Off-Axis Electron Holography of Isolated Ferromagnetic Nanowires

By

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Abstract

The investigations carried out in this thesis involved the nanoscale characterization of isolated ferromagnetic nanowires (NWs) using off-axis electron holography (EH), high-resolution transmission electron microscopy, scanning transmission electron microscopy and energy dispersive spectroscopy. The research focused on two categories of NWs, single phase CoFeB NWs and multilayer CoFeB/Cu NWs, which were fabricated by pulsed-current electrodeposition in nanoporous alumina membranes as an array of NWs. EH has been used to investigate the local magnetic behavior of the isolated NWs in their remanent state. In addition, the uniformity in diameter, composition, crystal structure of individual NWs were investigated.

Single phase CoFeB ferromagnetic NWs, with diameters ranging between 20 to 170 nm, were studied. Electron diffraction patterns indicated that the NWs were nanocrystalline, BCC CoFeB, with grain sizes up to 20 nm x 20 nm. Holograms from EH showed that the magnetization inside the NWs was uniform over most of their length, except at their edges. Since the NWs consisted of soft magnetic nanocrystals, the magnetic anisotropy was likely dominated by the shape anisotropy. Numerical simulations suggested that the stray field at the tips of the NWs was well reproduced by a truncated cone model, rather than a cylinder. The average magnetic induction was 1.4 ± 0.3 T.

Multilayer NWs consisted of periodic magnetic layers of CoFeB alloys and non-magnetic layers of Cu. Individual NW compositions, crystallinity, and layer thicknesses were calibrated using scanning transmission electron microscopy and energy dispersive spectroscopy. These properties were found to be significantly different from their expected nominal values assumed for the arrays, based on single-phase growth rates. Diffraction patterns obtained from the NWs again showed that both the CoFeB and Cu layers were nanocrystalline (BCC CoFeB, FCC Cu) but that the CoFeB layers had a significant atomic fraction of Cu, despite the small concentration of Cu used in the electrolyte. Nevertheless, the average magnetic induction of individual CoFeB layers ranged between 0.5 and 1.5 T, depending upon the thickness of the layer, from 50 nm to 250 nm, and the direction of an external magnetic field applied in situ. The magnetization was axial for all external field directions when the CoFeB layer was thicker than the diameter (45 nm), while for thin CoFeB and Cu layers (< 10 nm), magnetic vortices were detected, associated with opposing magnetization in neighbouring layers. These observations provided important insight for the interpretation of previously reported effective-anisotropy fields of similar NW arrays.
Keywords: Off-axis electron holography; Nanoscale characterization; Ferromagnetic nanowires; Magnetization; Nanocrystalline; Remanent magnetization
To: Maman (Hoora), Ali and Mohammadali
In memory of my dad, grandpa and grandma

تقديم به مامان، علي و ممديلى
به ياد بابا منصور، بابا جون و ننه جان
Only truth must be said, not all truth should be said

-Saadi Shirazi (1210-1291)
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List of Acronyms

ADF     Annular Dark Field
AFM     Atomic Force Microscopy
BF      Bright Field
CIP     Current In Plane vibrating sample magnetometry (VSM),
CPP     Current Perpendicular to the Plane
EDS     Energy Dispersive Spectroscopy
EELS    Electron Energy lost spectroscopy
EFTEM   Energy Filtered Transmission Electron Microscopy
EH      Electron Holography
FMR     Ferromagnetic Resonance
GMR     Giant Magnetoresistance
HRTEM   High Resolution Transmission Electron Microscopy
MFM     Magnetic Force Microscopy
SAD     Selected Area Diffraction
SEM     Scanning Electron Microscopy
SEMPA   Scanning Electron Microscopy with Polarized Analysis
SQUID   Superconducting Quantum Interference Device
STEM    Scanning Transmission Electron Microscopy
TEM     Transmission Electron Microscopy
VSM     Vibrating Sample Magnetometry
Chapter 1.

Introduction

1.1. Ferromagnetic nanowire arrays

Studying magnetic nanowires attracts considerable interest due to their potential for future technological applications, as well as, for the fundamental scientific insights they provide on the nanometer scale. Magnetic nanowires are confined in two dimensions because of their geometry. The only degree of freedom they have is associated with their length, which is an intrinsic shape anisotropy [1]. This degree of freedom influences the magnetic properties of magnetic nanowires, making them different from the properties of bulk materials or thin films. Moreover, a nanowire can be made from different segments along its length so that the shape of each segment and the interaction between the layers can add more degrees of freedom (complexity) to the system.

Magnetic nanowires have applications in many areas of nanotechnology, such as patterned magnetic recording media [2, 3, 4], and also have biological [5, 6], and optical and microwave applications [7, 8, 9]. These applications are possible due to the small scale (nanometer) of these wires. If the dimension approaches the characteristic lengths of the specific material they are made of, such as the spin diffusion length or the width of a magnetic domain wall, their magnetic characteristic will change. These different magnetic behaviors that are related to the material from which the nanowire structures are made, lead to specific applications [10].

To demonstrate a particular behavior useful for specific applications, nanostructures should meet two conditions: they need to have specific nanometer-scale structure; and should be producible on macroscopic scale [2, 3, 4, 7, 11, 12]. As a result,
one can have two different approaches for the fabrication of these nanostructures: the
top-down approach [13, 14, 15, 16, 17] and the bottom-up approach [18, 19, 20, 21],
with various techniques for production. These two approaches will be described in more
detail in Section 2.2.1. Moreover, fabricated magnetic nanowire arrays can be single
layer nanowires of the same component or multilayer ferromagnetic/nonferromagnetic
nanowires that demonstrate a diverse range of properties useful for different
applications. The magnetic characteristics of these nanowires can be changed by
varying their diameter, composition and layer thicknesses.

1.1.1. Single layer magnetic nanowire arrays

Single layer magnetic nanowire arrays have significant potential applications in
ultra-high-density magnetic storage devices. Each nanowire in an array can store one or
more bits of information (smallest unit of information). This is similar to continuous
magnetic thin films (made as a storage medium) where a group of crystalline grains act
as a bit.

Utilizing magnetic nanowire arrays as a medium for storing information can help
with some of the limitations in storage density of thin film media. To increase the storage
density of any media, the size of each representative bit needs to reduce. For thin film
media, this means the constituent grains have to reduce in size. However, there is a limit
to how small a magnetic grain size can be. Below that size, thermal instability
(superparamagnetism) [1] of the grains allows for spontaneous reversal of the grains’
magnetization and hence the recorded information is lost [10]. The minimum size of a bit
is therefore limited to the size of the single magnetic domain [22]. Magnetic nanowire
arrays with their inherent shape anisotropy can lower this limit. This is achieved through
the coupling of the grains in the nanowire (due to shape anisotropy), producing a single
magnetic domain [22].

In addition, the range of coercivity, $H_c$, of 500-3000 Oe [23] and high remanent
magnetization, $M_r$ (close to saturation magnetization, $M_s$) are two important properties of
the material used in any storage devices [10]. In the nanowire arrays of various magnetic
alloys, the range of desired $H_c$ can be achieved more easily than for thin films of the
same alloys due to the shape anisotropy of nanowires [12, 24, 25]. Also, a nanowire array structure with small enough wire diameter (to act as a single domain structure) and particular nanowire spacing in favour of no inter-wire interactions, can also demonstrate a high $M_r$.

### 1.1.2. Multilayer magnetic nanowire arrays

Multilayer magnetic nanowire arrays show promising giant magnetoresistance (GMR) properties with a current perpendicular to the plane (CPP) geometry [26-28]. The GMR effect was first observed in a film consisting of a magnetic-nonmagnetic multilayer structure, where by applying an external magnetic field, a relatively large change in the resistivity of the sample in the plane of the film was observed in the direction of the applied magnetic field [29, 30]. This was called the current in plane (CIP) GMR geometry. The CPP geometry mentioned above [31, 32] is more interesting to investigate since it is usually larger than the CIP-GMR effect [33].

The thickness of any multilayer thin film is smaller than its other two dimensions and hence, the resistance of the thin film across its thickness is very small. This small resistance makes the measurement of CPP-GMR effect challenging. In comparison, multilayer magnetic nanowire arrays (with high aspect ratio) are ideal candidates for accurate CPP-GMR measurement since they demonstrate higher resistance than the thin film made from the same material. For example, CPP-GMR measurement has been done successfully on several multilayers magnetic nanowires in [26-28, 34].

### 1.2. Magnetic properties of an isolated NW

The smallest structural unit of an array of single phase magnetic NWs is a cylindrical magnet, whereas for a multilayered NW array, this unit is a periodic row of magnetic - nonmagnetic cylinders of a radius, $r$. In both cases, the smallest magnetic structure has a cylindrical shape, where its magnetic properties will change depending on its thickness and radius. To better predict the remanent states of cylindrically shaped magnets, computational micromagnetic models [35] can be used. In Ref. [36] Ross et.
al, used a three-dimensional micromagnetic model [36-38] to calculate the remanent states expected as a function of the cylinder size and aspect ratio.

To calculate the remanent state of isolated cylindrical magnets using a three-dimensional micromagnetic model [36, 37], each cylinder is considered to be made of a number of unit cells with a cubic shape. Then the Landau-Lifschitz-Gilbert equations [38] are solved for each cubic cell, with its initial magnetization assumed to be uniform and parallel or perpendicular to the axis of the cylinder, or as a circumferential vortex. In this calculation, an external applied magnetic field, the magnetostatic interaction, the exchange interaction from neighbouring cells and magnetocrystalline anisotropy (if it exists) are included.

Depending on the aspect ratio (the ratio of the thickness of a cylindrical magnet to its radius), $t/r$, and radius of a cylindrical magnet, $r$, the three-dimensional micromagnetic simulation of the magnetic state with the lowest energy ranged from being a vortex to flower states [36]. For high aspect ratios ($t/r > 1$) with small $r$, simulations indicate that the remanent magnetization should be uniform along the axis of the wire, with small radial deviations at the top and bottom. This is called an out-of-plane flower state [36]. For this magnetization state, the axial remanence is large since magnetization is mostly axial for most of the volume of the cylinder. As $r$ increases, the out-of-plane flower state changes to a vortex state.

For thinner disc-shaped cylinders with smaller aspect ratios ($t/r < 1$), the lowest energy state leads to a magnetization called an in-plane flower state. This has a remanent magnetization nearly perpendicular to the axis of the disc, with opposite directions in alternating neighbouring discs. Here a transition from an in-plane flower state to a vortex state occurs for larger $r$.

For a multilayer NW, one would expect to see the magnetization states described above depending on the aspect ratio of each magnetic layer. However, because of dipolar interaction between the magnetic layers, the overall magnetization of the NW can be different. Carignan et. al, in Ref [8], calculated the effective magnetic field of arrays of multilayered NWs by considering an effective field model. In this model, it was assumed that the total field on each NW is the sum of the applied field and the magnetostatic
interaction (dipolar interaction) field. Magnetocrystalline anisotropy and exchange interaction between magnetic layers were not considered in their calculations. Under these assumptions, it was shown that a uniformly magnetized array of ferromagnetic NWs exhibits an effective anisotropy constant (due to dipolar interactions) that is approximately given by [8]:

\[ K_{\text{eff}} = \frac{\mu_0 M_s^2}{2} \left[ \frac{1 - 3(1 - f + fP)}{2} \right], \]  

(1.1)

where \( P \) is the porosity (or relative fraction of pores to the total surface) and \( f \) is the relative thickness of the magnetic layer compared to the total thickness of magnetic plus non magnetic layers.

For a single wire, corresponding to the limit of \( P = 0 \), the effective anisotropy field will reduce to

\[ K_{\text{eff}} = \frac{\mu_0 M_s^2}{2} \left[ \frac{1}{2} \right] = \frac{\mu_0 M_s^2}{2} \left[ \frac{3/2}{1 + t_N/t_{FM}} - 1 \right] \Rightarrow B_{\text{eff}} = \mu_0 M_s \left[ \frac{3/2}{1 + t_N/t_{FM}} - 1 \right], \]  

(1.2)

where the anisotropy constant can be associated with an effective anisotropy field, \( B_{\text{eff}} = 2K_{\text{eff}}/M_s \), parallel to the wire axis. For a thin magnetic layer compared to the nonmagnetic (high ratio \( t_N/t_{FM} \)), the bracket is -1, corresponding to an anisotropy dominated by the \(-\mu_0 M_s \) demagnetizing field. The remanent magnetization (assumed uniform in this simplified model) will be randomly oriented perpendicular to the wire axis. For a thick magnetic layer compared to a nonmagnetic one (small ratio \( t_N/t_{FM} \)), the bracket is 1/2, corresponding to a field of \( M_s/2 \) parallel to the wire axis. The thin magnetic layers can exhibit an out-of-plane remanent state due to the dipolar interaction of the other magnetic layers if the nonmagnetic spacers are much thinner [7, 39].

### 1.3. Nanoscale Magnetic characterizations

The magnetic properties of an individual magnetic entity at the nanoscale are hard to practically characterize, since the detectable signal is usually small. Therefore, most magnetic characterization techniques are based on measurement of and averaging
from collections of nanoscale material. This includes studies using such techniques as vibrating sample magnetometry (VSM), magnetic optical Kerr effect (MOKE), superconducting quantum interference device (SQUID), and ferromagnetic resonance (FMR) [40-41]. However, techniques such as Magnetic Force Microscopy (MFM), Scanning Electron Microscopy with Polarized Analysis (SEMPA), Lorentz microscopy, and electron holography (EH), are able to measure the magnetic properties with nanoscale resolution [40-41].

MFM, which is an Atomic Force Microscopy (AFM) technique with a magnetic probe, detects and images the stray magnetic field above the surface of a magnetic sample. This can be done through the interaction of the probe and the sample [42-43]. In MFM technique, the field dependence of domain structures and also magnetic reversal processes can be detected due to the possibility of applying different external magnetic fields. However, the influence of the magnetic sample on the magnetic probe (and vice versa) may affect the magnetic properties of the sample, which makes the quantitative characterizations of the MFM magnetic images hard [43]. Moreover, MFM, like SEMPA, only images the surface of magnetic features with limits on its capabilities for magnetic characterization of the bulk of the samples.

On the other hand, techniques based on transmission electron microscopy (TEM) for magnetic imaging, such as Lorentz microscopy and electron holography, can detect in-plane magnetic properties throughout the depth of samples. But, the samples must be thin enough to be transparent to the electron beam. The Lorentz microscopy is based on the magnetic image contrast due to deflection (by Lorentz force) of the electron beam passing through the magnetic sample. This technique has been used in the study of magnetization reversal mechanisms, as well as magnetic domain structure in magnetic samples [44]. But, obtaining quantitative information from the magnetic images and also the direction of magnetization in a single domain are difficult with Lorentz microscopy [45].

Off axis electron holography is a powerful technique that can image different states of the in-plane magnetization of samples as well as making quantitative measurements of these states.
1.4. Electron holography on isolated magnetic NWs

EH analysis has provided significant insights about the magnetic properties of individual magnetic NWs, including their magnetic anisotropy, interface anisotropy, and multilayer coupling as a function of their size, shape and structure [46, 47, 48]. The magnetic properties of ferromagnetic nanowires have previously been investigated for single phase (Co and Ni) and multilayer (Co/Cu) NWs of radii ranging from 20 to 150 nm, and a few microns in length using EH [46]. For single phase NWs of small radii in this study, the remanent magnetization state was uniform and directed along the wire axis, as theoretically expected. However, for larger radii (150 nm) the remanent magnetization became non-uniform likely due to an incomplete saturation of the magnetization. For multilayer NWs, in addition to the energetically favourable state of parallel-axial remanent magnetization, different anti-parallel alignments of magnetic segments have been observed. The spatial resolution of the magnetization from EH was limited to 70 nm, since a Lorentz lens was not available for imaging [46]. As a result, no information about the internal magnetic structure of individual NW structures was reported.

EH has recently been also carried out on 4-nm-diameter single-crystalline Co wires with spatial resolution of less than 10 nm [47]. The remanent magnetization state was also found to be along the axis of the wire, as expected, due to the high aspect ratio. However, the small radius of these NWs meant that their magnetic signal was also small and therefore, signal-to-noise was poor.

The goal of this dissertation is to probe the capabilities of EH for the high resolution characterization of the magnetic and morphological properties of individual nanoscale magnets. We will consider magnetic nanowire (NWs) fabricated by collaborators using electrodeposition in alumina templates. Besides investigating the capabilities of EH, we will show that understanding the crystallographic and magnetic characterization of individual NWs is crucial to optimizing the macroscopic magnetic properties of collections of NWs in the original templated arrays. In Chapter 4, single alloy CoFeB NWs are considered and the impact of the diameter of the NWs on their magnetic and morphological properties is investigated. In Chapter 5, we study the same
properties of multilayer CoFeB/Cu NWs as a function of their thickness and arrangement of the magnetic and non-magnetic layers.

For an individual NW, factors such as surface roughness, degree of crystallinity, shape, composition and the etchant used (for removal of the alumina membrane) will be seen to affect its overall magnetic behavior. Scanning and Transmission Electron Microscopy (STEM) techniques were employed to study these effects while electron holography was used to investigate the local magnetic behavior of an ensemble of these FMNWs.
Chapter 2.

Background

2.1. Magnetism and magnetic materials

2.1.1. Introduction

Magnetism is a physical phenomenon, which can be fully understood through quantum physics. The first thing that comes to mind when hearing this term is a magnetic bar underneath a sheet of paper with sprinkled iron particles forming a pattern. Michael Faraday was the first to carry out this experiment in 1831 [49] showing that the iron particles arrange in lines due to a force related to the magnetic bar. These lines then were known as magnetic field lines (lines of force) of the magnet.

A moving electric charge (an electric current) produces a magnetic field. If the charge moves in a closed loop, it produces a magnetic dipole, which generates magnetic field lines as illustrated in Figure 2.1. This loop of current, in other words this magnetic dipole, can be generated by any moving charge, ranging in scale from the current associated with the spin of an electron to the magnetic dipole of the earth.

One can define the magnetic dipole moment of a current loop as

$$
\mu = IA,
$$

(2.1)

where \( I \) is the current and \( A \) is the area of the loop. The magnetic dipole moment, \( \mu \), is a vector quantity, with its direction related to the orientation of the loop current following the right-hand rule. The magnetic field of a dipole is proportional to its magnetic dipolar moment, \( \mu \), and when located in an external magnetic field, the torque experienced by the dipole is
\[ \tau = \mu \times B. \]  

(2.2)

This torque forces the dipole to rotate such that \( \mu \) aligns with the magnetic field to minimize the energy of the system.

![Figure 2.1. A current loop with a current coming in and out of the page with the associated magnetic field lines.](image)

A conventional flow of charge produces a magnetic field that is maintained as long as the current is flowing. In atoms a permanent magnet can form by the current associated with electrons circling the nuclei and also from the intrinsic electron spin, as shown in Figure 2.2. The magnetic dipolar moments produced by these two currents are *orbital* magnetic moment, \( \mu_L \), and *spin* magnetic moment, \( \mu_s \), respectively.

For an electron (with charge \( e \) and mass \( m_e \)) orbiting with an angular speed of \( \omega \) around a nucleus, the angular magnetic moment \( \mu_L = e r^2 \omega/2 \) is related to the electron orbital momentum, \( L = m_e r^2 \omega \) as:

\[ \mu_L = \frac{\mu_B}{\hbar} L, \]  

(2.3)

where \( \mu_B = \frac{e \hbar}{2 m_e} = 9.27 \times 10^{-24} \text{ Am}^2 \) is the Bohr Magneton.
The equation for $\mu_s$ of an electron is similar to Eq. (2.3), when $L$ is replaced with the electron spin, $S$, and a factor $g = 2.0023$ is added. To have a net magnetic field associated with the electronic structure of an element, the element needs to have a large number of unpaired electrons contributing to an overall large magnetic moment. Elements such as Iron (Fe), Nickel (Ni) and Cobalt (Co), have such unpaired electrons, which contribute to a non-zero magnetic moment for these elements [50-51].

