) 70</td>
<td>220212</td>
<td>8.8</td>
</tr>
<tr>
<td>Sample Co/Pd (II) 70</td>
<td>130</td>
<td>8</td>
</tr>
<tr>
<td>Sample Co/Pd (II) 70</td>
<td>80720</td>
<td>8.4</td>
</tr>
<tr>
<td>Sample Co/Pd (II) 70</td>
<td>334653</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Weighted average: 8.86 ± 0.03, 0.50 ± 0.02, 1.85 ± 0.04
### Table 5.7: Fitted model parameter of the 60 nm period array for nine different array areas. Weighted average values are in the last line.

<table>
<thead>
<tr>
<th>Sample Co/Pd (I)</th>
<th>Fitted model parameter</th>
<th>Goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intensity</td>
<td>mean radius[nm]</td>
</tr>
<tr>
<td>60</td>
<td>169821</td>
<td>8.830</td>
</tr>
<tr>
<td></td>
<td>171445</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>187101</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>250213</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>413816</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>192343</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>2895</td>
<td>8.0</td>
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<td>342915</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>494600</td>
<td>9.8</td>
</tr>
<tr>
<td><strong>Weighted average:</strong></td>
<td><strong>8.56±0.04</strong></td>
<td><strong>0.53±0.03</strong></td>
</tr>
</tbody>
</table>

### Table 5.8: Fitted model parameter of the 50 nm period array for nine different array areas. Weighted average values are in the last line.

<table>
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<tr>
<th>Sample Co/Pd (II)</th>
<th>Fitted model parameter</th>
<th>Goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>Intensity</td>
<td>mean radius[nm]</td>
</tr>
<tr>
<td>50</td>
<td>196332</td>
<td>8.1</td>
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<tr>
<td></td>
<td>122544</td>
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<tr>
<td></td>
<td>72176</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>156944</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>115280</td>
<td>7.3</td>
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<tr>
<td></td>
<td>117648</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>3040</td>
<td>7.1</td>
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<tr>
<td></td>
<td>63</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>4787</td>
<td>7</td>
</tr>
<tr>
<td><strong>Weighted average:</strong></td>
<td><strong>7.43±0.06</strong></td>
<td><strong>0.6±0.05</strong></td>
</tr>
</tbody>
</table>

Table 5.7: Fitted model parameter of the 60 nm period array for nine different array areas. Weighted average values are in the last line.

Table 5.8: Fitted model parameter of the 50 nm period array for nine different array areas. Weighted average values are in the last line.
Table 5.9 summarises the weighted average of the obtained structural parameter from table 5.3 - 5.8.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>19.57±0.02</td>
<td>1.08±0.02</td>
<td>1.19±0.04</td>
</tr>
<tr>
<td>100</td>
<td>11.65±0.06</td>
<td>1.00±0.05</td>
<td>1.60±0.04</td>
</tr>
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<td>0.68±0.03</td>
<td>1.94±0.02</td>
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<td>0.60±0.05</td>
<td>2.02±0.05</td>
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</table>

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<td>1.28±0.04</td>
</tr>
<tr>
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<tr>
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<td>7.53±0.06</td>
<td>0.4±0.06</td>
<td>1.92±0.05</td>
</tr>
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</table>

Table 5.9: Summarised structural parameters obtained by weighted averaging of the nine individual fits of each array period. No measurements were taken for the 60 nm period array on sample Co/Pd (II) because the membrane was destroyed.

No fitting of the 40 nm period arrays was performed because no form factor oscillations were recognisable in the x-ray intensity distribution after background subtraction and exclusion. The membrane of the second 60 nm period array (sample Co/Pd (II)) broke before measurements could be taken therefore no data is tabulated. In the 50 nm period array (sample Co/Pd (II) table 5.8) one fit did not converge and was therefore not listed in the table.

The radius distribution of the nanostructures, determined from fitting the data to the model 3.23, is visualised in the plots in figure 5.18. For nanostructured arrays with large centre-to-centre distance (250 nm period) the radius of the fabricated nanostructures is large (≈ 19.5 nm) and the radius distribution broad (≈ ± 1 nm). With shrinking centre-to-centre distance of the nanostructures both the radius and the radius distribution decrease. The smallest radius distribution was found for the 50 nm period arrays with a mean of ≈ 7.5 nm and a standard deviation of ≈ ± 0.5 nm.
Chapter 5. Small Angle X-Ray Scattering

Figure 5.18: Probability distribution of nanostructure radii for different array periods deduced from SAXS analysis of identical Co/Pd samples. Large period arrays have a large nanostructure diameter and a broad distribution which becomes increasingly narrow with decreasing array period.
In figure 5.19 the mean nanostructure radius of the Gaussian radius distribution obtained from fitted scattering data is plotted as a function of period. The lines represent linear fits to the two data sets demonstrating a linear dependence between mean nanostructure radius and array period. The fits yield the following linear equations:

\[ y_{Co/Pd(I)}(x) = 0.06x + 5 \]  (5.2a)
\[ y_{Co/Pd(II)}(x) = 0.06x + 4.6 \]  (5.2b)

Figure 5.19: Plot of the mean (nanostructure radius) of the Gaussian radius distribution obtained from fitted scattering data as a function of array period. Both data sets (red/blue triangles) show a linear decrease (red/blue lines) in the nanostructure radius as the array period is decreased.

The fit parameters (from equation 5.2a and 5.2b) agree within the errors and have an adjusted \( r^2 \) value of \( \geq 0.987 \).

Figure 5.20 shows the relation between the standard deviation of the Gaussian distribution and the array period. The data sets were fitted with the linear functions:

\[ y_{Co/Pd(I)}(x) = 0.003x + 0.4 \]  (5.3a)
\[ y_{Co/Pd(II)}(x) = 0.002x + 0.3 \]  (5.3b)

The fit parameter (from equation 5.3a and 5.3b) agree within the errors and both fits have an \( r^2 \geq 0.93 \). One data point in the Co/Pd(I) data set was excluded from the fit (black circle). Both structural parameter, the mean and the standard deviation, of the Gaussian radius distribution of the nanostructures demonstrate a linear dependence on the array period as seen in figure 5.19 and 5.20.
Figure 5.20: Plot of the standard deviation of the Gaussian radius distribution obtained from fitted scattering data as a function of array period. The lines represent linear fits to the two data sets (red: sample Co/Pd (I), blue: sample Co/Pd (II)) demonstrating a linear dependence between standard deviation and array period. One data point of the Co/Pd (I) sample was disregarded for the fitting.
5.5 Alternative Analysis using Averaged Scattering Intensity Distribution Of A Co/Pd Nanostructure Array

Instead of evaluating each of the measured nine different areas of one sample/period individually all of the recorded scattering patterns (9 areas x 6 measurements =54 data sets) were summed up forming one data set (for evaluation methods of scattering patterns see figure 5.2). Thus a scattering pattern is created that comprises the scattering information from the nine measured areas. The creation of such an array is supposed to increase the signal-to-noise ratio of the measured x-ray intensity distribution because the Bragg-peak intensities add up whereas the randomly distributed noise does not. This in turn could lead to the appearance of higher orders of the form factor oscillations in the scattered x-ray distribution.

![Figure 5.21: Measured intensity (blue circles) overlaid with the fitted model intensities (red crosses) for the averaged 250 nm period Co/Pd (I) sample. The averaged x-ray intensity is composed of the summed up 54 individual measurements (9 positions × 6 measurements). Measurement error bars are given as black lines within the blue circles.](image-url)
<table>
<thead>
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<th>period [nm]</th>
<th>fitted model parameter</th>
<th>goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean radius [nm]</td>
<td>standard deviation [nm]</td>
</tr>
<tr>
<td>250</td>
<td>19.6 ± 0.1</td>
<td>1.04 ± 0.08</td>
</tr>
<tr>
<td>100</td>
<td>12.3 ± 0.2</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>80</td>
<td>9.6 ± 0.2</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>70</td>
<td>8.7 ± 0.2</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>60</td>
<td>8 ± 1</td>
<td>0.5 ± 1</td>
</tr>
<tr>
<td>50</td>
<td>9 ± 1</td>
<td>0.6 ± 1.6</td>
</tr>
</tbody>
</table>

Table 5.10: Fitted model parameter obtained from averaged x-ray SAXS measurements performed on nanostructured arrays with periods from 250, 100, 80, 70, 60, 50 nm.

Comparing the fitted model parameter of the individual positions in table 5.9 with the fitted model parameter obtained by averaging over all measured scattering patterns given in table 5.10 a good agreement between both parameter sets is shown, although the errors in table 5.10 are one order of magnitude larger.
5.5. MODELLING OF AVERAGED SCATTERING MEASUREMENTS

fitted with the following linear function:

\[ y_{Co/Pd(I)}(x) = 0.06x + 5 \]  
\[ y_{Co/Pd(II)}(x) = 0.06x + 5 \]

The fit parameter (in equation 5.4a and 5.4b) agree within the errors and approximate the data sets with a \( r^2 \) value \( \geq 0.95 \) for Co/Pd (I) and \( \geq 0.98 \) for Co/Pd(II). The dependence of the standard deviation of the Gaussian radius distribution as a function of period is shown in figure 5.23. Only the Co/Pd (I) data set was fit with a linear function. Similar to the fit in figure 5.20 the same data point (black circle) was disregarded for fitting. The fit function

\[ y_{Co/Pd(I)}(x) = 0.002x + 0.4 \]

approximates the data set with a \( r^2 \) value of 0.94.

Conversely, to the initial assumption of a better signal-to-noise ratio and higher order form factor oscillations, averaging the measurements of different positions increases the fit parameter error by an order of magnitude (compare table 5.9 and 5.10). The mean radius obtained from the two analysis methods (individual SAXS measurement analysis and averaged SAXS measurement analysis) is comparable but does
not lie within the error limits (periods not within error limits: 100 Co/Pd (I)/(II) and 80 Co/Pd (I)/(II), 70 Co/Pd (II) and 50 Co/Pd (I)). The position variance from both methods (individual SAXS measurement analysis and averaged SAXS measurement analysis) agree within the errors except for the 80 nm period in the Co/Pd (II) data set. For both methods the obtained mean radius and standard deviation follow a linear dependency of the array period. Although the absolute Bragg-peak intensity in the averaged SAXS intensity measurement did increase no higher oscillation orders could be found. Furthermore, the increased noise at large radii (shot noise level become comparable to the low Bragg-peak intensity) in the scattering measurement complicated the subsequent fitting which in return increases the error of the fit parameters. A comparison of the structural parameter obtained from both data processing methods shows that individual fitting of each data set obtained from a position and the subsequent calculation of the weighted average over all measurements gives more accurate values with lower errors.

Figure 5.23: Relationship between the standard deviation of the Gaussian distributed nanostructure radius and the period. Data points are shown as triangles superimposed by their linear fits (straight lines).
5.6 Comparison Between SEM Determined and SAXS Modelled Nanostructure Radius

In order to compare the averaged values obtained from the SAXS measurements the nanostructure radius was independently determined from Scanning Electron Microscopy (SEM) images. SEM technique is a well established imaging technique which allows the recording of sub-nanometer resolution images due to electron-sample interactions. In the recorded image, pixels defining the diameter of the structure were counted (by hand) and converted back into a radius. In order to minimise the counting error for the diameter the horizontal and vertical pixel diameter was determined and subsequently averaged. SEM images were taken for each fabricated array period (see table 5.1) to enable a comparison between the mean radii obtained from the the two methods (SAXS and SEM measurements). Figure 5.24 shows a section of a SEM image of a nanostructured Co/Pd array with a centre-to-centre distance of 70 nm.