Materials react differently when exposed to an applied external magnetic field, $H$ (units: 1 A/m = $4\pi \times 10^3$ Oe). One can classify them based on their magnetization, $M$ (the magnetic moment per unit of volume (m/V); units: 1 A/m = $10^{-3}$ emu/cm$^3$) in an external magnetic field. The response of materials to an applied magnetic field is described by the magnetic induction $B$ (units: 1 T = 10$^4$ G). One can define two quantities describing the response of a material to an external magnetic field: susceptibility, $\chi$, and permeability, $\mu$. Susceptibility is defined as the ratio of $M$ to $H$:

$$\chi = \frac{M}{H}.$$

Permeability defines the ease of having magnetic induction in a material when a magnetic field is applied:
\[ \mu = B / H. \]

The sign and amplitude of \( \chi \) and \( \mu \) play an important role in categorizing the magnetic properties of materials as explained in the next section. The relationship between the applied magnetic field, magnetic induction and magnetization of any material can then be described as:

\[ B = \mu_0 (H + M), \]  

(2.4)

where \( \mu_0 = 4\pi \times 10^{-7} \) (H/m), is the permeability of vacuum.

### 2.1.2. Types of magnetism

In any material, orbital angular momentum and spin of the electrons are the origins of magnetic field production in atoms. However, the overall magnetic characteristics of a material depend on the electronic configuration of its atoms and their response to an applied external magnetic field. When exposed to an external magnetic field, the electrons orbiting around a nucleus form a current loop and hence a magnetic field. They tend to align in a direction such that the resulting magnetic field opposes the direction of the external magnetic field. This effect is called diamagnetism and, depending on the other magnetic effects in a material, can be the dominant effect. Diamagnetic materials have atoms with paired electrons in their outer shells. Opposition of the induced magnetic field to the applied field results in a negative magnetization for diamagnetic materials and hence, the susceptibility \( (\chi) \) of these materials is negative.

For non-diamagnetic materials, a weak diamagnetic effect does exist but it is dominated by other stronger magnetic effects [23, 50-54].

Unpaired electrons in an electronic configuration, on the other hand, can generate a net magnetic moment in the atoms or molecules of a substance. If the interactions between these moments are weak and they are uncoupled (randomly oriented moments) in the absence of an applied magnetic field, then the net magnetization is zero and one would have a paramagnetic material. Figure 2.3 shows a schematic view of randomly oriented moments in a paramagnetic material.
A random orientation of magnetic moments in atoms and molecules is caused by thermal fluctuations. The presence of an external magnetic field works against this randomization by trying to align the moments with the magnetic fields. This leads to a partial alignment of magnetic moments with the applied magnetic field producing a small magnetization in the system. This magnetization is positive, which means it is in the direction of the applied magnetic field, and the susceptibility ($\chi$) is also non-zero and positive. However, in a paramagnetic material, the magnetization will disappear as soon as the applied magnetic field is removed.

In contrast to the paramagnetic effect, there is another form of magnetism with a strong coupling of the moments resulting in a nearly complete parallel alignment of magnetic moments with a large net magnetization, even in the absence of a magnetic field. This spontaneous magnetization is the characteristic of ferromagnetic materials. Figure 2.4 shows highly ordered magnetic moments in a typical ferromagnetic material.
Iron (Fe), Nickel (Ni) and Cobalt (Co) and some of their alloys are examples of ferromagnetic materials. The electronic configuration of the valence bands of elemental Fe, Ni and Co is a 3d shell that contains unpaired electrons giving rise to a spin magnetic moment. For ferromagnetic materials the total magnetic moment is a combination of electron spin and orbital magnetic moments [52]. At the Fermi level of these elements (in the 3d band), the majority of the electrons have the same spin direction resulting in a non-zero magnetic moment in the ground state.

Ferromagnetism is temperature dependent. When the temperature reaches a characteristic value, the Curie temperature $T_C$, thermal fluctuations become strong enough to disturb the ordering and the material acts like a paramagnet.

The spontaneous magnetization of a ferromagnet can also sometimes be zero depending on the interior structure of the total volume of a material. This happens when the material has several domains with random orientation of magnetization in each domain. An applied magnetic field, however, can orient the random magnetizations more and more as its amplitude increases. There is a saturation point when all domains have magnetizations in the direction of the applied magnetic field.

The resultant spontaneous magnetization of any material depends on the individual magnetic moments of possibly different kinds of atoms or ions. The key property of ferromagnetic materials is that coupling between magnetic moments results in a complete ordering of the moments. In other types of materials, these interactions force the moments to be anti-aligned with their neighbouring moments. This is what happens in anti-ferromagnetic materials where the neighbouring magnetic moments have opposite directions (Figure 2.5 (a)). This leads to a zero net magnetization due to the complete cancelation of the magnetic moments. In ferrimagnetic materials, however, the moments are still in an antiparallel configuration but they are not all the same (they have different magnitudes) giving a nonzero spontaneous magnetization to these materials (Figure 2.5 b). Hence, ferrimagnets have all the characteristics of ferromagnets, despite the different magnetic ordering.
2.1.3. Properties of ferromagnetic materials

Ferromagnetic materials have specific characteristics that can be totally different from one material to another. These properties can be associated with the structural details of the materials, their dimensions and even the environment they are exposed to. In this section, the characteristics of ferromagnetic materials are explained in more detail.

Curie temperature: As mentioned before, there is strong coupling between the magnetic moments in ferromagnets leading to an overall magnetization of the material. But this coupling must overcome the tendency towards randomization in the direction of the moments due to thermal motion. The outcome of the competition between these two effects is specific to the examined material and is characterized by $T_C$. Below $T_C$, the magnetic moments are ordered and the material is ferromagnet, while above $T_C$ the magnetic moments are disordered and the material is a paramagnet. Therefore, to maintain the same spontaneous magnetization of the magnetic structure above its $T_C$, an applied magnetic field is needed.

Magnetic Domains: Another feature that is a specific property of a ferromagnetic material is the presence of magnetic domains in their spontaneous magnetization. These domains have a direct effect on the spontaneous magnetization of the whole system through their size and magnetization.
Any ferromagnetic material is expected to have a large magnetization below $T_C$, even in the absence of an external magnetic field. However, they often present a zero magnetization. This is because the bulk of the ferromagnet is in its lowest energy configuration (the ground state), with a number of magnetic domains with random magnetization. In each domain, all the magnetic moments are ordered so that they produce a saturated magnetization in the domain. Moreover, there are no abrupt changes in magnetization between neighbouring domains. The region between two domains, where magnetization gradually changes, is called the domain wall. The width of a domain wall is determined by minimizing the total energy of the bulk material [23].

![Figure 2.6](image)

*Figure 2.6.* A ferromagnetic material (a) in the absence of an applied magnetic field, (b) in an applied magnetic field, and (c) in its saturated magnetization state when the applied magnetic field is increased (the blue arrow shows the direction of applied magnetic field).

At the ground state of the bulk ferromagnet, the domains have random magnetization in favour of a zero net magnetization (Figure 2.6 (a)). When a magnetic field is applied, the domains with magnetizations in the same direction as the external magnetic field grow larger, whereas the rest get smaller (Figure 2.6 (b)) [55]. When the ferromagnet reaches its saturation magnetization, all of the domains have combined into one domain oriented along the applied magnetic field (Figure 2.6 (c)).
Another property, called magnetocrystalline anisotropy (to be described in the following section), forces the magnetization to orient along a particular crystallographic direction, the easy axis. Both of the effects mentioned above are in favour of having a uniformly magnetized material with just one domain. This uniform magnetized volume produces a large magnetic field in the surrounding medium, which leads to large magnetostatic energy. The tendency of any physical system to move towards a minimized energy state forces the ferromagnet to form a number of domains with different magnetization orientations, sometimes leading to zero magnetization of the bulk ferromagnet.

Magnetocrystalline anisotropy: Magnetic anisotropy is a property of ferromagnetic materials whereby the magnetization is preferred along a specific direction, namely the easy axis of the ferromagnet. Along the easy axis, the susceptibility of the material has the smallest value.

One of the sources of this anisotropy is the presence of different crystallographic directions in a ferromagnetic structure called magnetocrystalline anisotropy. As mentioned before, the magnetic moment of any ferromagnet is the combination of the spin magnetic moment and the orbital angular moment. The interaction between these two moments is related to the crystalline structure of the material. Therefore, for any structure, there are generally more than one favourable orientation for the magnetization of the material to align along.

The direction of the easy axis of any crystal is the direction of their spontaneous magnetization when there is no applied magnetic field. In the presence of an external magnetic field, the magnetization of the ferromagnet can deviate from its easy axis if the applied field is not parallel to it. Again, by removing the applied magnetic field, the magnetization orients back along the easy axis. For example, in body-centered cubic (BCC) structure, the easy axis is in the <100> direction whereas in face-centered cubic (FCC) structure, the easy axis is in the <111> direction. These two anisotropies are called cubic anisotropy. For hexagonal close-packed (HCP), the easy axis is in the <0001> direction (c-axis) with an anisotropy called uniaxial anisotropy.
Shape anisotropy: another anisotropy, which makes the ferromagnet have a magnetic easy axis, is a geometric anisotropy. For any ferromagnet with a nonspherical or cubic geometry, there are preferred directions for the saturated magnetization that will occur with the smallest external magnetic field. This is called shape anisotropy. The easy axis for shape anisotropy is along the longest direction of a ferromagnet, since it is the most energetically favourable. This is because the further apart are the induced magnetic poles at the surface of a ferromagnet, the smaller is the magnetostatic energy of the system.

Hysteresis loops: A magnetic hysteresis loop demonstrates the change in the magnetization, $M$, of a ferromagnetic material in response to, and along the direction of an applied magnetic field, $H$. As shown in the hysteresis loop in Figure 2.7, ferromagnets are able to retain a memory of an applied magnetic field even when the external field is removed.

The shape of a hysteresis loop will change if the size, shape, microstructure or the angle of the applied field changes. From any hysteresis loop, various parameters including the saturation magnetization $M_s$, remanent magnetization $M_r$, and coercivity $H_c$, can be determined. These quantities are useful in the characterization of the examined material.

If a ferromagnet with initially zero $M$ is exposed to an increasing $H$, those domains that have magnetic moments in the direction of magnetization grow and the magnetization of the ferromagnet increases. The magnetization keeps increasing until it stops reacting to an increase of the applied field. This is when all the domains are completely aligned with $H$ and $M_s$ is achieved. Figure 2.7 demonstrates the variation of magnetization of a ferromagnetic sample from its initial state to its saturation through a M-H curve (gray curve).

As can be seen in the hysteresis plot, when the external magnetic filed starts to decrease from its maximum towards the reverse direction, the variation in the ferromagnetic magnetization does not follow the previous forward curve when the external field was increasing (gray curve). This means that the ferromagnetic material is able to retain a memory of the applied field. The remaining $M$ after the external field
vanishes is called the remnant magnetization, $M_r$. At this point, if $H$ is increased in the opposite direction the ferromagnet starts to nucleate domains in response. Domains with random magnetization grow such that for this new $H$, the ferromagnet has zero $M$. This reverse field, required to keep the magnetization zero, is called the coercivity, $H_c$.

By continuing to increase the reversal field, the magnetization of the ferromagnet domains will orient in the direction of the field and a negative saturation of the ferromagnet magnetization is achieved. The hysteresis loop will be complete by going to a zero magnetization and then to the positive saturation point.

![Hysteresis Loop](image)

**Figure 2.7.** A magnetization curve of a ferromagnetic and its related hysteresis loop.  
*Adapted from:* http://www.doitpoms.ac.uk/tlplib/ferroelectrics/switching2.php

The saturation magnetization $M_s$, remanent magnetization $M_r$ and coercivity $H_c$ are three important quantities of ferromagnetic materials and based on these quantities, different categories of ferromagnets can be defined. The ratio $M_r / M_s$ is a useful measure of the squareness of the M-H loop. It categorizes the ferromagnetic material into *soft* and *hard* magnets. Figure 2.8 shows typical hysteresis loops of both *soft* and *hard* magnets.
As illustrated by the hysteresis loop in Figure 2.8, soft ferromagnetic materials magnetize easily by a small applied magnetic field and achieve considerable saturation magnetization. As a result, the permeability for soft ferromagnetic materials is high. On the other hand, when the external magnetic field is removed, their remnant magnetization is very low leading to a small demagnetizing field or a low coercively. The ability of soft ferromagnetic materials to be easily magnetized and demagnetized is due to the ease of motion of their constituent domain walls. This makes these soft ferromagnetic materials good candidates as magnetic transformer cores.

For hard ferromagnetic materials, large applied magnetic fields are needed to fully magnetize them, as demonstrated by their typical hysteresis loop in Figure 2.8. This is due to difficulty in the motion of their domain walls in the presence of a small, applied magnetic field. These materials are also harder to demagnetize and have high coercivity. They also demonstrate high remnant magnetization, which makes them suitable candidates for magnetic recording applications and permanent magnets.

In the following section, we briefly describe the fabrication process and magnetic characterization of the NW arrays used for the study of this thesis.
2.2. Single layer CoFeB and multilayer CoFeB/Cu nanowire arrays

2.2.1. Fabrication

As mentioned in Chapter 1, there are two different approaches for the fabrication of NW arrays: the top-down approach and the bottom-up approach.

In a top-down approach where nanolithography techniques such as e-beam lithography, x-ray lithography or scanning probe-based lithography are used, nanostructures are made by patterning a large thin film of the same material. In this approach, the nanostructure arrays are fabricated by removing the unwanted parts from the patterns [13-16]. Although, in this approach, one can achieve a well-defined array configuration and a variety of structures with different shapes, the process of making these structures in a macroscopic scale is slow, costly and hard. Moreover, with this approach, it is not possible to make nanowires with high aspect ratios [17].

In the bottom-up approach, the nanostructures are made inside the pores of porous materials often as cylindrical fibers. This can be done either by electrochemical [18-21] or chemical deposition [19]. Depending on different factors, such as the deposited material or the chemistry of the pores, the deposited fiber can be nanowires or nanotubes [17]. Moreover, in the electrodeposition method, the length of the deposited feature can be controlled which is an advantage over chemical deposition of such features [19]. However, not all of magnetic materials can be electrodeposited.

The porous templates can be made by different methods including nanolithography techniques [55-58] where proposed templates with defined pore size and pore distance can be fabricated. This method has the same disadvantages as the top-down approach.

Fabricating the porous templates by either nuclear track etching of a polymer or anodizing aluminum plates are two other methods of making these templates [17]. Both of these methods lead to the deposition of nanowires with small diameter (10 nm) and an aspect ratio up to $10^3$. The track etched polymer membranes and anodic porous
alumina membranes can be easily made in macroscopic lengths and at low cost. This makes them more desirable as methods for fabrication of magnetic nanowire arrays [17].

**Fabrication of nanoporous alumina membranes**

Electrodeposited uniform magnetic nanowire arrays can be made in nanoporous alumina membranes, which have a hexagonally well-ordered pore structure [59-60]. The synthesis of these membranes is not complicated and they can simply be fabricated by anodization of aluminum in acid solutions. In addition to being economically favourable, another advantage is that the membrane can be a relatively thick template, which leads to deposition of long uniform nanowires vertically aligned with each other. Moreover, based on the choice of applied voltage and acid solution [61], various diameters of the pores as well as separation between the adjacent pores can be achieved. By anodizing aluminum twice (a two-step anodization process) the hexagonal ordering of the pores improves [62-63].

Figure 2.9 shows the three main steps of this process for obtaining high-quality nonporous membranes. Figure 2.9 (a) illustrates the first anodization step carried out by oxidation of highly pure aluminum (Al) in an acidic solution. At the end of the first step, the result is disordered nanoporous alumina. As shown schematically in Figure 2.9 (b), the second step of the process is to remove the prepared alumina completely by etching it in an acidic solution. This can be a phosphochromic acid solution (25 mL of H₃PO₄ and 45 g of H₂CrO₄ per liter of solution) at a temperature of 75 °C for one and half hours. This results in the surface of the Al plate having hexagonally ordered pits, and the plate is ready for the second anodization process. Figure 2.9 (c) shows the last step of the fabrication process. Now, anodization has initiated the desired hexagonally ordered pores, which are vertically well aligned in the positions of the pits made in the first step. Depending on the thickness of the nanoporous membrane, the duration of anodization in the third step can vary.

The temperature of the acid bath during the anodization process plays an important role in the thickness of alumina as well as the quality of the pores [50]. Increasing the temperature of the acid bath increases the anodization speed (the current is thermally activated so that the higher the temperature, the higher the current and
hence, a faster anodization). If the anodization is faster, there will not be enough time for the formation of a very dense layer of alumina [64]. When the temperature is low and well maintained, the process has time to generate dense alumina with the same rate everywhere on the surface of the sample. Therefore, keeping the bath cool helps maintain the overall quality of the alumina [62]. But if there are temperature variations in time, the pores will not be homogeneous along the axial direction [62,64].

Prior to the two-step anodization process, the pure Al plate (99.998%) [7] is polished mechanically (to obtain a mirror-like surface), followed by dipping it in acetone, propanol and then rinsing with deionized water for 2 minutes. The last preparation step is electropolishing of the Al plate (40% H$_2$SO$_4$ + 20% H$_3$PO$_4$ + 20% H$_2$O solution) to remove scratches on the surface and to obtain an optically bright surface. When the desired pores are made on top of the Al plate, the nanoporous alumina is removed from the Al plate by an electrochemical technique (dipping into a 70% perchloric acid solution with a voltage rapidly increased to 45 V [65]).

Figure 2.10 (a) shows a picture of a nanoporous alumina membrane with pores of an average diameter of 42 nm ± 4 nm, and an average intra-pore distance of 111 nm ± 8 nm. For this type of membrane, the last step of anodization was carried out in oxalic acid (C$_2$H$_2$O$_4$, 0.3 M) at an applied voltage of 40 V for four hours (the acid bath temperature is ideally kept at 1 °C). Figure 2.10 (b) presents a scanning electron microscopy (SEM) image of the same membrane, which clearly shows the quasi-hexagonally ordered holes in the nanoporous alumina membrane.
Fabrication of nanowire arrays

For the study described in this thesis, the ferromagnetic nanowires (FMNW) were fabricated by collaborators in the Department of Engineering Physics, Ecole Polytechnique, by members of Prof. David Menard’s group using electrodeposition in a nanoporous alumina membrane through a two-step anodization technique. Three
nanoporous alumina membranes with different pore size and intra-pore distance were used. The smallest pore size was 20 nm ± 3 nm within a membrane with inter-pore spacing of 60 nm ± 5 nm. The other two membranes had pore sizes of 40 nm ± 5 nm and 170 nm ± 30 nm, with inter-pore distances of 110 nm ± 10 nm and 300 nm ± 30 nm, respectively.

Prior to deposition of the NWs, an adhesion layer of titanium (Ti), with a thickness of 15 nm, and a 1 µm thick gold (Au) layer were sputtered on the backside of the alumina membrane. Two types of FMNW were fabricated by electrodeposition: uniform CoFeB (single layer) nanowire arrays with different diameters (20 nm - 170 nm), and multilayer CoFeB/Cu arrays with different spacing of CoFeB and Cu layers (uniform diameters 40 nm). The nanowires were grown inside the pores by pulse-current electrodeposition for the uniform CoFeB, and pulse-potential electrodeposition for the multilayer ones, inside a standard three-electrode cell [7, 8]. There, the Au/Ti/Al film acted as the working electrode in the cell (cathode) and a platinum sheet was used as the counter electrode (anode) with a saturated calomel reference electrode [7].