Figure 5.24: SEM image of a nanostructured array demonstrating the determination of the nanostructure radius by pixel counting (a)). The counting error at the edge (top and bottom) of the structure was estimated with 1 pixel (yellow circles). Additionally in image b), two structural variations (position and radius of the nanostructure) are shown which can be quantified by the model 3.23.

To increase the counting statistics the nanostructures for each period from the two samples (sample Co/Pd (I) and sample Co/Pd (II)) were counted together. The error for the diameter was estimated to be ±2 pixel - one pixel counting error at the top
and one pixel counting error at the bottom of the nanostructure (yellow dots in figure 5.24 a)). The histograms and the averaged values of the mean nanostructure diameter determined from the SEM images are shown in figure 5.25. For comparison, the mean values obtained from the individual SAXS measurement analysis, the averaged SAXS measurement analysis and the measured SEM images are summarised in table 5.11.

<table>
<thead>
<tr>
<th>period</th>
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<td></td>
<td>SEM</td>
</tr>
<tr>
<td>250 nm</td>
<td>18.8±1.9</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>100 nm</td>
<td>11.1±0.7</td>
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<td></td>
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<tr>
<td>80 nm</td>
<td>10±1</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>70 nm</td>
<td>10±0.7</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>60 nm</td>
<td>8.5±0.5</td>
</tr>
<tr>
<td>50 nm</td>
<td>7.6±0.7</td>
</tr>
</tbody>
</table>

Table 5.11: Comparison of the mean radius of the nanostructures obtained from SEM measurements (SEM) and from SAXS measurements following the two scattering pattern analysis methods (individual measurement of each position (indi. SAXS) and averaging over all positions (av. SAXS)). Except for the 100 nm and 70 nm period SEM and SAXS determined mean radius agree within the errors.
5.6. COMPARISON BETWEEN SEM DETERMINED AND SAXS MODELLED NANOSTRUCTURE RADIUS

Figure 5.25: Counting statistics of the nanostructure diameter for various array periods. To increase the counts for each array period structures from both samples (sample Co/Pd (I), sample Co/Pd (II)) were counted. The error was assumed to be ± 2 pixel.
The values measured from SEM images and the fitted values obtained from SAXS data agree very well as can be seen in table 5.11. An exception is to be found for the 100 nm and the 70 nm period. The agreement of the mean radius values for nanostructures independently measured by two different methods (SEM and SAXS) confirms that the model 3.23 can be used to describe the scattered x-ray intensity distribution and to deduce array parameter such as mean radius, standard deviation and misplacement of nanostructures.

5.6.1 Determination of the Oxide Layer in Co Nanostructures By SAXS

X-ray scattering not only offers the possibility to characterise the structural parameters of patterned arrays it might also allow for the chemical characterisation of patterned arrays of Co structures. This can be achieved by varying the energy of incident x-rays across the Co-absorption edge in SAXS experiments. For each energy a scattering pattern is measured and analysed following the methods described in chapter 5.2 and 5.3. Initial experiments were conducted to demonstrate that this class of experiments is possible. Preliminary results for two energies (7.71 keV at the Co K-absorption edge and 6.89 keV off the absorption edge - see figure 5.3) are shown in figure 5.26. Differences in the peak intensity and the period of the intensity oscillations are then related to different geometrical form factors of the scattering structures which could correlate to the formation of an oxidation layer around the Co structures.

The preliminary results provide an encouraging indication that SAXS can be used to investigate the internal chemical structure of the nanoislands which is then related to their magnetic properties. A comprehensive analysis of the measured energy dependent scattering patterns needs to be carried out to clarify the potential of this technique which is left as future work.
Figure 5.26: Preliminary x-ray scattering intensity measurements performed on Co structures at the K-absorption edge (7.71 keV) and off the edge (6.89 keV). Differences in the peak intensity and the period of the intensity oscillations could indicate different geometrical shapes of the scattering structures.
5.7 Satellite Peaks

When analysing the scattered intensity patterns it becomes noticeable that with decreasing array periodicity additional Bragg-peaks appear (satellite peaks) in the vicinity of the expected Bragg-peaks (see figure 5.27). The height of these satellite peaks is one to two orders of magnitude lower in intensity compared to the main Bragg-peaks. In the radially averaged intensity plots the satellite peak intensity follows the oscillating form factor behaviour but the graph is shifted towards lower intensities. These satellite peaks could be an indication of a possible superstructure within the array.

Figure 5.27: Close-up of a measured scattered x-ray intensity distribution from a 50 nm period array. Additional Bragg-peaks (within red circles) appear in the vicinity of the expected Bragg-peaks (caused by the underlying square lattice).