As mentioned above, for the fabrication of uniform CoFeB NWs, pulse-current electrodeposition was used which was preferred over direct current electrodeposition. This technique helps reduce the chance of blocking the pores of the membrane [66]. Hence, by applying a current for 10-20 ms time duration, CoFeB NWs grow inside the alumina pores (on the cathode), which are uniform in length and composition. When the current is turned off for a period of 150-300 ms, no metal is deposited but fresh electrolyte solution fills the membrane pores.

Single alloy, CoFeB FMNWs were fabricated [67] at room temperature using an aqueous electrolyte consisting of a solution of CoCl₂·6H₂O (0.35 M), FeCl₂ (0.025 M), H₃BO₃ (0.5 M), NaCl (0.5 M), Na₃C₆H₅O₇·2H₂O (sodium citrate dihydrate, 0.017M), CH₃(CH₂)₁₁SO₃Na (sodium lauryl sulfate, 5 ×10⁻⁴ M), CH₄N₄S₆ (thiourea, 2.8 × 10⁻⁴ M) and (CH₃)₂NH:BH₃ (dimethylaminoborane, 3.4 ×10⁻³ M) [42], at pH = 3.5. The electrodeposition was carried out with a constant current density of 100 mA/cm². Based on the concentration of Co and Fe in the electrolyte the nominal composition of the CoFeB NWs was Co₉₄Fe₅; with a Co/Fe atomic ratio of 94/5 = 20.
Multilayer FMNWs were fabricated using a single electrochemical bath, by switching the cathode potential, $V$, between two values of $V_m$ and $V_{nm}$ (−1 V and −0.56 V, respectively), where $V_m$ is the cathode potential used to deposit the magnetic metal layer (CoFeB), and $V_{nm}$ the same for deposition of the nonmagnetic metal layer (Cu). A voltage versus time plot is shown in Figure 2.11. Since $V_m$ was larger than $V_{nm}$, Cu would also be deposited during the deposition of the magnetic layer, at the voltage of $V_m$. Therefore, the electrolyte Cu ion concentration was very low compared to the magnetic metal ions. This helped to reduce the rate of Cu incorporation into the magnetic layers. Figure 2.11 illustrates schematically the electrodeposited NWs in a nanoporous alumina membrane and the characteristic geometry of the arrays and pores.

CoFeB/Cu multilayer NWs were fabricated using an electrolyte consisting of $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ (0.176 M), $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ (0.03 M), $\text{H}_3\text{BO}_3$ (0.7 M), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.003 M), ($\text{CH}_3)_2\text{NH} \cdot \text{BH}_3$ (0.007 M), and Na saccharin solution (0.005 M), at $p\text{H} = 3.5$. The NWs consisted of periodic M/nM (where M was CoFeB and nM was Cu) layers of different thicknesses and period, including M/nM: nominally 9/7 nm, 50/10 nm, 75/75 nm and 9/3/9/50 nm. These layer thicknesses were estimated based on the growth rates measured for thick uniform NWs, assuming 100% electrodeposition efficiency. The porosity of our membranes (measured using SEM) was 90 %.

To obtain individual NWs from a NW array, the alumina membrane can be removed by using sodium hydroxide [51] or phosphorhemic acid [7, 35]. An effective removal of the alumina, with a sample size of 4 mm in diameter, was obtained with a phosphorhemic acid solution (25 mL of H$_3$PO$_4$ and 45 g of H$_2$CrO$_4$ per liter of solution) used at a temperature of 75 °C for a duration of one and a half hours. In the case of sodium hydroxide, 1 M of NaOH solution was used for eight hours [7, 35, 65].
Figure 2.11. Schematic view of arrays of either CoFeB single layer NWs or multilayer CoFeB/Cu ones obtained by pulse-current or potential-current electrodeposition [7].

2.2.2. Magnetic characterization by static magnetometry

Magnetization hysteresis loop or the magnetostatic (dc) response of magnetic structures has been used in the characterization of magnetic behavior [1]. As mentioned, parameters such as saturation magnetization, remanent magnetization, and coercivity can be determined from a hysteresis loop. The magnetostatic response of the examined NWs in this thesis were measured using a commercial vibrating sample magnetometer (VSM) at the Department of Engineering Physics, Ecole Polytechnique by Prof. David Menard's group members. Each individual array of a particular NW was mounted on a quartz rod and the corresponding hysteresis loops were obtained in an applied dc field parallel and perpendicular to the NW axis. The results of VSM measurements on the reported NWs in this thesis ($M/M_s$ versus $H_{ext}$) are shown in Figures 2.12 and 2.13.
Figures 2.12 (a) - (c) show hysteresis loops from CoFeB NW arrays with expected average NW diameters of 170 nm, 40 nm and 20 nm for an applied dc field parallel (solid-blue curve) and perpendicular (dashed-red curve) to the wire axis. In all the examined NW arrays, their easy axes were parallel to the NW axis, meaning that the saturation of the NWs in an applied magnetic field is easier to happen in parallel direction to their axes. Meanwhile, $H_c$ and $M_r$ of these NWs changed with diameter [7]. Thus, the NW magnetic anisotropy could be varied by changing their geometry (diameter, length and inter-wire distance). For 20 nm CoFeB NWs in an applied external filed parallel to the axis of the NW, a nearly square hysteresis loop (Figure 2.12 (c)) was observed indicating high remanence and coercivity properties for this NW array. As the diameter of NWs increased, the squareness of the hysteresis loops decreased (Figure 2.12 (a) and (b)) resulting in smaller remanence and coercivity.

If the NW geometry (length and diameter) of the array is fixed, another way to change their magnetic anisotropy is by using multilayered NWs with controlled magnetic-nonmagnetic thicknesses, as shown in Figure 2.13 (a) - (d). This figure shows hysteresis curves for multilayered NW arrays consisting of M/nM layer thicknesses of nominal (a) 9/7 nm, (b) 50/10 nm, (c) 75/75 nm and (d) 9/3/9/50 geometries, as a function of the direction of the applied dc field with respect to the NW axes. It is clear that for NWs where their magnetic layer thickness was smaller than the diameter (rod shape magnetic segments) [1, 36], their easy magnetic axis was perpendicular to the wire axis. Moreover, the thickness ratio of magnetic-nonmagnetic layers could change the magnetic response of the NW arrays.

In particular, for CoFeB/Cu (nominally 9/7 nm) NW arrays, the hysteresis loops for the parallel and perpendicular external magnetic field almost overlapped each other (Figure 2.13 (a)). This was close to the expected response from a spherically shaped geometry, which is isotropic [7]. On the other hand, in the presence of a 50 nm Cu spacer in the triple layer arrays of CoFeB/Cu (9/3/9/50 nm) NWs, each segment (separated by 50 nm Cu) acts as a magnetically isolated layer and hence, the response to an external magnetic field was similar to a thin film behavior [7], with an easy axis in the plane parallel to the sample (perpendicular to the NWs).
Figures 2.13 (b) and (c) show hysteresis loops from NW arrays where the thicknesses of their magnetic layers were larger than their diameter (rod shape magnetic segments) [1,36]. For this geometry, the easy axis of the NW was parallel to the NW axis. In the case of CoFeB/Cu (75/75 nm) NW arrays, the hysteresis loops for parallel and perpendicular external magnetic field (Figure 2.13 (c)) were similar to the results for single layered CoFeB NWs with close to zero coercivity and remenance in a perpendicular applied field. In comparison, for arrays of CoFeB/Cu (50/10 nm) NWs in a perpendicular external magnetic field, the coercivity and remenance were comparable to the case of a parallel applied field. This is because of the specific geometry of these magnetic layers, where the diameter and the thickness of each layer were similar, making either perpendicular or parallel directions favourable.

All of the magnetic properties of NWs presented here were from macroscopic arrays. Since the pore density is high in alumina membranes, dipolar interactions between NWs were an important factor in determining their magnetic response [17]. Knowing the magnetic properties of individual NWs in the same array would add insight into the interpretation of the magnetic properties of the array itself.
Figure 2.12. VSM measurements of CoFeB NWs arrays with average diameters; (a) 170 nm, (b) 40 nm and (c) 20 nm for an applied dc field parallel (solid-blue curve) and perpendicular (dashed-red curve) to the wire axis [7].
Figure 2.13. Hysteresis loops (VSM measurement) of arrays of CoFeB (M) / Cu (nM) multilayer NWs with periodic M/nM layers of nominally (a) 9/7 nm, (b) 50/10 nm, (c) 75/75 nm and (d) 9/3/9/50 nm, for applied dc fields parallel (solid-blue curve) and perpendicular (dashed-red curve) to the wire axis [7].
Chapter 3.

Electron Holography

3.1. Introduction

The microscopic structure of materials was first studied using optical microscopy. However, the resolution of this technique is limited fundamentally by the wavelength of the photons used (100s nm), and therefore, it is not helpful for probing the atomic scale behavior of materials. In comparison, electrons with their smaller range of wavelengths can investigate structural properties of materials at resolutions down to 35 pm with the latest aberration-corrected transmission electron microscopes [68]. Photons and electrons differ not only in their wavelength but also in mass and charge. Since, electrons are charged particles that can also interact with other charges and any magnetic fields (through the Lorentz force) present in the material under study, electron microscopy can be used to investigate the electrical and magnetic properties of the desired materials with nano-scale resolution.

When an electron beam passes through a material, the amplitude and phase of the beam will change. In conventional TEM imaging, the amplitude and phase information are mixed and only the spatial distribution of the intensity (the square of the amplitude) of the electron wave is recorded in an image. While this recorded image, considered as a bright-field TEM image, has valuable information about the microstructure and chemistry of the material, any information about the phase of the electron wave function is lost.

Any sample has an electrostatic potential and possibly also an in-plane component of magnetic induction, which can affect the phase of electrons as a high-energy electron beam passes through. Measuring the change in the phase provides
information about these properties of the sample. Electron Holography (EH) is an interference-based technique, which enhances conventional TEM imaging by recovering the phase information of the electron beam in addition to their amplitudes.

The name “holography” originates from a Greek word meaning “whole writing”. Holography involves two steps for separating the phase and amplitude of any recorded image. Step one is to form an interferogram, called a hologram, by interfering two or more coherent electron waves; and step two: is the reconstruction of the hologram to regain the separated information. The concept of electron holography was initially proposed and developed by Denis Gabor in 1949 [69,70] who at the time, was primarily interested in overcoming electron microscope instrument limitations due to unwanted aberration in electromagnetic lenses [69, 71].

Gabor’s first idea was that if it was possible to transmit an unscattered electron wave through a thin weakly scattering object. Then, this unscattered wave could interfere with the electron wave scattered by the object. But, the lack of a sufficiently bright and coherent source of electrons stopped him from testing this idea experimentally. As a result, the first successful test of holography was carried out using laser beams [72] (optical holography). Electron holography would need to wait until the development of high-brightness field-emission guns, which eventually provided sufficient coherency for electron holography experiments to be feasible.

Since the original proposal of electron holography by Gabor, different methods of holography have been proposed and demonstrated. Cowley [73] described more than twenty holographic schemes, which could be set up in an electron microscope. All of these modes had the same principle of electron interference but for different applications. If the entire holography system was positioned between the illumination source and the object, then it was called a “projection method”. Another useful configuration, called the “transmission method”, or “in-line holography” had the whole holography set up placed between the object and the detector or photographic plate [74].
**In-line Holography**

Figure 3.1 illustrates a typical setup for in-line electron holography. The imaged hologram is the result of interference between the transmitted and the scattered plane waves at an out-of-focus image plane. The resultant hologram is a defocused (Fresnel) image. When the objective lens of the microscope is in its defocused state, it produces the image of the electron waves at a distance from the specimen plane.

![Diagram of in-line holography](image)

**Figure 3.1. The experimental setup of In-line holography in a typical TEM.**

As diagrammed in Figure 3.1, for in-line holography, both the scattered and transmitted waves travel along the same path. This helps minimize the effects of lens aberrations. However, since the original and conjugate waves both contribute to the reconstruction of the recorded hologram, one encounters difficulties in separating the two. This problem is known as the twin-image problem.

One method of resolving the twin-image problem is to record the hologram at a very high defocus state or in the Fraunhofer plane of the specimen. In this case, the conjugate image of the object will be far out of focus in the reconstruction process, and will therefore, have a small effect on the reconstructed image. Another way of dealing with the twin-image problem is to use off-axis holography where an electron biprism is added to split and recombine the illuminated and scattered beams [75].

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3.2. Off-axis electron holography

Off-axis electron holography was first realized as a reliable method by Leith and Upatnieks [72] in the development of laser techniques. The name “off-axis” comes from the relative tilt angle between the two interfering waves; one is a reference wave that passes through vacuum and the other the object wave that passes through the sample.

To implement off-axis electron holography in a microscope, three essential components are needed: (a) A coherent incident illumination, which can be provided by a field emission gun (FEG), (b) an electrostatic biprism that is below the sample and is used to tilt the reference and object waves to overlap and produce an interference pattern, and (c) a high resolution digital camera, for quantitative recording and processing of holograms on a computer.

(a) Field emission gun (FEG)

Performing electron holography with tungsten and LaB$_6$ filaments encounters issues including limited brightness, coherency and stability of illumination. These problems were reduced with the development of FEG sources. The brighter the electron source is, the greater its fraction of coherent current, and the greater the signal to noise ratio of the resulting holographic interference pattern in a given acquisition time will be. A typical FEG source has smaller emitting area than other sources (such as LaB$_6$), and therefore produces a higher brightness [75].

It should, however, be mentioned that a typical FEG source is not perfectly coherent, spatially and temporally, but it has sufficient coherency to produce the contrast and intensity required for an interference fringe pattern to be recorded within a sensible time. The necessary image recording time is still limited by the rate of drift of the beam, biprism and specimen which all must be negligible [75]. The spatial coherence, the size of the coherent electron source, is related to the beam convergence, semi-angle controlled by the condenser lens, and also the aperture size. By reducing the size of the condenser aperture, the spatial coherence increases (and the beam intensity decreases). Finally, temporal coherency, due to fluctuation in the energy of the beam, is reduced by using low noise high-tension voltage supplies [75].
(b) An electrostatic biprism

A biprism is a conducting rod with a diameter less than 1 micron that can act as a beam deflector in an electron microscope. Applying a voltage to the biprism tilts the beam on both sides of the biprism towards each other and they eventually interfere.

The first biprism was originally developed by Duker and Mollenstedt using a quartz wire with diameter less than 1 µm coated with gold [75]. To make a fine glass fiber, a high purity quartz rod and hydrogen-oxygen flame can be used. The quartz rod is melted over the flame and then rapidly pulled from the two ends to make two filaments with thin diameter, typically 50-100 µm. By connecting the tips of these two rods, melting them over the flame and pulling them apart, very thin fibers (300-500 nm) can be made and caught above the flame. The fine fiber must then be coated with a conducting layer such as gold. To promote adhesion of gold, an interlayer of Ti or Cr is usually applied prior to the gold coating.

The biprism is generally mounted by silver epoxy onto a special biprism holder. In most microscopes, the biprism holder is fitted to one of the openings in the selected aperture (SA) holder but it can also be mounted in a separate unit specific to the biprism. The optimum position of the biprism in the column has been calculated by considering all of the parameters influencing the quality of holograms [76]. Changing the position of the biprism can affect the angle of interfering beams, which directly changes the periodicity of the holograms as well as the related field of view for the same biprism voltage.

The biprism holder may have the ability to be rotated. This provides the freedom of aligning the biprism with a different edge or different area of the sample. There are also biprism holders that are fixed and not rotatable. In this case, the biprism itself is aligned perpendicular to the axis of the SA aperture holder. In this setup, the mechanical stability of the biprism due to vibration of the holder is maximized. Having a stable biprism is critical to a high signal to noise hologram.

A schematic diagram of a typical biprism in an electron microscope is shown in Figure 3.2. When a positive voltage is applied to the biprism, an interference pattern, a hologram, with a width $W$ is formed. The biprism creates two virtual sources, $S_1$ and $S_2$. 
which can then be considered as two sources in the standard Young’s slit experiment [74]. By increasing the voltage of the biprism, the deflection angle of the rays become larger and therefore, $W$ of the hologram will increase. In other words, increasing the biprism voltage pushes the two virtual sources further apart. The wave fronts from these two sources must be in phase over the interference region to form high contrast fringes in the interference pattern. This means that the spatial coherence of the sources puts a constraint on the maximum $W$. The wave fronts travel a greater distance for a larger $W$. Therefore, the fringe contrast in the interference region will disappear eventually by increasing the biprism voltage.

Figure 3.2. Schematic diagram showing the biprism operation in making a hologram.
Adapted from:
http://tudresden.de/die_tu_dresden/fakultaeten/fakultaet_mathematik_und_naturwissenschaften/fachrichtung_physik/isp/tbg/forschung/holography/basicsholography
As mentioned above, the off-axis electron holography set up is equivalent to the Young’s experiment. Hence, by analogy, $W$ and its fringe spacing, $s$, can be found based on the well-known experimental parameters [75]:

$$W = 2\left(\frac{a+b}{a}\right)(\alpha \frac{ab}{a+b} - R)$$

(3.1)

and

$$s = \lambda\left(\frac{a+b}{2aa}\right)$$

(3.2)

where $\alpha$ is the deflection angle of the wave caused by applying voltage to the biprism and $R$ is the radius of the biprism. As shown in Eq. (3.1), a larger $R$ means a smaller $W$. At zero voltage on the biprism, the wire makes a shadow and as the voltage increases, the first step is to overcome this shadow. Thus, $R$ should be minimized to improve $W$ for a given microscope spatial coherency [75].

Figure 3.3 (a) shows a reference hologram recorded with a biprism voltage of 120 V using a FEG source operating at an accelerating voltage of 200 kV. The fringes with a variable spacing at the edge of the hologram are Fresnel fringes formed by interference from the edge of the biprism. The finer fringes in the middle of the pattern are the ones containing information about any amplitude and phase shifts of the electron wave that passed through the specimen. To have a larger field of view or, in other words a larger $W$ with finer fringes, the Fresnel fringes must be subtracted. Their effects can be reduced by focusing on the central region of the hologram (away from the edges) and by applying a higher voltage to the biprism.

The fringe spacing (given by Eq. (3.2)) will decrease when the biprism voltage increases (increasing the voltage of biprism, increases the deflection angle $\alpha$). The width of three interference fringes is a good estimate of the resolution of the hologram [75]. Greater freedom to choose higher biprism voltages (which leads to a smaller fringe spacing and better resolution) is initially limited by the coherency of the source but eventually by the stability of the microscope and the resolution of the camera. The most coherent part of an electron beam is the brightest spot in the middle of the round beam.
Figure 3.3. A reference hologram recorded with a biprism voltage of 120 V using a FEG source operating at an accelerating voltage of 200 kV. The hologram shows Fresnel fringes at the edges and interference fringes, shown magnified in (b). (c) A line profile along the white line in (b), showing the fringe intensity variation.

As shown in Figure 3.4, if the round beam is elongated in one axis deliberately, an elliptical illumination can be achieved. The greatest coherency occurs along the elongated direction. Since the holographic fringes run parallel to the biprism wire, coherency is only required in one direction (perpendicular to the fringes). The elliptical illumination in a perpendicular direction (at exactly 90°) to the biprism wire can increase the coherent electron flux.