The possible effects of polydispersity and lattice mismatch on the measured x-ray intensity were already discussed in section 3.2. As a consequence of the e-beam lithographic process the nanostructured array is not written continuously but rather in fields having the size of the main (in the order of 100 µm) or sub (in the order of 1 µm) write field (as discussed in section 4.1.1). Stitching errors between the different write fields could have lead to a relative shift or tilt between the various nanostructured fields giving rise to the satellite peaks. A possibly additional disorder term needs to be added to account for this inherent fabrication problem in model 3.23 [46].
Figure 5.28: Fragmentation of a uniformly nanostructured area into subfields which could, due to relative tilting to each other, be the cause for satellite peaks. Due to the pattern writing process (main field, subfield) of the e-beam system the allegedly uniform nanostructured array (a)) is exposed in areas of different size (b)) . Relative orientation changes of the patterned area with respect to each other (c)) could lead to satellite peaks in the scattering pattern as seen in figure 5.27.
The aim of the scattering experiments was to structurally characterise large arrays of dense structures which have the potential to serve as recording media (BPM) in future hard disk drives by means of small angle x-ray scattering (SAXS). A scattering model for cylindrical nanostructures was proposed and it was demonstrated that structural parameters such as mean structure diameter, diameter distribution and position variance can be obtained by fitting the measured scattering intensity with the model. SEM measurements of the structure diameter were in good agreement with the modelled mean structure diameter. Fitting each data set individually and calculating the weighted average for the structural parameters yields lower error intervals and more accurate parameter values as compared to fitting an average of all data sets.
Chapter 6

Magnetic Interaction in Hybrid Anisotropy [Co/Pd]$_8$-Py Patterned Structures: A Static and Dynamic Study

Hybrid magnetic bilayer films (such as [Co/Pd]$_8$-Py), where one layer has perpendicular anisotropy and the other has in-plane anisotropy, have an interface region where the competing anisotropies control the magnetic structure. The Py (Ni$_{80}$Fe$_{20}$) layer has in-plane anisotropy and the Co/Pd multilayer has a perpendicular anisotropy with the easy axis of magnetization in the two layers being different in both magnitude and direction. While the domain structure and magnetic behaviour of the individual layers of such hybrid films are well understood, their combination can lead to a more complex three-dimensional magnetic domain structure with embedded magnetic vortices [13, 22, 89]. The investigation of magnetic vortices in patterned structures has received much attention in recent years because of the intriguing potential application in data storage [115] and microwave engineering [36, 103].

The samples consisted of 1.5 $\mu$m wide square elements of [Co/Pd]$_8$-multilayer with 20 nm Py on top, fabricated on $Si_3N_4$-membrane templates using electron beam lithography and sputtering. The perpendicular anisotropy layer [Co(0.3 nm) / Pd(0.9 nm)]$_8$ was deposited on a seed layer of Ta(1.5 nm)/Pd(1.5 nm). A Permalloy layer of 20 nm thickness, with in-plane anisotropy, was deposited directly on the final Pd layer and a 1 nm Al protective capping layer was deposited on top of the film stack. In order to be able to apply an oscillating magnetic field to excite patterned elements, an additional
lithographic step was used to overlay the elements with an evaporated 200 nm-thick copper stripline. A sketch of the STXM sample design, as described in detail in chapter 4.3.2, is shown in figure 6.1. The central membrane area was covered by a 150 nm-thick AlN heat-sink layer to distribute the thermal load generated during microwave excitation. The fabrication procedure is described in detail in chapter 4.1.

![Sample design for STXM experiments.](image)

Figure 6.1: Sample design for STXM experiments. The 1.5µm square magnetic structures are overlaid with an evaporated 200 nm-thick copper stripline. Adjacent to the stripline Platinum temperature sensors were fabricated in order to measure the sample temperature during rf power application.

The domain structure for individual square elements of Py and Co/Pd are well known. In figure 6.2 sketches of the magnetic domain patterns of the individual films of Py (a)) and [Co/Pd]₈-multilayers (b)) are shown. The Py layer shows a Landau domain pattern with a single vortex in the centre of the structure. The [Co/Pd]₈ multilayer shows a stripe domain pattern. The relative direction of magnetisation is indicated by the arrows and the relative magnetic contrast as imaged by the x-ray microscopy is indicated by the background colour of the corresponding domain.

Scanning transmission x-ray microscopy was employed to investigate the magnetic properties of the hybrid anisotropy square structures. The spin dependent absorption of circularly polarised x-ray light (see chapter 3.1.2) gives rise to the x-ray magnetic circular dichroism (XMCD) effect, which made an element specific (Co or Ni absorption edge) investigation of the magnetic pattern of individual layers possible.
Figure 6.2: Domain pattern sketches of non-interacting layer of Py in a) and [Co/Pd]$_8$ in b). The relative direction of magnetisation is indicated by the arrows and the magnetic contrast as imaged by the STXM is indicated by the colour of the corresponding domain.

Figure 6.3 shows a scanning transmission x-ray microscopy image of an as deposited 1.5 $\mu$m [Co/Pd]-Py square structures as grown imaged at (a) the Co and (b) the Ni absorption edge. The Co-layers show an out-of-plane stripe domain pattern while the Py layer reveals a faint in-plane Landau domain pattern. Unlike single anisotropy systems where the magnetisation remains constant as a function of depth the experimental images show the integrated intensities from a layer. The measurement integrates over the entire thickness of the Py layer where the magnetisation gradually changes from out-of-plane orientation, at the interface, to in-plane at the top of the layer [92]. This gradual magnetisation change across the Py layer gives rise to a blurring of the magnetisation pattern.
Figure 6.3: Scanning transmission x-ray microscopy image of two 1.5µm square structures as grown. Image a) shows the out-of-plane magnetic domain contrast in the Co/Pd-multilayer imaged at the Co absorption edge. Image b) shows the in-plane magnetic domain pattern in the Py-layer imaged at the Ni absorption edge. For convenience the measured domain patterns are illustrated in black/white contrast (c)) and in grey scale(d)) on the right hand side.
6.1 Mutual Domain Imprint in Hybrid Anisotropy Patterned Films

Static STXM-XMCD images of structures identified to exhibit a dynamic response after a previous microwave excitation of 15 dBm are shown in figure 6.4. In the Co/Pd layer (figure 6.4 a)) a stripe domain pattern is observed with locally circular domain structures. A rather indistinct black/white contrast is seen in the Py layer compared to the Landau pattern which is observed in single Py structures. However, careful analysis shows contrast variations (lighter and darker areas) in the Py layer image which can be related back to domain structures in the Py layer. The recognised broad domain configurations for the Py and the Co/Pd layer were traced and are shown in illustration c) and d). Both traced domain patterns (illustrations c) and d)) are superimposed in e). In red the magnetisation contrast in the Py layer is shown and in black the Co/Pd domain configuration. The superposition of the two domain structures in e) indicates a mutual domain imprint.