Figure 3.3 (c) shows a profile of the fringe intensity variation along a line perpendicular to the fringes (the white line in Figure 3.3 (b)). The maximum and minimum values of the intensity can be used in the calculation of an important parameter, the fringe contrast, which quantifies the achievable phase resolution of the hologram:

\[ \mu = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} \]

For the reference hologram in Figure 3.3 (a), the calculated fringe contrast is 52% with a fringe spacing of 4 nm. This could have been further improved by using a smaller condenser aperture, lower gun extraction voltage, and smaller beam spot size which provide better coherency.
One of the main steps in electron holography is recording the hologram, which has been significantly improved with the advent of digital cameras using charge coupled detectors (CCD). The original procedures involved recording the images on photographic films and reconstructing them through an *ex situ* optical process. This was a time-consuming process and would introduce optical artifacts and additional problems related to photographic film.

A CCD camera has several advantages. It produces a digital output and has a linear response to incident electron intensity [76]. The high resolution of CCD cameras helps record the position of the fringes accurately. However, there is a trade off between the resolution and the signal to noise of the image such that the higher the resolution, the lower the signal to noise and intensity of the images. The CCD camera used for the experiments here had a total size of 4096 x 4096 pixels. Due to acquisition constraints (image drift), only 2048 x 2048 pixels were typically used.

### 3.3. Acquiring Holograms

The first step in electron holography involves superimposing a reference wave on the object wave. This superimposed wave contains the amplitude and phase information about the specimen. When the sample is a magnetic material, an extra step is needed due to the fact that lenses in transmission electron microscopes have huge magnetic fields. Conventional TEM is carried out with the sample inside the pole pieces of the objective lens, which has a magnetic field (1.9 T for a Tecnai G2) along the beam direction. To enable off-axis EH in a field-free environment, the objective lens is switched
off and another lens (the so called Lorentz lens), which is below the specimen, is used as the imaging lens. The Lorentz lens is sufficiently weak and distant from the sample that it cannot influence magnetization at the sample plane. However, the magnification using a Lorentz lens is smaller (e.g. 40 kx in a Tecnai G2 at 200 keV).

In addition to the hologram obtained from the specimen, another hologram, the reference hologram, is obtained by removing the sample. One can process the reference and object holograms together to remove the artifacts introduced by the CCD, and biprism.

The intensity of the off-axis hologram is given by Eq. (3.3) where $A_i$ and $\phi$ are the amplitude and phase of an object wave, $r$ is a vector in the plane of the sample and $q_c$ is a two-dimensional reciprocal space vector which specifies the tilt of the reference wave [77,78].

$$I_{hot}(r) = 1 + A_i^2(r) + 2A_i(r)\cos(2\pi q_c \cdot r + \phi(r)).$$

One should note that there are three terms contributing to the total intensity: The intensity of the reference wave (assumed to have unit intensity and to be undisturbed in the presence of the specimen), image wave, and the interference consisting of a cosinusoidal fringe pattern modulated by the amplitude and phase of the image wave.

### 3.4. Hologram reconstruction

After acquiring the hologram, the amplitude and phase of the sample are extracted and processed (as described below) using an image-processing software, such as “Semper” [79]. We first need to Fourier transform the hologram, select a side band using an aperture, and then invert the Fourier transform using the selected side band. The final product is a complex image wave from which one can calculate the amplitude and phase.

The Fourier transform of the hologram is given by

$$FT[I_{hot}(r)] = \delta(q) + FT[A_i^2(r)]$$
where \( q \) is the carrier wave frequency. The first term in the above equation, corresponding to a peak at the origin \((q = 0)\), is Fourier transform of the uniform intensity component of the reference image, and the second term is the transform of the intensity distribution of the (normal) TEM image. The peaks centered at \((q = +q_c)\) and \((q = -q_c)\) are the transforms of the image wave function and the complex conjugate of the image wave function, respectively. Note that the two side bands carry the same information differing only in their phase sign [75].

One then obtains the phase image by selecting a side band and moving it to the origin of the Fourier space. Note that the selection of the side band, usually chosen to be a circular aperture, needs to be done carefully. The radius of the circular aperture determines the spatial resolution of the extracted information. By increasing the size of the side band mask (increasing the radius of the mask in Fourier space), one achieves a higher spatial resolution but at the cost of introducing additional noise to the image. A reduction in the radius of the mask, on the other hand, can help to remove high frequency noise.

The artifacts introduced by the edge effects of the mask must also be taken care of. A circular aperture with diffuse edges helps avoid the introduction of such noise compared to a sharp edged mask. Also, choosing accurately the center of the side band is important. An inaccurate center selection introduces a ramp in the reconstructed phase image [75]. It is easier to select the center in the Fourier space, from the Fourier transform of the reference hologram, where there is no perturbation to the fringe patterns by the specimen.

Finally, we invert the Fourier transform using the selected side band back into real space. The product of the transform is a complex image. The amplitude image, \( A(r) \), is calculated as

\[
A(r) = \sqrt{Re^2 + Im^2}
\]

and the phase images as
\[ \phi(r) = \tan^{-1}\left(\frac{\text{Im}}{\text{Re}}\right), \]

where \( \text{Re} \) and \( \text{Im} \) are the real and imaginary parts of the reconstructed complex image, respectively.

![Figure 3.5](image)

**Figure 3.5.** Reconstruction steps for an electron hologram of a CoFeB nanowire. (a) unprocessed hologram, (b) Fourier transform of the hologram with selected side band, (c) magnified region of the hologram to show a close up of the fringes, (d) a modulo \( 2\pi \) phase image and (e) final unwrapped phase image.

A summary of the steps described above is schematically shown in Figure 3.5 (a)-(e) for the analysis of a CoFeB nanowire, as an example. It can be seen in Figure 3.5 (d) that the reconstructed phase shows some discontinuity. This is because the reconstructed phase image is modulo \( 2\pi \), which introduces \( 2\pi \) phase discontinuities. These artifacts, therefore, are not related to the specimen and can be removed by
“unwrapping” algorithms. This produces a smooth phase image representing the actual phase image of the specimen, as shown in Figure 3.5 (e).

### 3.5. Electrostatic and magnetic contributions to the phase

When passing through a sample, the electron wave acquires a phase shift due to the electrostatic potential and magnetic induction in the sample and through the Lorentz force acting on the electrons in the electromagnetic field. If electron waves go through different paths (two different paths in an electron microscope), such as when electrons pass through either the sample or vacuum, it can be shown that the phase difference between the two electron rays depends on the magnetic flux surrounded by the rays. This phase shift can be described in quantum theory through the work done by Aharonov and Bohm [80] as follows.

The electron wave function, $\Psi(\vec{r}, t)$, satisfies the Schrödinger equation:

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = H \Psi(\vec{r}, t),$$

(3.5)

where the Hamiltonian, $H$, describes the interaction of electrons with the surrounding medium. For free electrons, the Hamiltonian is time-independent and the solution of the Schrödinger equation is a plane wave:

$$\Psi_0(\vec{r}, t) = |\Psi_0| e^{i \frac{e}{\hbar} (Et - \vec{p} \cdot \vec{r})}.$$  

(3.6)

In the presence of an electrostatic potential, $V(\vec{r}, t)$, the Hamiltonian is modified by a potential energy term, $e V(\vec{r}, t)$:

$$H = H_0 + e V(\vec{r}, t).$$

(3.7)

The solution to the new Schrödinger equation is

$$\Psi(\vec{r}, t) = \Psi_0(\vec{r}, t) e^{\frac{-i}{\hbar} \int eV(\vec{r}, t) dt} = \Psi_0(\vec{r}, t) e^{-i\Phi(\vec{r}, t)},$$

(3.8)
which can be shown by substituting Eq. (3.8) into the Schrödinger equation, Eq. (3.5), giving:

\[
\ii \hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = \ii \hbar \frac{\partial \Psi_0(\vec{r}, t)}{\partial t} e^{-i\Phi(\vec{r}, t)} + \ii \hbar \Psi_0(\vec{r}, t) \left(-i \frac{\partial \Phi(\vec{r}, t)}{\partial t}\right) e^{-i\Phi(\vec{r}, t)} \\
= H_0 \Psi_0(\vec{r}, t) e^{-i\Phi(\vec{r}, t)} + e V(\vec{r}, t) \Psi_0(\vec{r}, t) e^{-i\Phi(\vec{r}, t)} = H \Psi(\vec{r}, t),
\]

where the presence of the electrostatic potential produces a phase shift:

\[
\Phi(\vec{r}, t) = \frac{1}{\hbar} \int eV(\vec{r}, t) dt. \tag{3.9}
\]

Figure 3.6 shows two different paths that an electron could take. In the absence of any electrostatic potential, the wave equation is

\[
\Psi_0(\vec{r}, t) = \Psi_{01}(\vec{r}, t) + \Psi_{02}(\vec{r}, t). \tag{3.10}
\]

The presence of different electrostatic potentials along the two paths changes the wave function as

\[
\Psi_0(\vec{r}, t) = \Psi_{01}(\vec{r}, t) e^{-i\Phi_1(\vec{r}, t)} + \Psi_{02}(\vec{r}, t) e^{-i\Phi_2(\vec{r}, t)}, \tag{3.11}
\]

where \(\Phi_1(\vec{r}, t)\) and \(\Phi_2(\vec{r}, t)\) correspond to the phase shifts along the paths 1 and 2, respectively.

From Eq. (3.9), the phase difference between the two paths can be calculated as:

\[
\Delta \phi = \frac{e}{\hbar} \int_{A_1}^{B} V(\vec{r}, t) dt - \frac{e}{\hbar} \int_{A_2}^{B} V(\vec{r}, t) dt.
\]

Switching the limits of the integral along path 2, the phase difference can be rewritten as

\[
\Delta \phi = \frac{e}{\hbar} \int_{A_1}^{B} V(\vec{r}, t) dt + \frac{e}{\hbar} \int_{A_2}^{A} V(\vec{r}, t) dt,
\]

which then gives a loop integral around the closed path:
Figure 3.6. Schematic diagram of a free electron’s path starting from point A and passing through different regions 1 and 2, and reaching point B with different phase shifts.

\[ \Delta \phi = \frac{e}{h} \oint V \, dt. \quad (3.12) \]

One should note that in addition to the scalar potential \( V \), the vector potential \( A \) of the electromagnetic field can also affect the phase of the electron wave. This means Eq. (3.12) should be modified as:

\[ \Delta \phi = \frac{e}{h} \left( \oint V \, dt - \oint \vec{A} \cdot d\vec{r} \right). \quad (3.13) \]

Eq. (3.13) looks like a relativistic representation of the phase difference as an integral along a closed loop in space-time. By applying the Stoke’s theorem, the phase difference can be simplified as:

\[ \Delta \phi = \frac{e}{h} \left( \oint V \, dt - \iint \vec{B} \times \vec{A} \cdot d\vec{s} \right), \]
\[ \Delta \phi = \frac{e}{h} \left( \oint V \, dt - \iint \vec{B} \cdot d\vec{s} \right). \quad (3.14) \]
For calculating the phase shift in off-axis electron holography, an analogy to what shown in Figure 3.6 can be used. As mentioned before, two electron waves are interfering to form a hologram in off-axis electron holography. The path of the reference wave (the electron wave passing through vacuum) can be considered as one of the paths in Figure 3.6 and the path of the object wave through the sample as the other one. Therefore, Eq. (3.14) can be used in electron holography for evaluating the phase shift due to the electrostatic and magnetic influences of the specimen.

When the specimen does not have any magnetic properties, the phase shift has only the electrostatic interaction, under the influence of an effective electrostatic mean inner potential (MIP) of the specimen, $V_{\text{MIP}}$. $V_{\text{MIP}}$ can be estimated by averaging the potential of the single atoms, which gives the additional energy of $eV_{\text{MIP}}$ to any electron wave passing through the specimen. Moreover, the energy of the reference electron wave depends only on the acceleration voltage of the electron microscope, $U$, and is $eU$.

For calculating the phase shift due to electrostatic interaction, the first term in Eq. (3.14) should be considered. This term can be expressed in terms of the difference between the momenta of the object wave and the reference wave (instead of their difference in energy) as:

$$
\Delta \phi = \frac{1}{\hbar} \int eV dt = \frac{1}{\hbar} \int \frac{\hat{p} \cdot d\vec{r}}{h} = \int \frac{P_0 - P_r}{h} \, dz,
$$

where $P_0$ and $P_r$ are the magnitudes of the reference and object wave momenta, respectively. This integral is calculated along the $z$ direction, which is the direction of the electron beam in the microscope column. Since we are dealing with high-energy electrons, they can be treated as relativistic particles and their momentum can be expressed as

$$
P_0 = \frac{1}{c} \sqrt{2eUE_0 + (eU)^2}
$$

$$
P_r = \frac{1}{c} \sqrt{2e(U + V_{\text{MIP}})E_0 + e(U + V_{\text{MIP}})^2},
$$

where $E_0$ is the rest energy of the electron (the $E_0^2$ term is negligible here). Substituting these equations into the integrand of Eq. (3.15), and using a Taylor expansion up to
second order (the higher order terms can be ignored since $U >> V_{MIP}$), the integrand can be written as:

$$\frac{P_0 - P_r}{h} = \frac{2\pi}{\lambda} \left( 1 + \frac{eUV_{MIP} + V_{MIP}E_0}{2UE_0 + eU^2} - 1 \right)$$

$$\frac{P_0 - P_r}{h} = C_E \cdot V_{MIP}, \quad (3.16)$$

where

$$C_E = \frac{2\pi}{\lambda} \frac{eU + E_0}{U(2E_0 + eU)},$$

is an electron beam energy-dependent constant. By substituting Eq. (3.16) into Eq. (3.14), the total phase shift for an electron wave passing through a specimen with $V_{MIP}(x,y,z)$ (which for each material is determined by its composition) and in-plane magnetic induction $B_\perp(x, z)$ can be expressed as

$$\Delta \phi(x,y) = C_E \int V_{MIP}(x,y,z)dz - \frac{e}{h} \int B_\perp(x,z)dzdx. \quad (3.17)$$

Here, the x-y plane is the plane of the specimen and z is the direction of the electron beam.

Note that this phase shift is for a thin and weakly diffracting specimen where dynamical diffraction is neglected [81]. In general, magnetization and magnetic induction distributions are three-dimensional vector fields. However, in Eq. (3.17) it is assumed that the magnetic induction is along the y direction. For even greater simplicity, one can assume in a limited case that the in-plane component of B and $V_{MIP}$ are constant through the thickness of the specimen, and that the specimen thickness profile, $t(x)$, is known. With the above assumptions, the phase shift in x direction can be written as

$$\Delta \phi(x) = C_E V_{MIP}(x) t(x) - \frac{e}{h} \int B_\perp(x) t(x) dx. \quad (3.18)$$

Moreover, the gradient of the phase can be expressed by differentiating Eq. (3.16) with respect to $x$:

$$\frac{d\phi(x)}{dx} = C_E \frac{d}{dx} \left\{ V_{MIP}(x) t(x) \right\} - \frac{e}{h} B_\perp(x) t(x). \quad (3.19)$$
The calculation of $V_{\text{MIP}}$ and in-plane magnetic fields of the desired specimen is based on utilizing Eqs. (3.18) and (3.19), and the phase shift obtained from electron holography.

The above equations can also be used for a non-magnetic specimen to measure its $V_{\text{MIP}}$ with a known thickness, or measure its thickness for a known $V_{\text{MIP}}$. For a more accurate measurement of either the thickness or the $V_{\text{MIP}}$ of any specimen of interest, the effect of dynamic scattering needs to be included [82]. If the specimen is sufficiently non-conductive, the incident electron beam can cause an electrostatic charging, which can develop artifacts in the processing phase up to a point of making electron holography impossible for the particular specimen. To reduce electrostatic charging, either the specimen can be well attached to a conducting support such as carbon-coated grids, or a thin layer of carbon (less than 50 nm) can be coated on the specimen to increase its conductivity. This thin layer of carbon is assumed to not disturb the process of holography since it is amorphous and a weak scatterer.

In any phase image obtained by electron holography of a magnetic material, we have the contributions of both $V_{\text{MIP}}$ and in-plane magnetic field of the magnetic specimen as expressed in Eqs. (3.18) and (3.19). To distinguish the magnetic contribution from $V_{\text{MIP}}$, one can acquire two holograms of the same specimen, one from the sample in the upright orientation, and the other when the specimen is flipped upside down. In this method, the phase change from the magnetic contribution of the two holograms, has opposite sign and the related $V_{\text{MIP}}$ contributions have the same sign. Therefore, to separate the two contributions, these two reconstructed phase images can be either subtracted (for magnetic contributions) or added (for $V_{\text{MIP}}$ contributions) [83].

Another way of separating the magnetic contribution from the $V_{\text{MIP}}$ contribution is to acquire two holograms from the same specimen with two different accelerating voltages of the electron beam. The two phase images reconstructed from these two holograms have the same magnetic contributions since it is independent of the acceleration voltage of the electron beam (as can be seen from Eq. (3.19)). However, the $V_{\text{MIP}}$ contributions have different energy-dependent constants, $C_E$, which can be calculated from Eq. (3.16). By knowing these two different constants and subtracting the two phase contributions, one can calculate the $V_{\text{MIP}}$ contribution. It should be noted that
there are some difficulties associated with this method, which sometimes make it hard to perform. For example, different acceleration voltages have different imaging conditions, which add extra necessary steps (such as resizing the images) to the phase calculation [84].

A more practical method is to tilt the specimen by ± 30° and switch on the objective lens at each angle to apply a magnetic field parallel to the beam direction [83,85]. This then generates components of magnetic field along the axis of the specimen (an in-plane component) and perpendicular to the axis. Tilting the specimen with the same angle in two opposite directions helps generate two equal in-plane magnetic fields with opposite directions. Once the sample is magnetized in either direction, the objective lens is turned off and the specimen tilted back to 0° to record a hologram of the area of interest for each tilt. By taking the difference in the total phase shift from the two holograms, one obtains twice the magnetic contribution of the specimen to the phase shift. In this method, the MIP contribution is calculated by adding the same two terms and dividing by two.

The method explained above, i.e. reversing the magnetic field and then subtracting the phase to see the magnetic component, relies on the assumption of having identical magnetic structures (with different magnetic signs) between the reversal experiments. For samples such as nanowires (NWs), with large aspect ratios \( t/r > 1 \), elliptical shape), a complete reversal of magnetization is feasible. But, for NWs with smaller aspect ratios \( t/r < 1 \), disk-shape), the reversal pairs may not have identical magnetic structures. This can lead to artifacts in the magnetic induction maps. To account for irreproducible magnetic states, one can reverse each wire more than once and consider the average of the measurements.

To calculate the magnetic induction \( B_z \) from Eq. (3.19), one needs to know the magnetic thickness of the specimen, which is likely to be smaller than the true (physical) thickness. This is because of factors such as surface oxidation. In the case of NWs, if the actual diameter of NWs is considered in the calculation of magnetic induction, the measured induction would be an upper limit, which could be off from the true values.
Moreover, for the NWs with small aspect ratio ($t/r < 1$, disk-shape), the self-demagnetizing fields from the NWs further reduce the measured magnetic induction.

Figure 3.5 (a)-(e) show the reconstruction steps for a CoFeB NW specimen with a $+30^0$ tilt with respect to the applied magnetic field. The same procedure has been carried out with an acquired hologram at $-30^0$ tilt to calculate $V_{MIP}$ and the magnetic phase images of the NW. Figure 3.7 (a)-(c) show the corresponding total phase shift, the $V_{MIP}$ phase contribution and the magnetic phase contribution. Each individual phase image has a line profile across a selected region showing the phase profile across the NW. Using the magnetic phase contribution, one can also produce the magnetic induction map related to this phase shift, as shown in Figure 3.7 (d).

![Figure 3.7](image)

Figure 3.7. (a) same total phase image as Figure 3.5 (c), with an inset that represents the line profile across the phase image (red line). (b) $V_{MIP}$ phase contribution and (c) Magnetic phase contribution. (d) Magnetic flux lines generated from the image in (c) with a contour spacing of 0.15 radians (0.2 T).
Chapter 4.