A detailed comparison of the magnetic domain pattern between the Co/Pd and the Py layer, specifically at the position of the circular domain structures in the Co/Pd layer is shown in figure 6.5. The recognised faint circular domain pattern in the Py layer is highlighted in red in image 6.5. The reasonable correspondence of the highlighted Py domains (red) with the locally circular Co/Pd domain pattern in figure 6.5 d) is indicative for a mutual domain imprint between both layers.

Micromagnetic simulations performed by Hrkac and Bryan (PRL in preparation), discussed in section 6.4, indicate the formation of a magnetic vortex in the Py layer close to each of the locally circular domain configurations seen in the Co/Pd layer.
Figure 6.4: Comparison between broad domain configurations in the Co/Pd and Py layer. Image a) and b) show the obtained static domain configurations for the Co/Pd layer (imaged at the Co absorption edge) and the Py layer (imaged at the Ni absorption edge). Image c) and d) show the traced domain structures as recognised in the images a) and b). In e) the traced domain structures from c) and d) are superimposed showing a reasonable correspondence.
6.1. MUTUAL DOMAIN IMPRINT IN HYBRID ANISOTROPY PATTERNED FILMS

![Image of domain patterns]

Figure 6.5: Comparison between locally circular domain configurations in the Co/Pd and Py layer. Image a) shows the Co layer domain structure and a close-up of the locally circular domain configuration. Image b) shows the static domain configuration in the Py layer. In c) the recognised circular magnetisation contrast in the Py layer is highlighted in red (compare with b)). In d) the traced Py domain configuration and the Co domain pattern are superimposed showing reasonable correspondence. This indicates mutual imprint between the layers.
6.2 Dynamic Properties of Hybrid Anisotropy Samples

In order to investigate the dynamic response of the hybrid system, an oscillating magnetic field with an excitation frequency of 250 MHz was applied by passing an ac current through the copper stripline with an input power of 15 dBm. This frequency coincides with the excitation values reported in the literature for Py elements with similar dimensions \[133\].

The magnetic structures are excited by the fast oscillating Oersted field generated by the ac current flowing through the stripline. (Spin) Angular momentum transferred from the (unpolarised) electron current passing through the stripline to the magnetic structures (spin-torque transfer) could contribute to the excitation of magnetic domains \[14, 67\]. However, spin-transfer torque contributions can be neglected \[14\] in this experimental set-up due to the \(\approx 10\) times larger dimensions of the stripline compared to the nanoscale structure and the \(\approx 10\) times higher conductivity of the copper stripline (\(\sigma_{\text{Cu}} \approx 5.9 \times 10^7 \Omega^{-1} \text{m}^{-1}\) at 20°C) compared to the Py film layer (\(\sigma_{\text{Py}} \approx 5.8 \times 10^6 \Omega^{-1} \text{m}^{-1}\) at 20°C).

The assumed uniform current distribution through the stripline can be significantly altered at high ac current frequencies. This effect, known as the skin effect, confines the majority of the current distribution to a thin layer below the surface (penetration depth is called the skin depth \(\delta_s\)) and scales with \(f^{-0.5}\). The skin depth can be calculated as follows: \(\delta_s = \frac{1}{\sqrt{\pi \mu_r \mu_0 \sigma f}}\), which gives for a 250 Mhz ac current a skin depth of \(\delta_s \approx 4 \mu m\). The stripline height is 200 nm therefore skin effects can be excluded from further considerations.

Dynamic images in figure 6.6 c) and d) taken at the Ni-absorption edge (Py layer) show two distinct (black/white) excitation spots with opposite colour contrast. As a result of the pixel-by-pixel imaging (image resolution 80x80 pixel) and time integration (20 ms/pixel) in our measurements, the position of the vortex core as a function of time was not resolved precisely, but rather black/white clouds are seen. The black/white contrast associated with the vortex core precession result from the fact that the two vortex cores with opposite polarity (with moments pointing out of/in to the image plane) have been formed. The excitation of the vortex cores from the equilibrium position due to the magnetic field causes a gyrotropic motion in opposite directions (see chapter 3.1.1 ).

The formation of a magnetic vortex configuration in the Py layer is preferred because it reduces the total magnetic energy in the layer. However, due to close proximity of the orthogonal anisotropy layer dipolar and exchange interactions result in an altered
domain structure as already confirmed by the mutual imprint revealed by the static images in figure 6.4 and 6.5. A vortex forming in the Py layer has a strong out-of-plane vortex core which couples to the underlying Co/Pd domain pattern, thereby altering the simple stripe domain pattern into a locally circular domain regions (see 6.4 a)). The coincidence of the appearance of locally circular domains at the same lateral dimensions as the vortex core strongly suggests that the two features are correlated. This modified domain structure represents a localised energy minimum pinning the vortex. The different polarities of the vortex cores in the dynamic images (figure 6.6 c)) and the corresponding oppositely magnetised central domains in the Co/Pd circular domain pattern in figure 6.5 a) provide further evidence of the mutual interaction between the different layers of the hybrid film.

Changing the phase of the rf excitation by $180^\circ$ relative to the synchrotron clock (see chapter 3.1.2) causes the image contrast to reverse, unambiguously confirming true vortex core motion of two vortices with opposite vortex core polarity in figure 6.6 c) $\mapsto$ d).