Characterization of Single-layer CoFeB Nanowires

In this Chapter, magnetic properties of three types of CoFeB NWs with different diameters, 20 nm, 40 nm and 170 nm, have been investigated. After a brief review of the electrodeposition procedure used in their fabrication, we present results on the structural, morphological and magnetic properties of each type.

The electrodeposition procedure was as described in Section 2.2.1, with an expected composition of Co$_{95}$Fe$_4$B for all diameters. However, two types of alumina membranes were used for fabrication of the NWs and they differed in the degree of temperature control during the membrane anodization process. For a “well controlled” process, the temperature was kept at 4 ± 0.1 °C while for the case of “less controlled” process the temperature was at 4 ± 1 °C.

For an individual NW, factors including surface roughness, degree of crystallinity, shape, composition and the effect of different etchants (for removal of the alumina membrane) can affect its overall magnetic behavior. An investigation on the impact of these factors was carried out using scanning and transmission electron microscopy (STEM) techniques. These techniques included bright field TEM imaging (BF), with selected area diffraction (SAD), high resolution transmission electron microscopy (HRTEM), and annular dark field (ADF) scanning TEM with energy dispersive spectroscopy (EDS) and energy filtered (EF) TEM for structural and compositional analysis. For the magnetic analysis, off-axis electron holography was conducted to map the magnetic induction of individual wires.
4.1. Large CoFeB NWs

Individual large CoFeB NWs are classified here as having diameters between 100 nm to 200 nm. They were fabricated using a well-controlled temperature giving membranes each with a distribution of hole diameters of 170 ± 30 nm. NaOH was used to remove individual NWs from each alumina membrane. For structural and morphological characterization, a Tecnai T20 STEM with a tungsten filament electron source (200 keV) was used at the Center for Electron Nanoscopy (CEN), Technical University of Denmark by a collaboration with Dr. Takeshi Kasama while for magnetic characterization, a Titan Analytical STEM (300 keV) with a field-emission source was used.

4.1.1. Structural and morphological characterization

Bright field TEM images of two large NW examples are shown in Figure 4.1 (a)-(b). The wire in (a) has a relatively uniform diameter of 100 nm as compared to the wire in (b) which is apparently tapered from 150 nm to 100 nm towards the tip. The expected range of diameters was between 140 nm to 200 nm, based on the distribution of hole diameters of 170 ± 30 nm for alumina membranes. However NWs with smaller diameter were also seen. Figure 4.1 (a) showed an example of a 100 nm diameter NW. As can clearly be seen, an amorphous layer with random thickness also existed everywhere around each NW.

Figure 4.2 shows an Electron Energy loss spectroscopy (EELS) spectrum obtained from the same NW as shown in Figure 4.1 (a). The spectrum has elemental edge absorption peaks from Co, Fe, and O on top of a large background signal from the zero-loss beam. The largest peak is the Co-L₁ edge peak at 780 eV with a smaller Fe-L₃ peak at 710 eV. These show that the wire contained mainly Co, O and Fe. The significant O peak observed is primarily related to debris from the alumina (Al₂O₃) removal that is visible covering much of the wire, combined with any oxidation of the wire after removal of the alumina.
Figure 4.1. (a) and (b) BF TEM images of two CoFeB NWs (acquired at 300 keV).

Figure 4.2. EELS spectrum of the wire in Figure 4.1 (a) obtained using a Tecnai T20 -STEM (200 keV).

Figure 4.3 (a) shows another BF TEM image of the same NW as Figure 4.1 (a) followed by energy filtered (EF) TEM maps of O, Co and Fe signals from the same NW in (b), (c), and (d), respectively. These elemental maps show that Co and Fe are distributed over the entire NW while O is mostly present on the surface of the wire. The Co concentration in the middle of the wire seems to be less than expected for a cylinder, which could be an artifact as the sample was too thick for the internal structure to be distinguished from TEM BF imaging. Such artifacts are indeed more pronounced in thicker wires. In the Fe map, on the other hand, the concentration is smaller compared to Co except for a brighter line-like contrast at one side of the NW, which is again an artifact. This artefact was due to an imperfect cross correlation of the pre-edge and post-edge EFTEM maps of Fe.
At the end of the wire, Co and O are observed together, suggesting the presence of Co oxides (probably CoO) in this region. The rest of the O map has no overlap with either the Fe or Co maps, which indicates that the observed O is mostly due to residual Al₂O₃ covering the NW. This shows that NaOH could not remove the alumina around the NWs completely.

Figure 4.3. (a) Bright Field (BF) TEM image of a CoFeB NW (acquired at 200 keV). (b), (c) and (d) energy filtered TEM images of O, Co and Fe, respectively. In the Fe map, the brighter line-like contrast at one edge is an artifact.
4.1.2. Magnetic characterization

Bright field (BF) images and their corresponding magnetic induction maps of four selected NWs with different diameters are shown in Figure 4.4 (a) - (d) (acquired at 300 keV). All four contour maps were calculated from the phase images reconstructed from holograms of the same NWs. These holograms were acquired at remanence with the magnetic field within the sample environment < 5 Oe using the Lorentz lens of a 300 keV beam, with a biprism voltage of 150 V. Prior to collecting the holograms, the NWs saw an applied magnetic field (objective lens current) that was in a direction almost parallel to the axis of the NWs. The holographic fringe spacing was 3.1 nm in these measurements, implying that the magnetic resolution was 9 ± 1 nm.

Magnetic induction, $B_\perp$, is calculated (Eq. (3.19)) from the measured (by EH) phase change across the NW when the cross-sectional area of the NW perpendicular to the plan of the specimen is known. For a cylindrical shaped NW, this area is $\pi r^2$, where $r$ is the radius of each NW.

For the NWs shown in Figures 4.4 (a) - (d) with diameters of 120 nm, 148 nm, 97 nm, 183 nm, the average $B_\perp$ was estimated to be 0.9 T, 1.3 T, 1.4 T, and 0.6 T, respectively. These measurements are also listed in Table 4.1. The contour spacing is 2 radians (equivalent to 0.2 T for a 100 nm NW).

As can be seen from Figures 4.4 (b) and (d), the magnetization inside the wires is uniform and follows the shape of the wires. Since the wires consisted of nanocrystals (based on diffraction patterns not shown), it is a reasonable observation that shape anisotropy is the dominant factor determining magnetization. The wires have a relatively large magnetization even at the regions close to their surfaces. But in Figure 4.4 (a) and (b) a lack of magnetization at some regions close to the surface may be due to the presence of $\text{Al}_2\text{O}_3$. At the end of wire 3 in Figure 4.4 (c), the magnetic induction becomes weaker. This is perhaps due to the presence of a significant degree of out of plane (OOP) magnetic components since the wire is twisted at its end as was confirmed by tilting the sample using a dual-tilt axis, tomography holder. Moreover, the demagnetizing field may also have a contribution to this weak induction.
Figure 4.5 shows simulated magnetic fields of magnetic wires with a tapered cone shape (without the top) (left) and a cylinder shape (right). The simulated magnetic induction was 1.5 T with a contour spacing of 1 radian. One can see that the shape of the NW has influenced the measured field lines consistent with the degree of taper. Moreover, comparison with the measured $B_\perp$ from the four NWs in Figure 4.4 shows that the $B_\perp$ lines are more consistent with those of a tapered geometry.

![Figure 4.4](image)

**Figure 4.4.** (a) - (d) BF and magnetic contour maps from EH of four selected NWs with different diameters (acquired at 300 keV). The contour spacings are 2 radians (equivalent to 0.2 T for a 100 nm NW).

The $B_\perp$ measured by holography are summarized in Table 4.1. All of the investigated NWs had some angle with respect to the specimen holder plane. These angles were measured using a dual-tilt axis, tomography holder, which can had errors up to ±10 degrees. The measured values represent the component of the actual magnetic induction of the NWs, in the plane perpendicular to the beam (see Eq. (3.19)). By considering the measured tilt angle for each individual NW, one can calculate the
actual magnetic induction in the NWs as shown in the last columns of Table 4.1 (corrected $B_\perp$). These values are consistent with literature reports for CoFeB thin films with similar compositions [86-89].

Table 4.1. Magnetic induction, $B_\perp$, of four selected NWs measured by electron holography. Wires 1 to 4 are shown in Figure 4.4 (a) to (d), respectively. * The error in corrected $B_\perp$ is primarily due to the 10-degree error in the measured sample tilt angle.

<table>
<thead>
<tr>
<th>Wire</th>
<th>Diameter (nm) ± 5</th>
<th>Tilt angle of wire (deg) ± 10</th>
<th>Measured $B_\perp$ (T)</th>
<th>Corrected $B_\perp$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>30</td>
<td>0.9 ± 0.2</td>
<td>1.0 ± 0.1*</td>
</tr>
<tr>
<td>2</td>
<td>148</td>
<td>20</td>
<td>1.4 ± 0.2</td>
<td>1.5 ± 0.1*</td>
</tr>
<tr>
<td>3</td>
<td>97</td>
<td>25</td>
<td>1.3 ± 0.3</td>
<td>1.4 ± 0.2*</td>
</tr>
<tr>
<td>4</td>
<td>183</td>
<td>50</td>
<td>0.6 ± 0.1</td>
<td>0.8 ± 0.2*</td>
</tr>
</tbody>
</table>

Figure 4.5. Simulated magnetic induction of wires with a tapered shape (left) and a cylindrical shape (right). Parameters used in the simulations were: $B$, 1.5 T; length, 926 nm; diameter of the end of the wires, 62 nm; diameter of the bottom of the cone-like wire, 103 nm; and contour spacing, 1 radian.
4.2. Effect of alumina membrane fabrication and removal

In this section, we consider the impact of using different types of alumina membranes and how the membranes affect the morphology of the NWs after they were removed. We have seen already that there was residual alumina left after sodium hydroxide etching of NWs from large alumina membrane. We consider the impact of two different etchants, sodium hydroxide and phosphorochromic acid, which were used to remove the NWs from the membrane. We compare three sets of NWs made with a smaller average membrane pore size of 40 nm; set A: fabricated in a membrane anodized at a less controlled temperature, and removed in NaOH solution, set B: fabricated in the same membrane as set A but removed in phosphorochromic acid, and set C: fabricated in a membrane anodized at a well-controlled temperature and removed in NaOH solution.

4.2.1. Structural and morphological characterization

Set A

BF TEM and STEM images of a NW are shown in Figure 4.6 (a) - (b), respectively. As seen from both images, this NW has a half arrow-head profile instead of the expected rectangular profile consistent with a cylinder. Therefore, the diameter of this NW varied from 45 nm to 80 nm in this region of its length. However, the majority of the NW was cylindrical shaped. One can question whether the variation in diameter of the NW could be related to the impact of the etchant used (NaOH) but like the larger NWs of the last section, there was a non-uniform amorphous layer visible (debris of alumina) on all periphery surfaces. Therefore, NaOH did not remove all of the alumina and the shape of the NW was likely conserved. The arrow-head shape is more likely due to a fluctuation in the alumina pores along their length originating when they were first anodized.

Details of the features inside and around the NW from regions 1 and 2 in Figure 4.6 (a) were obtained from HRTEM images shown in Figure 4.6 (c) and (d), respectively. In both images the amorphous layer is present everywhere around the NW consisting of regions with varying thickness (black arrows in Figure 4.6 (c)) or with a uniform average
thickness of 5 nm that followed the shape of the NW (white arrows in Figure 4.6 (c)). The thin uniform amorphous layer may be a Co/Fe oxide layer that formed after complete removal of alumina from those areas.

Figure 4.7 (a) and (b) shows more examples of the same kind of NWs having a combination of the two amorphous layers but without the arrow-shaped features. The average diameter of cylindrically shaped regions of these NWs was 40 ± 5 nm and 45 ± 5 nm (except at the tip) with an average surface roughness of 5 nm. In this set, the two amorphous layers were seen in all of the NWs with similar percentage, consistent evidence of less efficiency of NaOH in removing the alumina membranes.

It was expected that the NWs would consist of amorphous CoFeB, due to the presence of boron in the alloy, but crystalline features were seen in all three set of NWs, both from the images and SAD patterns. The image in Figure 4.6 (d) shows the existence of Moiré fringes (areas marked by arrows in Figure 4.6 (d)), which indicate that the NWs had different crystalline grains with different orientations or lattice constants on top of each other.

Most of the NWs were cylindrical with an average diameter of either 45 ± 5 nm or 40 ± 5 nm. Figure 4.8 (a) and (b) show a BF TEM image and SADP for another NW of this set, followed by an STEM image of the same area. The BF and STEM images show uniform amorphous layers for the areas where NaOH has removed the alumina. Otherwise, randomly shaped debris of alumina is present around the NW. The SADP indicates that there is a background of random nanocrystalline CoFeB, as shown by rings. Also, a single crystalline phase of CoFe is obvious from the dot pattern. Analysis of the ring diameters and spacing indicated the expected phases, body-centered cubic (BCC), for CoFeB.

Figure 4.8 (c) and (d) show HRTEM images of areas 1 and 2 of the same wire in Figure 4.8 (a). Figure 4.8 (c) shows a part of the NW, with average diameter of 40 nm, where alumina has been removed. A 5 nm amorphous layer has formed around the wire and follows closely the shape of the NW. Moiré fringes with different orientations can be seen everywhere confirming the nanocrystallinity of the NW.
Moreover, the details of the features in Figure 4.8 (d) demonstrate areas with single crystalline phase. The arrows in Figure 4.8 (d) indicate single grain areas with lattice fringes with spacing of 0.16 nm. The black box in Figure 4.8 (d) was magnified in Figure 4.8 (f) to show the mentioned lattice fringes. The fringes are visible along the axis of the wire and their lattice spacing of 0.16 nm is consistent with the (111) planes of the CoFe BCC alloy (with average lattice constant of 0.28 nm) [90-91]. The grain sizes seen for this set typically had an area of 20 nm × 20 nm. Smaller grain sizes were also possible, as shown by white arrows in Figure 4.8 (d), having areas of 15 nm × 15 nm and 8 nm × 8 nm, respectively.

Figure 4.8 (e) shows an indexed SADP of the same NW when the ring pattern was suppressed. The indexed spots are consistent with a [110] electron beam direction for a BCC structure. Hence, [112] and [111] would be two perpendicular directions in the plane of NW’s image. As noted before, since the (111) lattice fringes were mostly seen parallel to the axis of the NW, crystallographic growth was in the [112] direction for these areas.

EDS line profiles have also been obtained for this type of NW (not shown). Integration of the EDS peak intensities found that the Co/Fe EDS peak ratio was 90/4 ± 2.5. No signal was detected for boron. Since the cross-section for detection of Co and Fe is identical, the Co/Fe ratio is equivalent to their peak ratios, which was close to the expected composition of Co$_{96}$Fe$_4$. The B composition was not greater than the estimated detectable level (2 at %).
Figure 4.6. (a) Bright field TEM and (b) STEM images of a CoFeB NW (acquired at 200 keV). (c) and (d) show, respectively, magnified views of the areas in box 1 and 2 in (a). Black arrows in (c) show amorphous layers of alumina whereas the white arrows show an amorphous layer that follows the shape of the NW with an average thickness of 5 nm. The black arrows in (d) show Moiré fringes with different orientations, evidence for differently oriented crystalline grains on top of each other.
Figure 4.7. (a) and (b) BF TEM images CoFeB NWs (acquired at 200 keV). The average diameter of these NWs is 40 nm (a) and 45 nm (b).

Set B

A BF TEM image of a CoFeB NW (deposited in the same kind of alumina membrane as set A, giving 40 nm NWs) and the STEM image of the same wire, are shown in Figure 4.9 (a) - (b), respectively. The difference between this set and set A is that phosphorchoromic acid (instead of NaOH) was used to remove NWs from the alumina membrane. Although one would expect to see the same roughness in set A and B NWs, BF and STEM images show clearly that the NWs look rougher in set B. Again, BF and STEM images show that there is an amorphous layer around the NW, which follows the shape of the NW, and its thickness varies from 5 to 9 nm. Compared with set A, there is no evidence of large alumina debris on this NW, suggesting a complete removal of the alumina membrane by phosphorchoromic acid.
Figure 4.8. (a) BF TEM image and SADP and (b) STEM image of a CoFeB NW (acquired at 200 keV). (c) and (d) show, respectively, magnified views of the areas in box 1 and 2 in (a). Black arrows in (c) indicate amorphous alumina regions. Black lines in (c) show the amorphous layer with an average thickness of 5 nm. The arrows in (d) show single grain areas with different orientations, with the white arrows marking the grains with sizes of 15 nm × 15 nm and 8 nm × 8 nm. The black-boxed region in (d) has been magnified in (f). (e) SADP of the same wire. (f) (111) lattice fringes of a BCC CoFe alloy (average lattice constant 0.28 nm). The line shows twenty CoFe lattice fringes with a length of 3.2 nm.

To know more about the composition of the amorphous layer, an EDS map along a line (the red line in Figure 4.9 (b)) across the same wire was acquired. The integrated peak intensities from O and Al are shown in Figure 4.9 (c). The EDS profile of O shows that its concentration is more at the edge with the same thickness as the amorphous layer around the NW. However, the Al profile is not following the same shape as the O, suggesting that the amorphous layer around the NW cannot be just alumina but must also be partially due to oxidation of the NW after alumina removal. Similar to set A, the Co/Fe ratio was found to be 90/4 ± 2.5 from EDS analysis.

The HRTEM images of the areas 1 and 2 of the same wire are shown in Figure 4.9 (d) and (e). The wire’s average diameter is 40 ± 5 nm, with the same roughness of 5 nm as for set A. Many other NWs were observed to have such areas with the same thickness. On the other hand, several NWs in this set showed a larger variation in thickness, as shown in Figure 4.9 (e), where the variation in thickness was as high as 25 nm (indicated by the white line). Moreover, the amorphous layers around these narrower parts were thicker (like in Figure 4.9 (e) which was 15 nm).

The largest variations in thickness were observed in areas which were thinner than average. The thickness variation in all measured NWs showed a random behavior that could be the result of etching by phosphorochromic acid. More examples of the same effect are shown in Figures 4.10 (a), (b) and (c) showing a portion of the NW where it is half of the average thickness. The black arrows in Figure 4.10 (a) - (c) point to areas where the thickness of the NWs has changed. In particular, in Figure 4.10 (c), the impact
of phosphorchromic acid etching is demonstrated by the random variation in the thickness of the NW.

The black arrows in Figure 4.9 (d) and (e) show the orientation of lattice fringes in each area and one can see that areas with the same crystallographic orientation exist in the NWs of this set. The white box in Figure 4.9 (e) was magnified and shown at the corner to demonstrate the lattice fringes, mentioned above, with a spacing of 0.16 nm. These are consistent with the (111) planes of the CoFe BCC alloy (with an average lattice constant of 0.28 nm). The typical grain sizes in this set are close to those of set A and varied between 20 nm × 20 nm and 25 nm × 25 nm.
Figure 4.9. (a) BF TEM and (b) STEM images of a CoFeB NW (acquired at 200 keV). (c) Plots of the integrated peak count from EDS perpendicular to the axis of the same wire (red line) from O and Al spectra. Images (d) and (e) show, respectively, magnified views of the areas in box 1 and 2 in (a). Black arrows in (d) and (e) indicate areas of single grains of different orientations. At the corner of (e) a magnified view of the white-boxed area is shown, where (111) lattice fringes of a BCC CoFe alloy are visible.