A three-dimensional visualisation of the vortex gyration in the sample is shown in figure 6.7. The vortices and their polarity are indicated by arrows. The pixel-by-pixel intensity integration caused a blurring of the gyrating vortices (black/white excitation spots).
Figure 6.6: Dynamic vortex excitation images of hybrid Co/Pd-Py sample. Image a) and b) show static magnetisation contrast images taken at the Co and Ni absorption edge respectively. The individual position of the vortex core as a function of time was not resolved precisely, but rather black/white clouds (excitation spots) are seen in the area where the vortex gyrates (red circles). The black/white contrast associated with the vortex core precession result from the fact that the two vortex cores with opposite polarity (with moments pointing out of/in to the image plane) have been formed. A phase shift in the excitation frequency of 180° caused a contrast reversal which indicates that the excitation spots are truly of magnetic origin.
6.2. DYNAMIC PROPERTIES OF HYBRID ANISOTROPY SAMPLES

Figure 6.7: Three-dimensional schematic with the static magnetisation contrast image of the Co/Pd domain structure (bottom) and the dynamic image of the Py layer on the top. The position of the excitation spots in the Py correspond with the underlying circular domains in the Co/Pd. The schematic indicates a vortex pair with reversed polarities, represented by arrows, circulating in opposite directions and coupled to the Co/Pd circular domains.
6.3 Magnetic Properties of Hybrid Anisotropy Bilayer Samples as a Function of Temperature

In order to excite the hybrid anisotropy structures rf power is applied to the stripline which causes an increase in temperature of the sample. To characterise the influence of elevated temperatures on the magnetic properties of hybrid anisotropy bilayer samples accurate temperature measurements need to be taken (shown in figure 6.8) and the magnetic properties need to be investigated as a function of temperature.

Figure 6.8 shows a calibration measurement of a sample similar to the one on which the dynamic measurements were performed. The sample was put on a hotplate at predefined temperatures and the resistance was measured in a four-point measurement set-up. Plotted is the temperature as measured by Platinum sensors on the Si₃Ni₄ membrane as a function of resistance. A linear correlation is clearly recognisable as discussed in chapter 3.1.5. A linear regression of the data was calculated (red line) yielding the fit function: \( \Delta T (\Delta R) = 3.5 \degree C/\Omega \times \Delta R + 21 \degree C \).

Figure 6.8: Four-point measurement of the sample temperature as a function of the normalised Platinum temperature sensor resistance. The measurements were performed on a sample similar to the one on which the dynamic measurements were performed. The red line shows a linear fit of the measured data points.
During the dynamic measurements the initial resistance of 227 Ω (at 25°C) of the temperature sensors change to 248 Ω. Using the linear fit function with \( \Delta R = 21 \Omega \) gives a temperature increase of about 95°C and a final temperature of approximately 120°C. However, since the temperature sensor is spatially separated from the stripline (to prevent short cuts) the temperature at the stripline is expected to be higher. In order to estimate the effect on the magnetic properties of the hybrid anisotropy sample, vibrating sample magnetometry measurements where conducted as a function of sample temperature. The sample temperature was increased in steps of 25°C and an in-plane and out-of-plane hysteresis loop was measured. Beyond 100°C intermediate measurements were conducted at 25°C after each elevated temperature measurement in order to compare the magnetic properties and identify irreversible magnetic alterations in the sample. By measuring the saturation magnetisation \( M_S \) - shown in figure 6.9) and the anisotropy field \( H_a \) - see chapter 2.1) from a hard axis hysteresis loop the uniaxial anisotropy constant \( K_{Uni1} \) can be calculated according to:

\[
K_{Uni1} = \frac{M(T)S}{2} \frac{H(T)a}{2} + 2 \pi M(T)^2
\]  

(6.1)

The measurement error for \( M_S \) and \( H_a \) was estimated to \( \approx 5\% \) - the error for \( K_{Uni1} \) calculates to 10%. The highlighted blue region denotes the temperature interval at which the sample temperature is expected to be during the measurement. Beyond a temperature of \( \approx 175°C \) thermal effects cause an irreversible change in the magnetic properties of the sample indicated by the change of \( K_1 \) at 25°C. The increased temperature lowers the uniaxial anisotropy during excitation allowing the hard magnetic Co/Pd domain pattern to interact with the vortex core. This mutual interaction changes the Co/Pd stripe domain pattern into locally circular domain patterns as observed in the simulations and the measured XMXD contrast images in figure 6.6.

The measured magnetic properties of the samples (lower magnetic anisotropy and decreased saturation magnetisation) at increased temperature were used as input parameter for the micromagnetic simulations in section 6.4.
CHAPTER 6. STUDY OF HYBRID ANISOTROPY PATTERNED STRUCTURES

Figure 6.9: Saturation magnetisation \( (M_S) \) as a function of temperature. The highlighted region identifies the temperature interval during the application of 250 MHz 15 dBm rf power. Beyond \( \approx 175^\circ C \) thermal effects alter the magnetic properties of the sample (indicated by black line).

Figure 6.10: Uniaxial anisotropy constant \( (K_{Uni}) \) as a function of temperature. The highlighted region identifies the temperature interval during the application of 250 MHz 15 dBm rf power. Beyond \( \approx 175^\circ C \) thermal effects alter the magnetic properties of the sample (indicated by black line).
6.4 Comparison between Simulations and Experimental Results

In order to confirm the hypothesis of mutual domain imprint which affects the static and dynamic properties of the hybrid anisotropy structures micromagnetic simulations were carried out by collaborators Hrkac (Univ. of Exeter) and Bryan (Univ. of Sheffield) on a 1.5 \( \mu \)m square structure comprised of [Co/Pd]$_8$ + 30 nm Py. The simulations are therefore based on a similar, but not identical, structure to that which was measured. However, the data show that the model provides a reasonable description of the underlying magnetic interactions and is capable of reproducing the essential features of the measurements.