Figure 4.10. (a), (b) and (c) BF TEM images CoFeB NWs (acquired at 200 keV). The BF images show the effect of alumina etching by phosphorhromic acid. All the black arrows point at the variation in thickness of the NWs. At the corner of (a) a magnified view of the black-boxed area is showing a 15 nm variation in thickness presumably caused by phosphorhromic acid etching.
**Set C**

A BF TEM image of a CoFeB NW (fabricated in a membrane anodized at a well-controlled temperature) and the STEM image of the same wire are shown in Figure 4.11 (a)-(b) respectively. This NW was removed from the membrane (of 40 nm diameter with smooth edge pores) by NaOH. Although a new alumina membrane was used in order to get smoother NWs, it can be seen clearly that the NW looks very rough (up to a 30 nm roughness). This roughness, however, is not related to the NW itself. It seems to be a non-uniform amorphous layer (alumina) everywhere around the NW. One can then conclude that NaOH was not able to remove alumina from the NW and debris is present everywhere.

Figure 4.11 (c) shows an EDS map of integrated peak intensities from Co and Fe along the red line in Figure 4.11 (b). The EDS profiles show that Co concentration is roughly an order of magnitude larger than Fe concentration. The Co/Fe EDS peak ratio is 90/3 ± 2 and no EDS peak was detected for B (Similar to previous sets, B composition was too small to be detected (< 2 at%).) The Co/Fe ratio found from EDS analysis is larger than the expected composition of Co$_{95}$Fe$_4$.

More details of the roughness of the NW, as well as features inside it, are shown by HRTEM images of same NW in Figure 4.11 (d) and (e). In both images the amorphous layer (alumina) is obviously present everywhere around the NW with no pattern (the back arrow in Figure 4.11 (d)). In some areas the thickness of the alumina debris were larger than the actual thickness of the NW itself. However, in most of the NWs in this set, the average thickness of the alumina debris were 20 nm to 30 nm, suggesting the less efficiency of NaOH in removing alumina. Unfortunately, phosphorchromic acid was not used for this set and we cannot compare the performance of phosphorchromic acid versus NaOH. One can still speculate that, since for these NWs it is harder to remove alumina compared to set A, the effect of phosphorchromic acid will not be as destructive as in set B.

White lines in Figure 4.11 (d) show the actual thickness of the NW. Ignoring the alumina debris and looking at the morphology of the NW, one can see that this set has smoother surface and the roughness is about 3 nm. The average thickness of this set is
35 ± 3 nm and similar to the previous sets, crystalline features were seen here. As shown in Figure 4.11 (e) (by black arrows, small areas (from 3 nm × 3 nm to 8 nm × 8 nm) with single crystalline (with lattice fringes spacing of 0.2 nm) phase can be seen everywhere. The typical grain sizes related to this set are smaller than the two other sets. The black box in Figure 4.11 (e) was magnified and shown at the corner to demonstrate the lattice fringes with spacing 0.2 nm. They are consistent with the (110) planes of the CoFe BCC alloy (with average lattice constant of 0.28 nm).

Figures 4.12 (a), (b) and (c) show the effect of NaOH as well as the typical thicknesses for other wires in this set. Similar to Figure 4.11 (a), the NWs show random-shaped alumina debris everywhere around the actual smooth NWs (see the magnified image at the corner of 12 (c)).

Figure 4.13 (a)-(d) shows an EF TEM image of a typical NW in set C followed by the corresponding maps of O, Co and Fe. The debris of alumina is clearly present everywhere around the NW. O is present around the NW more than Co, which is concentrated inside. At the edge, there is almost no Co but O is present. This is evidence of alumina but not NW oxides (like Co oxide) in that region. In the Fe map, the concentration is very small compared to Co, or even O.

From a comparison of Co and Fe concentrations in Figure 4.13 (c) and (d), one can find the ratio of Co/Fe in this NW. Figure 4.13 (e) shows the intensity of the brightness profiles (concentration of the element) from the red box for both Co and Fe. The Co/Fe ratio found from the analysis of the Co and Fe peaks was 90/3 ± 1.5, the same value as was found from the EDS analysis. The artefact (similar to what was seen in Figure 4.3 (d)) in the wire results in a large peak for Fe in the profile and instead, the small peak in the middle was considered for calculating this Co/Fe ratio.
Figure 4.11. (a) BF TEM and (b) STEM images of a CoFeB NW (acquired at 200 keV). (c) Plots of the integrated peak count from EDS perpendicular to the axis of the same wire (red line) from Co and Fe spectra. (d) and (e) show, respectively, magnified views of the areas in box 1 and 2 in (a). Black lines in (d) indicate fluctuations in thicknesses of the NW and black arrows in (e) show the area of single grain with different orientations. At the corner of (e) a magnified view of the white-boxed area is shown, where (110) lattice fringes of a BCC CoFe alloy are visible.

Figure 4.12. (a), (b) and (c) BF TEM images CoFeB NWs (acquired at 200 keV) removed from alumina using NaOH. At the corner of (c) a magnified view of the black-boxed area shows a smooth surface NW when the alumina debris is ignored.
Figure 4.13. (a) EFTEM image a CoFeB NW (acquired at 300 keV). (b), (c) and (d) Elemental maps of the same NW for O, Co and Fe. (e) Profiles of the EDS intensity (concentration of the element) from the red box areas for Co and Fe. In the Fe map, the brighter contrast around the small noisy signal in the middle was assumed to be the actual intensity related to Fe.
In summary, we considered three sets of CoFeB NWs in this section: Set A and B were fabricated in membranes anodized at a less controlled temperature and were removed by sodium hydroxide solution and phosphochromic acid, respectively. It was observed that sodium hydroxide is less efficient in removing the alumina while phosphochromic acid not only removed the Alumina but also etched the wire itself to some extent. Both sets had NWs with average diameter of either $45 \pm 5$ nm or $40 \pm 5$ nm, the Co/Fe ratio of $90/4 \pm 2.5$ and nanocrystalline structure (BCC CoFeB) with average grain size of 20 nm $\times$ 20 nm. Set C, on the other hand, was fabricated in membranes anodized at a well-controlled temperature and was removed by sodium hydroxide solution. For this set, the efficiency of NaOH in removal of alumina was worse compared to set A. The average diameter of NWs in this set was $35 \pm 3$ nm, with the Co/Fe ratio of $90/3 \pm 2$ and nanocrystalline structure with average grain size of 10 nm $\times$ 10 nm. For this set, compared to the other two, the NWs showed less roughness and smaller grain sizes.

### 4.2.2. Magnetic characterization

In this section, we report results from the magnetic characterization of the NWs described above by EH. Unless mentioned otherwise, the holograms were acquired at remanence ($< 5$ Oe) using a 200 keV beam with a biprism voltage of 140 V. The holographic fringe spacing was typically between 3.3 nm and 5 nm, implying that the magnetic resolution was between 10 nm to 15 nm.

#### Set A

Figure 4.14 and 4.15 show the results from EH from CoFeB NWs similar to those shown in Figures 4.8 and 4.6, as a function of the direction of the applied external field (1 T). Panel (a) in each figure shows the acquired hologram while panels (b) and (c) show the corresponding phase images of their MIP and magnetic contributions, respectively. The observed lower-density outer layer around the NWs in the MIP images is consistent with alumina debris and/or a Co/Fe oxide that had grown during or after alumina removal by NaOH.
Examples of line profiles across the NW (red lines shown in (b)) are shown in the panel insets (b) and (c). The magnetic contour maps, generated from the magnetic phase contributions ((c) panels), are also shown in panels (d).

In Figure 4.14 the external magnetic field, $H$, was applied almost parallel (15 degree deviation) to the NW axis. This produced a uniform magnetization as shown in the corresponding magnetic contour map. The magnetic contour lines followed the shape of the NW, likely due to the significant effect of shape anisotropy in the magnetic behavior of these NWs. The calculated $B_\perp$, of this NW is $1.7 \pm 0.4$ T, based on its average thickness, $40 \pm 5$ nm, and total phase shift of $3.2$ radian. The two boxed-areas shown in the MIP and magnetic phase contribution images, panels (b) and (c), show features resulting in local deviations in the contour lines seen in panel (d) which are not real and are related to phase unwrapping artifacts.

In Figure 4.15, $H$ was applied perpendicular to the NW axis. This NW had a large fluctuation in its diameter due to an arrowhead feature on its surface. The effect of this shape can then be seen in the magnetic phase image, Figure 4.15 (c), and its magnetic contour map, Figure 4.15 (d). Figure 4.14 (c), shows a sigmoidal change in phase across the NW that results in magnetic contour lines along the axis of the NW (Figure 4.14 (d). There are also small phase changes along the NW that are likely due to the rough profile of the NW.

The corresponding $B_\perp$ of this NW can be calculated as a function of position depending on the local diameter that varies between 40 nm to 80 nm across the NW from tip to end. $B_\perp$ varied from 0.76 T, to 1.5 T. The smallest value was near the tip partially due to a twist of the wire at the end (as was confirmed by tilting the NW) and also the demagnetizing field. However, the value of the magnetic induction in the middle of the NW (1.5 T) is the same as (to within the error) as that of the NW shown in Figure 4.14 (1.7 T).
Figure 4.14. CoFeB (40 nm) NW with an external magnetic field applied almost parallel (15 degree deviation) to the axis of the NW (a) Hologram (acquired at 200 keV) in a < 5 Oe field with a magnified view of a portion (insert image) showing holographic fringes, and (b) MIP phase contribution from a reconstruction of the hologram in (a). The insert image shows a line profile across the NW along the red line. (c) Magnetic phase contribution with an insert showing a line profile at the same location as in (b). This profile shows the total magnetic phase shift across the NW. (d) Contours of equal phase displaying the associated $B_\perp$ contour map (average magnetic induction map, contour spacing is 0.5 radian). These contours were generated from the magnetic phase image, (b).
Figure 4.15. CoFeB (40 nm) NW with an external magnetic field applied perpendicular to the axis of the NW. (a) Hologram in a < 5 Oe field, (b) MIP phase contribution, (c) Magnetic phase and (d) $B_\perp$ contour map (magnetic flux lines, contour spacing 0.67 radian) of the same NW.

Another example of the same type of NW with an average thickness of 45 ± 5 nm saturated in a perpendicular $H$ is shown in Figure 4.16 (a) with its magnetic contour map in Figure 4.16 (b). In contrast to the first, this NW did not have a large fluctuation in thickness that the NW in Figure 4.15 had and hence, its magnetic contour map shows a uniform magnetization, exactly along the axis of the NW. The corresponding average $B_\perp$ of this NW is 1.7 ± 0.3 T, the same as for the other two NWs (within error). Moreover, these values are close to the $B_\perp$ measured for the larger NWs with diameters of 170 nm.
Figure 4.16. CoFeB (40 nm) NW with an external magnetic field applied perpendicular to the axis of the NW. (a) Hologram in a < 5 Oe field, and (b) $B_\perp$ contour map (magnetic flux lines, contour spacing 0.67 radian) of the same NW.

Set B

Figures 4.17 and 4.18 show the results of EH on two CoFeB NWs and as a function of the direction of the applied magnetic field of 1 T. The NW in Figure 4.17 is the same as was shown in Figure 4.9. The lower-density outer layers around the NWs in the MIP images (panels (b)) follow the shape of the NWs. As concluded before, this layer is related to the oxide made after alumina removal by phosphochromic acid. Examples of line profiles across the NW (red lines shown in (b)) are shown in the panel insets (b) and (c).

In Figure 4.17, the $H$ field was applied parallel to the NW axis whereas in Figure 4.18, $H$ was applied making a 60-degree angle with the axis of the examined NW. As can be seen from the magnetic contour maps, Figures 4.17(d) and 4.18 (d), the resultant magnetization is uniform and the magnetic contour lines follow the shape of the NWs. Figures 4.17 (c) and 4.18 (c) show that the phase variations are mostly sigmoidal across the NWs assuming a cylindrical shape, but some fluctuations can also be seen along the NWs. As before, these fluctuations cause deviations in the magnetic contour lines from being along the axis of the NWs, and are likely the result of thinning and roughening of the NWs during the acid etching.
Figure 4.17. CoFeB (40 nm) NW with an external $H$ field applied parallel to the axis of the NW. (a) Hologram (acquired at 200 keV) in < 5 Oe field, and (b) MIP phase contribution from a reconstruction of the hologram in (a). The insert shows a line profile from across the NW along the red line. (c) Magnetic phase contribution with an insert showing a line profile at the same location as in (b). This profile shows the total magnetic phase shift across the NW. (d) Contours of equal phase displaying the associated $B_{\perp}$ contour map (magnetic flux lines, contour spacing 0.25 radian).
Figure 4.18. CoFeB (40 nm) NW with an external $H$ field applied almost with an angle 60 degree to the axis of the NW (a) Hologram in a < 5 Oe field, (b) MIP phase contribution, (c) Magnetic phase and (d) $B_{\perp}$ contour map (magnetic flux lines, contour spacing 0.5 radian) of the same NW.

The average $B_{\perp}$ of these NW was $1.0 \pm 0.3$ T (Figure 4.17) and $1.6 \pm 0.4$ T (Figure 4.18) calculated using an average thickness of $40 \pm 5$ nm, and a total phase shift of 2 radians for NW in Figure 4.17, and 3.1 radians for NW in Figure 4.18. The smaller value for $B_{\perp}$ of the former can be due to the presence of an OOP magnetic component (if the wire is twisted at the end the demagnetizing field). The estimated $B_{\perp}$ of the latter NW (Figure 4.18) is the same (to within error) as for those of set A (average of 1.6 T).
Set C

Figure 4.19 (the same CoFeB NW as in Figure 4.11 and 4.20 show EH results for CoFeB NWs with an average thickness of 35 ± 3 nm. The wires were exposed to an applied external magnetic field of 1 T, parallel to the NW axis (Figure 4.19) or with an angle of 30 degrees to the axis of NW (Figure 4.20). In both cases, non-uniform lower-density outer layers are present around the NW as can be seen in the MIP images. These are alumina debris, which were not removed by NaOH. Examples of line profiles across the NW (red lines shown in (b)) are shown in the panel insets (b) and (c). The magnetic contour maps are shown in panels (d).

As mentioned in the morphology section, we expected to see more uniform NWs in this set compared to sets A and B. This was in fact the case where the wires here have a roughness of 3 nm instead of 5 nm. However, the MIP images (Figures 4.19 and 4.20 (b)) show a non-cylindrical profile (compared to the other two sets). This is due to a larger layer of alumina around these NWs. On the other hand, the magnetic contour maps, Figures 4.19(d) and 4.20 (d), do not show a similarly rough shape. Instead, the corresponding magnetic contour lines show a uniform magnetization that follows the shape of the NWs.

The deviation of magnetic contour line in the left side of Figure 4.20 (d) is due to the presence of alumina debris, which has been charging when the hologram was acquired. The phase image (Figure 4.20 (c)) of the same area also shows a phase gradient that is then combined with the gradient from the magnetic effect of NW. The observed deviation of magnetic contour lines is the net effect.

With an average cross-section diameter of 35 ± 3 nm the average magnetic induction is 1.2 ± 0.2 T and 0.8 ± 0.1 T. There is probably an OOP magnetic component (NW could be twisted) for the NW in Figure 4.20, since the magnetic induction is below average. The overall magnetic induction from the examined NWs in this set (average of 1.2 T) is smaller than for sets A and B.
Figure 4.19. CoFeB (35 nm) NW with an external magnetic field applied parallel to the axis of the NW. (a) Hologram (acquired at 200 keV) in < 5 Oe field with a magnified view of a portion (insert image) showing holographic fringes, and (b) MIP phase contribution from a reconstruction of the hologram in (a). The insert shows a line profile from across the NW along the red line. (c) Magnetic phase contribution with an insert showing a line profile at the same location as in (b). This profile shows the total magnetic phase shift across the NW. (d) Contours of equal phase displaying the associated magnetic induction contour map (magnetic flux lines, contour spacing 0.25 radian).
Figure 4.20. CoFeB (35 nm) NW with an external magnetic field applied with an angle 45 degree to the axis of the NW. (a) Hologram in a < 5 Oe field, (b) MIP phase contribution, (c) Magnetic phase and (d) magnetic induction contour map (magnetic flux lines, contour spacing 0.25 radian) of the same NW.

The magnetic contour lines have been observed to be uniform in all the magnetic induction maps of the studied NWs. This outcome, however, is limited by the resolution of the EH measurement which, in our case, is 10 nm to 15 nm for the holograms acquired at 200 keV using a Tecnai. This limits our ability to measure any magnetic fluctuations in the sample due to the presence of, for example, grains inside the sample. To check for such a possibility, EH with a better resolution (7.5 nm - 9 nm, 120 keV) was performed on two NWs from set C and the results are shown in Figure 4.21. Even the EH measurement had a better resolution, the resultant magnetic induction maps still show a uniform magnetization along the axis of the NWs, with no evidence for small
magnetic features inside the NW (Figure 4.20 (c) and (d)). The shape anisotropy still governed the magnetic behavior of these NWs. The calculated average magnetic induction of these NWs (diameter $35 \pm 3\,\text{nm}$) was $1.1 \pm 0.2\,\text{T}$ for the NW in Figure 4.21 (a) and $0.8 \pm 0.1\,\text{T}$ for the NW in Figure 4.21 (b).

Figure 4.21. CoFeB (35 nm) NWs with an external magnetic field applied with an angle 30 degree to the axis of the NW. (a) and parallel to the axis of the NW (b), (a)-(b) Holograms (acquired at 120 keV) in < 5 Oe field with a magnified view of a portion (insert image) showing holographic fringes, and (c)-(d) Contours of equal phase displaying the associated $B_{\perp}$ contour map (magnetic flux lines, contour spacing 0.14 radian in (a) and 0.16 radian in (b)).
In summary, the NWs in the three studied sets all have uniform magnetization along their axis. In all the sets, magnetization was mainly controlled by the shape anisotropy of the wire. Due to the rougher surface in sets A and B (specially in set B with more roughness resulted from the etchant) one could see deviations in the magnetic field lines. The average magnetic induction for sets A and B was $1.7 \pm 0.3$ T and $1.6 \pm 0.3$ T, respectively, which are essentially the same (within error). But for set C the average magnetic induction is $1.2 \pm 0.2$ T, smaller that the other two which can be due to larger ratio of Co/Fe compared to the other two sets [89].

4.3. Small CoFeB NWs

4.3.1. Structural and morphological characterization

Small NWs are classified here as having diameters smaller than 30 nm. BF TEM and STEM images of a NW fabricated in a membrane made by a temperature-controlled anodization method are shown in Figure 4.22 (a) - (b). NaOH was used in this case for the removal of alumina membrane. For 40 nm CoFeB NWs made from the same type of membrane (set C in section 4.2.1), the NWs were found to be in a non-uniform cloud of alumina but smooth on their surfaces. Here, however, the NW looks rough in some areas and there is no evidence for large alumina debris. In both BF and STEM images of the NW, there is an amorphous layer following the shape of the NW with an average thickness of 3 nm. Some areas with alumina debris remain as shown, for example, in the regions indicated by arrows in Figure 4.22 (a) and (b).

An EDS map along the red line in Figure 4.22 (b) shows the integrated peak intensities from Co and Fe in Figure 4.22 (c). The EDS profiles demonstrate that the Co density was an order of magnitude larger than Fe. The Co/Fe EDS peak ratio was 80/7 which is smaller than the expected composition of Co$_{95}$Fe$_{4}$ with twice as many Fe atoms as expected. No EDS peak was detected for B here as the B composition was too small to be detected (< 2 %).