The sample structure is discretised by a three-dimensional tetrahedral tessellation yielding a three-dimensional finite element mesh. The Landau-Lifshitz-Gilbert equation (see chapter 3.1.1) was solved for a Co/Pd-Py mixed anisotropy system using a hybrid finite element/boundary element method [45, 72, 117], with a linear basis function and a 14 nm finite element mesh. The model takes magnetocrystalline, dipolar and interface exchange coupling between the magnetic layers into account. Due to the non-uniform current path through the different materials the effect of Oersted fields were included in the simulations. Spin current interactions have shown only marginal contributions (as explained in section 6.2) and are omitted in this study. The simulations used the following parameters based on magnetic measurements made as part of the work on related samples. The Co/Pd multilayer was treated as a single material with electrical conductivity \( \sigma_{Co/Pd} = 3 \text{MSm}^{-1} \), exchange stiffness \( A_{Co/Pd} = 10 \text{pJm}^{-1} \), saturation magnetization \( M_{Co/Pd} = 400 \text{kAm}^{-1} \), an out-of-plane magnetocrystalline anisotropy \( K_{Co/Pd} = 250 \text{kJm}^{-3} \) and a damping constant \( \alpha_{Co/Pd}=0.02 \). The corresponding material parameters for the Py layer were \( \sigma_{Py} = 3 \text{MSm}^{-1} \), \( A_{Py} = 13 \text{pJm}^{-1} \), \( M_{Py} = 800 \text{kAm}^{-1} \), \( K_{Py} = 0 \text{kJm}^{-3} \) and \( \alpha_{Py}=0.02 \). The surrounding Cu-stripline had a conductivity of \( \sigma_{Cu} = 45 \text{MSm}^{-1} \). All initial remanent states were achieved following saturation in the out-of-plane direction.

The domain patterns shown in figure 6.11 represent magnetisation cross-sections at the surface of the Py layer and bottom of the Co/Pd layer of the element as shown in the inset in figure 6.11. Images a)-d) in figure 6.11 show the remanent state after relaxing from an initial out-of-plane saturation. The strong out-of-plane domain structure in the Co/Pd layer (image b)) penetrates into the Py layer (image d)). Conversely, the in-plane domain structure that dominates in the Py layer (image c)) maps onto the
Co/Pd layer (image a)). The mapping is particularly clear for the out-of-plane domain structure as shown in image b) and d). The simulations indicate the appearance of multiple vortex cores (black/white spots) in the Py (image d)) having the same polarity as the underlying Co/Pd domains (image b)). The reason for this is the strong coupling between the in-plane and out-of-plane domain structures, which induces metastable pinning site potentials, as a consequence of the mutual spin structure interaction. The simulated static domain configurations figure 6.11 b) and d) are in good agreement with the experimental static domain images shown in figure 6.5 a) and b) and demonstrate a domain imprint from the Co/Pd into the Py layer. However, the simulations represent an idealised system with uniform material parameters whereas in reality the material properties have a distribution (e.g. distribution of anisotropy) which leads to preferential pinning sites with an enhanced stability of vortex formation.

In the simulations a dramatic change is noticed when the rf current is applied to the stripline in both the Co/Pd domain structure and in the Py layer. The snapshots are taken after 20 ns of excitation with five complete current cycles (amplitude 36 mA which is equivalent to the experimental conditions of 15 dBm rf power and a period of 4 ns) applied. The previous Co/Pd domain pattern (figure 6.11 b)) now exhibits a strong circular symmetry (image f)) around the centre of the square, which couples to a single vortex in the Py-layer (black spot in image h)). During the excitation most of the simulated vortices were driven out of the system and only a central one remained. The gyroscopic vortex core motion also influences the in-plane domain pattern in the Py changing it into a Landau pattern (compare figure c) and g)). Furthermore, a mutual domain imprint of the newly created domain pattern can be seen. In the simulations of dynamic behaviour, the domain pattern in the Co/Pd layer is modified by the vortex core in the Py layer as it orbits around its equilibrium position (centre of the square) giving rise to the circular symmetry in the Co/Pd domain pattern.

In this chapter the excitation of mutually imprinted domains in micrometer-sized Co/Pd-Py hybrid anisotropy elements using continuous microwave excitation at 250 MHz and 15 dBm power was demonstrated. The mutual influence of the domain structures is reflected in an imprint of the Co/Pd stripe domain pattern in the Py, and in a position match between the circular stripe domain pattern and the excitation spots corresponding to vortex core precession in the Py-layer. Micromagnetic simulations reproduced the imprint of the stripe domains from the Co/Pd layer into the Py layer and demonstrate how the vortex in Py layer writes its orbital motion onto the Co/Pd layer.
6.4. COMPARISON BETWEEN SIMULATIONS AND EXPERIMENTAL RESULTS

Figure 6.11: Static and dynamic domain configurations calculated from micromagnetic simulations by Hrkac and Bryan. Static simulated remanent magnetic states of a 1.5 \( \mu m \) square taken at \( z=-9.6 \) nm for Co/Pd and \( z=+30 \) nm for Py. The frame of reference for the different \( z \) heights is shown in the inset. Mutual domain imprint is visible from the Co/Pd stripe domains to the Py layer (compare image b) vs. d)) and vice versa (compare image c) vs. a)). A clear circular domain structure is visible in b) and a complex magnetisation pattern resembling Landau state forms on top of it in the Py c). Black/White spots in d) indicate vortex core positions in the model. The dynamic simulations e) to h) show a snapshot of the domain pattern that evolves from the static domain configuration (a)-d)). The curling stripe domains in b) rearranged around the centre of the square f) where the vortex is located as shown in g) and h). The vortex core appears as the central black spot in h) representing the out-of-plane magnetization component.
Chapter 7

Conclusion and Future Work

7.1 Conclusions

The work in this PhD thesis covers two strands of x-ray experiments - firstly, the characterisation of large arrays of dense structures by means of x-ray scattering and secondly, the investigation of hybrid anisotropy square structures with x-ray microscopy. The aim of the scattering experiments was to structurally characterise large arrays of dense structures which have the potential to serve as recording media (BPM) in future hard disk drives by means of small angle x-ray scattering (SAXS). Since scattering is a collective phenomenon with contributions from many structures averaged structural array values with statistical significance can be obtained compared to conventional investigation techniques such as SEM or Drag Tester experiments. Large arrays of nominally identical structures were fabricated by electron beam lithography and sputtering covering an area of 500x500µm² with centre-to-centre distances ranging from 250 nm down to 50 nm. A scattering model was proposed and implemented as an analysis program in order to derive structural parameters (mean structure size, structure size distribution and position variation). The highly ordered arrays allow the assumption that the structure factor (Z(q)) in the model is unity. Different background subtraction methods and data fitting methods were tested to find the most appropriate data reduction algorithm. The patch approach, in which the Bragg-peaks were covered by gradient adjusted intensity patches, provided the best approximation of the background. Subsequently, the x-ray scattering pattern, which was measured for nine different positions within the array, was analysed according to two different methods - in method one the nine different measurement positions were
individually evaluated and in method two the nine measured positions were superimposed prior to evaluation in order to improve the signal-to-noise ratio. The individual fitting of each of the nine measured areas of the array yielded lower errors (by one order of magnitude) and better agreement with the experimental SEM measurements of the structure dimensions as compared to the superposition of the intensities of the measured positions. It was demonstrated that the structure radius and the Gaussian radius standard deviation have a linear dependency on the centre-to-centre of the structures.

It was demonstrated that SAXS measurements are an excellent investigation method to quickly (in the order of seconds) and accurately (sub-nanometer precision) determine the structural parameters of large arrays of patterned structures with statistical significance. The obtained structural array parameters can then be used as input parameters for read/write channel simulations to assess the potential of large arrays of dense structures as future BPM [94, 112, 120]. This method is not restricted to the investigation of the structural parameters of BPM but can be applied to all samples of nominally identical structures (regardless of shape) with translational symmetry (arranged in a lattice) such as spin ice [40], plasmonic [147] or self-assembled [80] structures.

The aim of the x-ray microscopy experiments was to investigate the static and dynamic domain configuration in patterned structures of hybrid anisotropy bilayer magnetic films. In these materials the magnetisation in the layers is different both in direction (orthogonal) and magnitude which gives rise to interesting new magnetic properties due to mutual interaction between the layers. Scanning transmission x-ray microscopy (STXM) was employed with X-ray magnetic circular dichroism (XMCD), where the ability to tune the x-ray energy to element specific absorption edges allows the observation of the domain patterns in the individual layers. In the transmission geometry, the measured signal is integrated over the whole volume of the structure rather than just the surface which allows for the investigation of buried layers. The structures were fabricated on Si$_3$N$_4$-membranes by means of electron beam lithography and sputtering. Additionally a Copper transmission stripline covering the structures and Platinum temperature sensors adjacent to the stripline were fabricated as part of the sample layout. Static XMCD images of the domain configuration in the two layers showed a mutual
domain imprint between the layers due to exchange and dipolar coupling. An oscillating Oersted-field generated by an rf current passing through the stripline excited the domain configuration in the Py-layer indicating the formation of two topological entities (magnetic vortices) which couple to the Co/Pd domain pattern. A mutual interaction between the vortex formation in the Py layer and the formation of locally circular Co/Pd domain patterns was observed. Time resolved micromagnetic simulations of the domain configurations in the different layers which were conducted by Hrkac and Bryan reproduce the observed mutual domain imprint and the formation and evolution of magnetic vortex states during excitation. The excitation of locally confined magnetic vortices was demonstrated, which arise due to a mutual coupling (exchange and dipolar) between the Co/Pd stripe domain pattern and the vortices in Py layer, in micrometer-sized Co/Pd-Py hybrid anisotropy elements using continuous microwave excitation at 250 MHz and 15 dBm power. The interaction between the two layers offers the possibility of creating vortex oscillators in which the underlying Co/Pd domain pattern defines through its alternating circular domain pattern the gyration radius of the core.

7.2 Future Work

7.2.1 Continuation of the Investigation of the oxide layer in Co Nanostructures By SAXS

The experiments have the potential to provide relevant information about the oxidation and internal chemical structure of the nanoislands which can lead to improved manufacturing processes and engineered nanostructures with specific magnetic properties. Preliminary results on the energy dependence of the SAXS patterns in chapter 5.6.1 show that a thorough analysis of the measured scattering patterns, the form factor determination (solid cylinder/hollow cylinder) and the energy dependent fitting of the intensity oscillations needs to be carried out.
7.2.2 Experimental Parameter Space Exploration and Vortex Core Reversal In Hybrid Anisotropy Bilayer Samples

In the future, the control of the motion of the vortex core in the Py layer via the coupled Co/Pd perpendicular domains could allow for control of its path and amplitude, something that could provide additional functionality in vortex oscillators. Therefore, a continuation of the dynamic STXM-experiments on hybrid anisotropy bilayer samples is suggested with a focus on the vortex dynamics as a function of excitation frequency and rf-power level. Additionally, field driven vortex core reversal and its effects on the underlying Co/Pd domain structure would be an interesting scientific aspect to explore and open up new potential applications e.g. in data storage [34] or new functionality in spintronics [103].
Bibliography