HRTEM images of areas 1 and 2 in Figure 4.22 (a) are shown in Figure 4.22 (d) and (e). The amorphous layer around the NW is following the shape of the NW and
clearly formed after the removal of alumina. The average thickness of the NW was 22 ± 3 nm.
Figure 4.22. (a) BF TEM and (b) STEM images of a small CoFeB NW (acquired at 200 keV). (c) Plots of the integrated peak counts from EDS perpendicular to the axis of the same wire (red line) from Co and Fe spectra. (d) and (e) show, respectively, magnified views of the areas in box 1 and 2 in (a). Black arrows in (d) and (e) show areas with lattice fringes or areas with Moiré fringes. At the corner of (e) a magnified view of the white-boxed area showing (110) lattice fringes of a BCC CoFe alloy.

Figure 4.23. (a) and (b) BF TEM images of small CoFeB NWs (acquired at 200 keV). Inserts show a magnified view of the black-boxed areas in each case showing details of the amorphous layer around each NW.
For this set, the dominant shape of the NWs was not what is shown in Figure 4.22 (a), although NWs like this were seen in many cases. More example of this set are shown in figures 4.23 (a) and (b). Figure 4.23 (a) shows a NW that has large variation in its thickness, which is not just due to alumina etching by NaOH, but some of them were also formed during deposition. They are similar to the dent shape feature formation seen for CoFeB (40 nm) NWs in set A. The thickness variation is measured to be between 15 nm and 35 nm.

The commonly observed NW shape in this set is shown in Figure 4.23 (b), which is similar to what was seen for CoFeB (40 nm) NWs in set C. The average thickness of the NW is 22 $\pm$ 3 nm and NaOH could not completely remove the alumina. Hence, there exists a cloud of alumina with a thickness close to the thickness of the NW itself. However, there are also regions, like the one magnified at the corner of Figure 4.23 (a), with a shape that has not been observed frequently.

This set also has lattice fringes from nanocrystalline regions as indicated by black arrows in Figures 4.22 (d) and (e). Moreover, areas with the Moiré fringes were seen throughout this set. The white box in Figure 4.22 (e) was magnified and shown in the corner to demonstrate the mentioned lattice fringes with a spacing of 0.16 nm. They are consistent with the (111) planes of the CoFe BCC alloy (with average lattice constant of 0.28 nm). The typical grain size in this set is 15 nm $\times$ 15 nm.

4.3.2. Magnetic characterization

Figures 4.24 and 4.25 show EH results from the same NWs as in Figure 4.23 ((b) and (a)), in parallel and perpendicular orientations with respect to an external magnetic field (1 T). We see the same low-density outer layer that we saw in previous samples, which either formed after alumina removal by NaOH or are the debris of alumina itself. The $B_\perp$ contour maps confirm the presence of a uniform magnetization along the axes of the NWs as before. In Figure 4.24 (d), the $B_\perp$ contour lines follow the shape of NW but it seems in the middle that they are moving apart. This is again an artifact. Since the NW had a small curve, the cross correlation of the two phase images from +25 and –25
degree tilts could not be done perfectly, causing the resultant distance between contour lines in the middle (seen also in the middle of phase image).

For the NW in Figure 4.24, the average $B_{\perp}$ is $1.3 \pm 0.3$ T for a diameter of $22 \pm 3$ nm. This is equal to the estimated $B_{\perp}$ for the NW in Figure 4.25, which was $1.4 \pm 0.3$ T for the same average diameter. As can be seen from Figure 4.25 (a) and (c), the measured NW has a larger fluctuation in thickness with areas where the diameter is as high as 35 nm. For these areas, $B_{\perp}$ was calculated based on their corresponding phase shift, and was close to the average value. An average value of $1.4 \pm 0.3$ T is the $B_{\perp}$ for this set, which is equivalent (within errors) to the result for other NWs examined in this chapter, except for the 40 nm diameter NWs in set C.
Figure 4.24. CoFeB (22 nm) NW with an external $H$ field applied parallel to the axis of the NW. (a) Hologram (acquired at 200 keV) in < 5 Oe field with a magnified view of a portion (insert image) showing holographic fringes, and (b) MIP phase contribution from a reconstruction of the hologram in (a). The insert shows a line profile from across the NW along the red line. (c) Magnetic phase contribution with an insert showing a line profile at the same location as in (b). This profile shows the total magnetic phase shift across the NW. (d) Contours of equal phase displaying the associated $B_\perp$ contour map (magnetic flux lines, contour spacing 0.13 radian). These contours were generated from the magnetic phase image, (b).
4.4. Discussion

The diameters of the NWs investigated by STEM and HRTEM were in the same range as those of the pore sizes of the associated alumina membrane. The two different etchants, sodium hydroxide and phosphoric acid, that were used to remove the NWs from the alumina membranes, had different effects on the CoFeB NWs. Sodium hydroxide was not able to remove alumina completely and its debris was present around the NWs. In comparison, phosphoric acid was more effective at dissolving alumina, leaving little residue with the side effect of attacking the NWs and making them
rougher, resulting in deviations in $B_\perp$ inside the NWs. However, the average $B_\perp$ of NWs extracted using either etchant method was overall the same, indicating that these two methods did not significantly change the average magnetic properties of the NWs.

It was expected that amorphous CoFeB would be found due to the introduction of a third element (boron), known to induce amorphization in both thin films and NW arrays [67]. However, based on selected area diffraction patterns, the CoFeB NWs were all nanocrystalline (BCC). Reasons for this may have been a smaller B concentration than expected, but even 1 at% is difficult to detect in individual NWs using EDS.

Similar to reported results for Co$_{94}$Fe$_{5}$B$_{1}$ thin films [67], CoFeB NWs that are grown with the same electrolyte in current-controlled electrodeposition, yield a typical composition of Co$_{94}$Fe$_{5}$B$_{1}$, with a Co/Fe atomic ratio of $94/5 = 20$. EDS investigation of the examined NWs in this work showed that the measured Co/Fe ratio was the same as the expected value (to within error), except for the smallest diameter NWs (22 nm). In that case the Co/Fe ratio from EDS analysis was half of the expected value. This could have been due to a difference in the parameters used in electrodeposition, which were optimized for larger diameter NWs.

For magnetic NWs, the shape and magnetocrystalline anisotropies, as well as their roughness, can change the magnetic characterization of the NWs. If the surface of a NW is smooth and they are nanocrystalline, the shape anisotropy of the NW plays a major role in determination of their magnetization [2,36]. For a magnetically isolated cylindrical (NW) magnet, where its magnetic structure is dominated by shape anisotropy, the remnant magnetization tends to be parallel to the symmetry axis (its easy axis). However, as the diameter of NW increases, there is a possibility of having some degree of random orientation in the magnetization [2,36].

The off-axis EH technique was able to resolve magnetic volumes as small as (15 nm)$^3$ using a single biprism in a field-emission electron column at 200 keV. All examined NWs showed uniform magnetization along their axes for an applied magnetic field parallel, perpendicular, or with an angle to the axis of the NW. This means that the magnetizations were mainly controlled by the shape anisotropy of the wire. For some
portions of the NWs, small deviations in the magnetization from away from the axis of the NW, were seen which were likely caused by the rougher surfaces of those NWs.

For a thin film of Co$_{94}$Fe$_5$B$_1$, electrodeposited in similar conditions as to the examined NWs, a magnetization of 1.7 T was reported [67]. The measured average $B_\perp$ of CoFeB NWs with different diameters were the same, to within errors, and close to the magnetization of Co$_{94}$Fe$_5$B$_1$ thin film, 1.7 T. However, there were NWs with a smaller average $B_\perp$, which could have been due to their larger Co/Fe ratio [89].
Chapter 5.

CoFeB/Cu multilayer nanowires

In magnetic nanowires, the overall magnetic behavior depends on several factors, including shape anisotropy, crystallinity and interaction between the internal layers of the NW. In this chapter, impact of these factors are investigated using scanning and transmission electron microscopy (STEM) techniques on four different types of multilayered CoFeB/Cu NWs. The STEM techniques include bright field TEM imaging (BFI), selected area diffraction (SADP), high resolution transmission electron microscopy (HRTEM), annular dark field detection (STEM) with energy dispersive spectroscopy (EDS). Finally, off axis electron holography was conducted to map the magnetic induction of individual wires. The effects due to the shape and magnetocrystalline anisotropies, as well as magnetic interaction between the layers were utilized in the interpretation of each magnetic induction map.

In order to help interpret the magnetic contour maps, obtained from the holograms, magnetostatic simulations (performed by collaborators) were carried out using a commercial, finite-element software package (CST Microwave Studio, www.cst.com). For these, a magnetic structure consisting of uniform magnetization with predetermined and identical orientation for all tetrahedral mesh cells was assumed within the magnetic layers. In other words, each magnetic layer was treated as a permanent magnet with predefined magnetization direction. The uniform magnetization values and the layer thicknesses for the simulations were taken as the average induction and thicknesses measured by EH and EDS analysis. A permeability of unity was used for the non-magnetic layers, and as such, they had no influence on the field produced by the magnetic layers. The background was treated as vacuum, with permeability of unity, and was increased in size until the boundaries had essentially no influence on the field produced by the magnetic layers. The magnetic induction vector map was observed on a sagittal plane passing through the center of the wire.
5.1. Bilayer NWs (50/50 nm) Diameter 45 nm

5.1.1. Structural and morphological characterizations

A bright field (BF) TEM image and selected area diffraction pattern (SADP) of a typical CoFeB/Cu (nominally 50/10 nm) multilayer NW are shown in Figure 5.1 (a). Phosphochromic acid was used to dissolve the alumina membrane and to collect the individual wires such as this one. Note that no apparent amorphous alumina debris is visible around the wire but its surface is not smooth. The average diameter of the wire is 45 ± 5 nm and the SADP indicates that both the Cu and CoFeB regions are random nanocrystalline materials. Analysis of the ring diameters and spacing indicated the expected phases, namely, face-centered cubic (FCC) Cu and body-centered cubic (BCC) CoFeB.

A STEM image of the same wire is shown in Figure 5.1 (b), where the presence of multilayers is evident from the periodic contrast in the image. Note that all interfaces are aligned perpendicular to the axis of the wire. An EDS map along a line at the centre of the same wire showed integrated peak intensities from Fe, Co and Cu as shown in Figure 5.1 (c). The Co and Fe distributions are observed as the darker regions of the STEM image while those with predominantly Cu peaks are the brighter regions.

The EDS profiles show that the magnetic-nonmagnetic interfaces are abrupt to within 5 nm, a factor of 10% -15% of the peak width. But Cu is found in the magnetic layers with a composition that varies from 5% to 50% of the signal in the nominally pure Cu layers. The nonmagnetic Cu layers are apparently 50 ± 5 nm, thicker than the expected width, 10 nm, and have therefore, the same thickness as the magnetic layers. The Co:Fe EDS peak ratio was 2.7 ± 0.3. Note that the B composition was too small to be detected (< 2 at%).

Figure 5.2 (a) and (b) show STEM and TEM images from another example of a CoFeB/Cu (50/50 nm) multilayered NW. Towards one end there is a short piece of a second NW overlapping the main NW while at the opposite end there is a feature that was observed in more than one NW, sometimes at more than one location on the NW.
and in both TEM and STEM images. Otherwise, for most of the NWs, the average diameter was either $45 \pm 5$ nm or $40 \pm 5$ nm. In this case, it can be seen that the diameter of the wire is different before and after the dented region varying between 45 nm and 65 nm. We concluded in the previous chapter, that these are not a side effect of removing the NWs from the alumina membranes with phosphochromic acid. They likely originate from a defect in the alumina template or discontinuity in the applied voltage during growth that is replicated in the NWs.

Figure 5.2 (c) and (d) show HRTEM images of areas 1 and 2 from the same wire as indicated in Figure 5.2 (b). It is clear that in both images an amorphous layer with a thickness between 3 and 5 nm has formed around the wire. Since it follows closely the shape of the NW, and has a very uniform thickness, this is unlikely to be residual alumina debris. More likely this is an oxide layer that formed during or after removing the NWs from the alumina membrane. This layer did not form from a beam-generated process, as it was visible on many NWs independent of the time spent focused on any one section. Ignoring the amorphous layer, the NW in Figure 5.2 (c) and (d), has a diameter that was smallest at each grain boundary and larger within each grain varying by 5 nm from grain to grain. The NWs are not atomically smooth, with an average roughness of 5 nm. This observed variation could be due to the presence of two kinds of layers causing fluctuations in the diameter of the NW in the process of switching between CoFeB and Cu layers.

As mentioned before, SADP showed that the NWs were nanocrystalline. The details of the features in Figure 5.2 (d) also confirmed that the wires were crystalline. The existence of Moiré fringes (white box in Figure 5.2 (d)) indicates that the NWs had different grains with different orientations on top of each other. Other areas showed single grains. Figure 5.2 (f) shows a magnified view of the area in the black box in Figure 5.2 (d) where the lattice fringes visible are along the axis of the wire. Their lattice spacing, 0.16 nm, are consistent with the (111) planes of the CoFe BCC alloy (with average lattice constant of 0.28 nm). This area, 25 nm × 25 nm, is a typical grain size.

Figure 5.2 (e) shows a typical SADP of the NW. The indexed spots are consistent with a [110] electron beam direction for a BCC structure. If the plane (110) is
perpendicular to the plane of the NW’s image, [112] is a direction perpendicular to the (111) fringes and in the plane of the wire. Therefore, for any grain with (111) lattice fringes parallel to the axis of the wire, they are consistent with a preferred [110] crystallographic growth direction of the NW.

Figure 5.1. (a) Bright field TEM image and selected area diffraction pattern and (b) STEM image of a CoFeB/Cu (50 / 50 nm) NW (acquired at 200 keV). (c) Plots of the integrated peak counts from energy dispersive spectroscopy along the axis of the same wire (red line) from Cu, Co and Fe spectra.
Figure 5.2. (a) STEM image and (b) bright field TEM image of a CoFeB/Cu (50 / 50 nm) NW (acquired at 200 keV). Panels (c) and (d) show, respectively, magnified views of the areas in box 1 and 2 in (b). At the corner of (c) a magnified view of the box area is shown, showing an amorphous layer of thickness 3 nm to 5 nm around the wire. The white-boxed region in (d) has been magnified to show more clearly Moire fringes, evidence of differently oriented grains on top of each other. (e) SADP of the same wire. (f) (111) Lattice fringes of a BCC CoFe alloy (average lattice constant 0.28 nm). The line shows 20 of the CoFe lattice fringes with a length 3.2 nm.

5.1.2. Magnetic characterization

Figure 5.3 and 5.4 show the results from EH on the same CoFeB/Cu (50/50 nm) NWs, as a function of the direction of the applied external magnetic field (1 T). Panel (a) in each figure shows the acquired hologram while panels (b) and (c) show the corresponding phase images of their MIP and magnetic contributions, respectively. The observed lower-density outer layer (3-5 nm) around the NWs in the MIP images indicates that Co/Fe oxide had grown during or after alumina removal by phosphochromic acid. The bulk NW is inside this thin layer and has a rough surface in some parts.

Examples of line profiles across the NW (red lines shown in (b)) are shown in the panel insets (b) and (c). The shape of the profile from the MIP phase image confirms a cylindrical morphology as expected. The magnetic contour maps, generated from the magnetic phase contributions ((c) panels), and magnetostatic simulation of the induction vector map are also shown in panels (d) and (e).

In Figure 5.3 the external magnetic field was applied parallel to the NW axis. In this case, the magnetic phase image in Figure 5.3 (c) shows a sigmoidal phase change that is more rapid or less rapid depending on whether the part of the NW is magnetic or not. Figure 5.3 (d) shows the resulting magnetic induction contour map generated from the magnetic phase contribution (Figure 5.3 (c)). The average \( B_\perp \) of the magnetic layers is \( 0.5 \pm 0.1 \) T, based on its average thickness, \( 40 \pm 5 \) nm, and a total phase shift, 0.9 radian. Each contour represents a phase shift of 0.1 radians, which is equivalent to 0.05 T of magnetic induction, \( B_\perp \). This is calculated (Eq. (3.19)) from the phase shift by
knowing the cross-sectional area of the NW perpendicular to the magnetic line. For a cylindrical shaped NW, this area is $\pi r^2$.

The magnetic induction $B_\perp$ map in Figure 5.3 (d) shows that the magnetic contours are almost exactly aligned with the axis of the wire with a radial deviation at both ends of each layer. For an individual magnetic layer with an aspect ratio larger than 0.9, one expects to see such an out-of-plane flower state in the magnetic contour lines [36]. The interaction between each magnetic layer modifies the flower state of each layer and makes small radial deviation at both ends of each magnetic layer. The magnetic induction is not perfectly parallel to the axis of the NW and the small deviations in alignment (< 5 degrees) could be due to a slight effect of the magnetization of each magnetic layer from their magnetic layer neighbours. The average $B_\perp$ of the magnetic layers is $0.5 \pm 0.1$ T, as determined from the number of magnetic contours in each layer. The magnetostatic simulation of the induction vector map, in Figure 5.3 (e), assumes a uniform longitudinal magnetization in each magnetic layer and displays the expected direction of the magnetic field induction to help interpret the hologram.

In Figure 5.4 the external magnetic field was applied perpendicular to the NW axis. In this case, the magnetic phase map shows phase changes not only across the NW, but also inside the NW with different angles with respect to the axis. Two different profiles of the magnetic phase shift are shown in the inserts of Figure 5.4 (c). Due to the interaction between magnetic layers in this case, it was expected that each layer would show a deviated magnetization orientation with respect to the applied magnetic field, which could have an in-plane flower state. Figure 5.4 (d) shows the magnetic contour map of the same NW, where in some parts of the wire, magnetic contour lines have angles with the external field (e.g. areas 1 and 2). Fluctuation in $B_\perp$ of the magnetic layers along the NW is observed from variation in the number of the contour lines. This can be explained by the presence of an out-of-plane component of magnetic induction, which cannot be depicted by EH. The magnetostatic simulation in Figure 5.4 (e) shows the $B_\perp$ vector map of a CoFeB/Cu (50 / 50 nm) nanowire, with the magnetization of the magnetic layers alternating between $+45^\circ$ and $-45^\circ$ relative to the wire axis.
Figure 5.3. CoFeB/Cu (50 / 50 nm) NW with an external $H$ field applied parallel to the axis of the NW (a) Hologram (acquired at 120 keV) in zero field with a magnified view of a portion (insert image) showing holographic fringes, and (b) MIP phase contribution from a reconstruction of the hologram in (a). The insert shows a line profile from across the NW along the white line. This phase image with the associate profile shows the actual shape of the wire. (c) Magnetic phase contribution with an insert showing a line profile at the same location as in (b). This profile shows the total magnetic phase shift across the NW. (d) Contours of equal phase displaying the associated $B_\perp$ contour map (magnetic flux lines, contour spacings 0.1 radians (equivalent to 0.05 T for a 40 nm NW)). These contours were generated from the magnetic phase image, (b). (e) Magnetostatic simulation of the $B_\perp$ vector map of a CoFeB/Cu (50 / 50 nm) NW, with axially magnetized magnetic layers.
Figure 5.4. CoFeB/Cu (50 / 50 nm) NW with an external $H$ field applied perpendicular to the axis of the NW (a) Hologram image (acquired at 120 keV) at zero field. The insert is a magnified image of the region shown, and (b) MIP phase contribution. The insert shows a line profile across the NW along the line 1. This phase image with associate profile shows the actual shape of the wire. (c) Magnetic phase contribution with two line profiles along lines I and 2 depicted on (c). (d) Contours of equal phase displaying the associated $B_\perp$ map (magnetic flux lines, contour spacings 0.1 radians (equivalent to 0.05 T for a 40 nm NW)). (e) Magnetostatic simulation of the $B_\perp$ vector map of a CoFeB/Cu (50/50 nm) NW, with the magnetization of the magnetic layers alternating between $+45^\circ$ and $-45^\circ$ relative to the wire axis.

5.2. Bilayer NW (200 / 75 nm) diameter 40 nm

5.2.1. Structural and morphological characterizations

Sodium hydroxide (NaOH) was used in this case to dissolve the alumina membrane. Figure 5.5 (a) shows a STEM image of a typical NW showing a rough surface, with no clear evidence of a multilayer structure. The roughness is apparently due to alumina debris on the surface of the NW. This can be seen by looking at a magnified view of the region in the white box where there is a cloud of material around the wire. The presence of the same kind of material was obvious on the TEM grid since it caused charging effects. The BF image of the same NW is shown in Figure 5.5 (b) where more evidence of alumina debris is seen based on the lower contrast and the random shape of this amorphous material. The NW itself looks rough with an average thickness of 40 nm. An SADP (not shown) produced ring patterns, indicating nanocrystallinity, and the same phases present Cu (FCC) and CoFeB (BCC) as for the (50 / 50 nm) NWs.

More details about the crystallography and morphology of the NW were acquired via HRTEM on the same wire. Figure 5.5 (c) and (d) show HRTEM images of areas 1 and 2, as indicated in Figure 5.5 (b). In both images, an amorphous layer around the NW has a random shape and does not follow the shape of the NW. The thickness of this layer could become larger than the thickness of the NW itself. The average diameter of the wire, ignoring the amorphous layer, was 40 ± 5 nm. The region in the black box in Figure 5.5 (c) has been magnified in the insert in the right corner. This shows the typical...
roughness of the NW, 5 nm, ignoring the alumina debris, similar to the roughness of the (50 / 50 nm) NWs.

Figure 5.5 (e) shows a magnified image from the white square area in Figure 5.5 (c) where one can see lattice fringes (spacing 0.21 nm) throughout the area. These lattice fringes are consistent with (111) Cu fringes (lattice constant 0.36 nm). The Cu is nanocrystalline. Grains with similar fringe spacing ranged in size from 3 nm to 15 nm with random orientations with respect to the axis of the wire (as shown by black arrows).

Figure 5.5 (f) shows a magnified image of the white square area in Figure 5.5(d) where the lattice fringes spacing 0.16 nm are consistent with CoFe (111) fringes. The (111) CoFe lattice fringes were always parallel to the axis of the wire, similar to those in the (50 / 50 nm) NWs, but with a larger average grain size of 30 nm × 30 nm. Moiré fringes were clearly seen in the CoFeB parts of the wire identified by their larger spacings compared to lattice fringes, evidence of slightly differently oriented grains on top of each other.

A typical SADP of the NW, when the ring pattern was suppressed, is shown at the corner of Figure 5.5 (f). The indexed spots are consistent with a [112] electron beam direction for a BBC structure. If the image plane of the NW is (112) therefore, the [110] direction is parallel to long axis of the NW and is the predominant growth direction, given the (111) planes are predominantly perpendicular.
Figure 5.5. (a) STEM image and (b) bright field TEM image (acquired at 200 keV) of a CoFeB/Cu (200 / 75 nm) nanowire. Panels (c) and (d) show HRTEM images of the boxed regions indicated as 1 and 2 in (b), respectively. At the right bottom corner of panels (c) and (d) the insert image is a magnified view of the black box area of each panel. Panels (e) and (f) show magnified images of the white square regions in panels (c) and (d), respectively.

STEM imaging with EDS mapping along the wire was carried out on several of these NWs to check the presence of multilayers and their actual thicknesses. Based on previous examples, the Co and Fe distributions should be observed as the darker regions of the STEM image while those of the Cu should be seen at the brighter regions. However, as mentioned before, in most of the STEM images, clear evidence in the image of the presence of multilayers was not observed, except for the (50 / 50 nm) NWs. If evidence for such contrast was observed in some of the STEM images it was confirmed by performing EDS point analyses. However, the layers more often were unclear and the EDS line scans very noisy and impossible to detect in most cases. This could be due to the existence of alumina debris in all of the NWs, which causes charging, and image drift and blurring of the related EDS mapping.

Figure 5.6 (a) – (d) show two examples of STEM imaging with their related EDS profiles where the magnetic layers with different thicknesses could be resolved. Figure 5.6 (a) shows a STEM image of a NW with a dent shape. This dent shape was seen in this type of NWs but less frequently than in the (50 / 50 nm) NWs. This could be explained by the larger layer thickness such that errors associated with voltage switching during growth would have been less frequent.

An EDS map along a red line at the center of the same wire resolved peaks from Fe, Co and Cu, as shown in Figure 5.6 (b). The profiles are noisy, but Co and Fe peaks are clearly showing a thickness of 100 ± 10 nm for the magnetic layer. In the middle of the same layer, the Cu peak with a thickness of 50 ± 5 nm is feasible. In the EDS profiles there is an area with smaller thickness, which does not show Cu signal. A Cu signal will be observed in the magnetic layer as a result of its lower threshold voltage for deposition compared to that of magnetic layer.
Figure 5.6 (c) and (d) show another STEM image and the related EDS profiles. From the EDS profile, a large thickness of the magnetic layer, 200 ± 10 nm, with another 50 ± 10 nm thick Cu layer in a magnetic layer is observed. The EDS analysis confirms that the magnetic layers can be larger than 75 nm. However, a reproducible EDS profile with obvious magnetic non-magnetic layers could not be resolved.

We will confirm from EH analysis of these NWs in the next section that the actual layer thicknesses were 200 ± 10 for each magnetic layer and the expected value of 75 ± 10 nm for non-magnetic layers.
Figure 5.6. (a) and (c) are STEM images (acquired at 200 keV) of a CoFeB/Cu (200 / 75 nm) NW. (b) and (d) are plots of the integrated peak counts from energy dispersive spectroscopy along the axis of the same NWs in (a) and (b) (red line) from Co, Fe, and Cu spectra.

5.2.2. Magnetic characterization

Figure 5.7 (a) shows an example of a hologram (120 KeV) of this type of NW where the applied magnetic field is parallel to their axis. The MIP phase contribution and the magnetic phase of the reconstructed hologram are shown in Figure 5.7 (b) and (c), respectively. The MIP of the NW (Figure 5.7 (b)) has areas (like the one shown in the black box) with sharp contrast variation compared to neighbouring areas, which is an artifact. This is caused by phase unwrapping errors during the processing stage. A profile across the MIP phase of NW (Figure 5.7 (b)) clearly shows the effect of alumina debris, which affected the roundness of the NW expected to be symmetric in shape. However, in the areas with no clear alumina debris, the NW shape is cylindrical. The effect of unwrapping errors is to add unreal phase changes in the same area as MIP for magnetic phase (Figure 5.7 (c)). This unreal phase shift can lead to vortex-shaped magnetic contours or can create unreal deviations in magnetic contours. Another contrast change in the magnetic phase image is seen in the white box. This is a charging effect of alumina debris, which also can disturb the magnetic contour map of the NW.

The magnetic induction contour map of the same NW is shown in Figure 5.7 (d). The map clearly shows that the magnetization is along the axis of the NW. The average $B_z$ of the magnetic layers is $1.0 \pm 0.2$ T, based on its average thickness, $40 \pm 5$ nm, and a total phase shift, $1.85$ radian. Each contour represents a phase shift of $0.125$ radians, which is equivalent to $0.08$ T of $B_z$. The thickness of each magnetic layer is observed to be $200 \pm 10$ nm, larger than the expected value of 75 nm. This does not, however, change the expected magnetization. Given the large aspect ratio, we would expect that the magnetization would be along the wire axis after application of an external magnetic field in any direction. The non-magnetic layer ($75 \pm 10$ nm) shows a demagnetizing field effect as an unreal vortex shape, caused by the unwrapping artifact.

The acquired holograms and magnetic contour maps of two other wires of the same kind are shown in Figure 5.8 (a) – (d) (120 kV) for an applied external magnetic
field at an angle of 45 degrees with respect to the axis. In both cases, the magnetization inside the wires is uniform and follows the shape of the wire. However, in Figure 5.8 (b) $B_\perp$ contour map shows an asymmetric shape. This suggests that although the high aspect ratio of the magnetic layers forces the magnetization to be along the NW, the interaction between the layers or any magnetic crystallographic axis, with a slightly deviated angle with respect to NW axis, can cause small deviation in the magnetization of the magnetic layers. In the single Cu region of Figure 5.8 (b), the $B_\perp$ becomes weaker due to a demagnetization field from the magnetic layers, as expected. The contour line spacing is 0.08 T, giving a total average measured $B$ of $1.0 \pm 0.2$ T for the magnetic layers. The thickness of the magnetic layers in Figure 5.8 (c) and (d) was even larger such that the entire imaged section of this NW was composed of one magnetic layer with a $B_\perp$ as large as $1.5 \pm 0.25$ T (The magnetic contour line spacing is 0.14 T). The magnetostatic simulations in Figures 5.7(e) and 5.8 (e) show the induction vector map of a CoFeB/Cu (200 / 75 nm) nanowire, corresponding to the measured layer thicknesses, with axially magnetized layers.

As observed in the images of this type of NW, the alumina debris is around most parts of the NW. This debris is also all over the TEM grids and since they are not conductive, the electron beam can charge them up affecting the acquired hologram. Basically, the total effect of charging should be part of the MIP phase contribution, unless variations in the charging patterns form in two consecutive acquired holograms with $\pm$ tilts. In this case, the difference of the two charging patterns will appear in the magnetic phase contribution and, depending on its strength, can disturb the magnetic induction contour map. To correctly interpret the magnetic signal, one needs to separate the magnetic signal form this charging effect.
Figure 5.7. (a) Hologram image (acquired at 120 keV) with magnified holographic fringes, and (b) MIP phase contribution with a line profile across the NW along the white line. This phase image with associate profile shows the actual shape of the wire. (c) Magnetic phase contribution with a line profile along the same direction as the MIP phase contribution. This profile shows the total phase shift across the NW. (d) Contours of equal phase demonstrating the associated $B_\perp$ contour map (magnetic flux lines) of a CoFeB (200 nm) / Cu (75 nm) NW for a magnetic field applied parallel to the axis of the NW (the contour spacing are 0.08 T). These contours were generated from the magnetic phase image (b), The apparent vortex state in the nonmagnetic layer is not real, due to artifacts from image processing. (e) Magnetostatic simulation of the induction vector map of a CoFeB/Cu (200 / 75 nm) nanowire, corresponding to the measured layer thicknesses, with axially magnetized magnetic layers.
Figure 5.8. (a) and (c) Hologram images (acquired at 120 keV) and (b) and (d) magnetic contour maps of two examples of CoFeB (200 nm) / Cu (75 nm) NWs for an applied magnetic field with a 45 degree angle with respect to the axis of each wire. The contour spacings are 0.08 T and 0.14 T in (b) and (d) respectively. (e) Magnetostatic simulation of the $B_\perp$ vector map of a CoFeB/Cu (200 / 75 nm) nanowire, with axially magnetized magnetic layers.

Figures 5.9 (a) - (d) show the acquired hologram (spatial resolution of 12 nm and the electron beam voltage of 200 keV), MIP phase contribution, magnetic phase contribution and the $B_\perp$ contour map of a similar NW. Obvious from the hologram and its MIP, there are large regions of alumina debris in an area underneath and close to the NW. This can be a source of charging in the acquired holograms. Moreover, the NW itself also has a large alumina debris in the same region. By looking at the right side of the $B_\perp$ contour map (Figure 5.9 (d)) of the NW, one can see clearly that the magnetic contour lines are parallel to the axis of the NW (Figure 5.9 (d)). This is related to the phase change observed from the magnetic phase image (Figure 5.9 (c)). One would expect to see a demagnetizing effect in the magnetic contour map, right after the magnetic layers. The inner contour lines show the demagnetizing effect but the rest are deviating far from the NW. This can be explained by charging of alumina debris close to the NW, changing the overall phase image of the NW to a unreal $B_\perp$ map.
5.3. Bilayer NW (8 / 12 nm) Diameter 40 nm

5.3.1. Structural and morphological characterizations

Sodium hydroxide (NaOH) was used here to dissolve the alumina membrane and obtain individual NWs for magnetic measurement. Figure 5.10 (a) shows a STEM image of a section of a CoFeB/Cu (nominally 9 / 7 nm) NW followed by Figure 5.10 (b), where a BF image of the same NW is shown. A multilayer characteristic is obvious in some parts.
of both the BF and STEM images. It is also obvious that the alumina membrane was not removed completely with NaOH since there is alumina debris with a random shape and lower contrast in some areas around the NW. However, in some parts of the NW, there is an amorphous layer, which follows closely the shape of the NW, and has a very uniform thickness. This is likely an oxide layer that formed during or after removing the NWs from the alumina membrane.

The SADP shows a ring pattern like those observed in the other NWs, indicating that both the Cu (FCC) and CoFeB (BCC) regions were random polycrystalline materials.

Figure 5.10 (c) and (d) shows HRTEM images acquired from the areas 1 and 2 of the NW in Figure 5.10 (b), showing details of the crystallography and morphology of the NW. It is clear from these images that there is alumina debris present in some areas, with an average thickness smaller than was detected for the CoFeB/Cu (200 / 75 nm) NWs. Moreover, the areas with a considerable size of alumina debris were less frequent. As before, the areas without alumina debris showed an amorphous layer, which followed the shape of the NW, with an average thickness of 3 nm.

Ignoring the amorphous layers, the average bulk diameter of this NW was 40 ± 5 nm. The region outlined by the black box in Figure 5.10 (d) is shown magnified in the insert image in the corner. This shows that the typical roughness of the NW was 5 nm on average. The multilayer pattern of the NW can be seen in both figures 5.10 (c) and (d). Each layer is separated from the neighbouring layers by a narrow brighter interface. The region in the black box in Figure 5.10 (c), is magnified in the inserted image at the corner. The grains in each layer are randomly oriented with lattice fringe spacing proportional to the lattice constant of Cu (0.361 nm). In addition, small grains, 2 nm × 2 nm, were detected. A similar nanostructure was seen in every alternate layer. The copper layers showed a variation in thickness from 10 nm to 15 nm, twice as large as the nominal value of 7 nm.

The regions outlined by white boxes 1 and 2, in Figure 5.10 (c), show two other alternate layers, which have larger areas with lattice spacing proportional to the lattice
constant of CoFe alloy (0.28 nm). Box 1 includes the example of an area 7 nm × 7 nm which shows (100) lattice fringes of a CoFe alloy. The magnified view of the region in box 2 is shown in Figure 5.10 (e), where another large grain (7 nm × 7 nm) of a CoFe alloy is visible with (110) lattice fringes spacing of 0.2 nm. The CoFeB layers show a variation in their thickness from 7 nm to 9 nm, close to the predicted thickness of 9 nm. The average thickness of the interface between the layers is 2 nm.

Figure 5.10 (f) shows a magnified view of the region in the white box of Figure 5.10 (d). It shows the interface and a portion of each layer on either side. It is clear that both layers have randomly-oriented grains with different sizes. As mentioned before, the SADP of this NW showed the ring pattern of a nanocrystalline material. In the two NW types studied in the previous sections, one could index spots from individual grains by filtering the ring pattern from the dominant CoFeB layers. Here, it was hard to find the spot pattern related to any of the individual layers.

STEM imaging with EDS mapping along the NWs axis were carried out on several wires. Figure 5.11 (a) – (d) shows two examples where magnetic layers could be resolved. The NW in Figure 5.11 (a) has a relatively smooth surface and multilayers are clearly present. Note that not all the layers have the same thickness and orientation with respect to the axis of the NW. Some of them show a slight deviation from the axis and some show variations in their thickness across the NW in the same layer.

Figure 5.11 (b) shows an EDS map along a red line at the left corner of the same NW, which has resolved peaks from Co, Fe, and Cu. The Co and Fe peaks clearly demonstrate a thickness of 8 ± 2 nm for the magnetic layer, also seen in HRTEM images (Figure 5.10 (c-d)). The Cu signal followed the periodicity of the Fe and Co (valley for Cu where there was a peak for Fe or Co), with an average thickness of 12 ± 3 nm, larger than expected. The EDS profile in Figure 5.11 (b) is a typical profile seen in several NWs.

Figure 5.11 (c) and (d) show another STEM image and the related EDS profiles. We can see layers in some parts from the STEM image, which have a larger deviation away from the axis of the NW. From the EDS profile, a larger thickness for the Cu layers
was seen, $20 \pm 5$ nm, with a thickness of $8$ nm $\pm 2$ nm for the magnetic layer. The EDS analysis confirmed that the non-magnetic layers were larger than the 7 nm expected value. However, the magnetic layer had the expected thickness.
Figure 5.10. (a) STEM and (b) bright field TEM images (acquired at 200 keV) of a CoFeB/Cu (8 / 12 nm) multilayer nanowire. Images (c) and (d) show HRTEM images from the regions indicated as box 1 and 2 in panel (b), respectively. At the corner of panel (c), the black box area has been magnified to show randomly oriented Cu grains. Similarly, the black box in (d) is shown magnified in the corner image showing the typical roughness of the NWs. Panel (e) shows (110) lattice fringes of a CoFe alloy (average lattice constant 0.28 nm) (the 2 nm line shows 10 lattice fringes). Panel (f) shows randomly orientated Cu and CoFe grains.
Figure 5.11. (a) and (c) are STEM images (acquired at 200 keV) of a CoFeB/Cu (9 / 15 nm) NW. (b) and (d) are plots of the integrated peak counts from EDS along the axis of the same NW in (a) and (b) (red line) from Co, Fe, and Cu spectra.
5.3.2. Magnetic characterization

Figures 5.12 (a) - (d) show the acquired hologram (200 keV), MIP phase contribution, magnetic phase contribution, and the magnetic contour map, respectively, at zero fields, after a parallel applied magnetic field. The MIP image (Figure 5.12 (b)) shows the presence of alumina debris in some areas and artifacts related to the unwrapping errors. Sometimes there is a misalignment between some parts of two phase images producing a false contrast in the image. Such false contrast is seen, for example, in the upper part of the magnetic phase image (Figure 5.12 (c)). The line profile across the NW at this area did not show any magnetic signal while the bottom part showed a weak magnetic signal (Figure 5.12 (c)). For the part of the wire where the detection of magnetic signal was confirmed (bottom part of the NW), $B_\perp$ contour lines parallel to the axis of NW are observed (Figure 5.12 (d)). These lines can be interpreted to have been produced from a combination of all the layers along this part of the NW. However, these $B_\perp$ contour lines are concentrated in the middle of NW and no $B_\perp$ contour lines can be seen inside NW toward the edge of it. This could result from having out of plan induction at these parts of the NW [48]. Such geometry in NW layers is expected to produce a random remnant magnetization in the plane of the NW.

The magnetostatic simulation of the induction vector map of a CoFeB/Cu (8 / 12 nm) nanowire, in Figure 5.12 (e), corresponds to the measured layer thicknesses, with axially magnetized magnetic layers. The $B_\perp$ is mostly concentrated within the wire due to the proximity of the axially magnetized layers.

For a perpendicular applied magnetic field, no magnetic signal was detected, likely due to limited spatial resolution. Figure 5.13 (a) and (b) show a hologram and associated $B_\perp$ contour map from a similar NW with a perpendicular magnetic field applied. As it is clear from the $B_\perp$ contour map, no magnetic signal is visible in the NW area.
Figure 5.12. CoFeB/Cu (8 / 12 nm) multilayer NW for a magnetic field applied parallel to the axis: (a) Hologram image (acquired at 200 keV), (b) MIP phase contribution with a line profile across the NW along the white line. This phase image with the associate profile shows the actual shape of the wire. (c) Magnetic phase contribution with a line profile of the same line as the MIP phase contribution. This profile shows the total phase shift across the NW. (d) Contours of equal phase showing the associated $B_L$ contour map (magnetic flux line) (contour spacings 0.1 T) generated from the magnetic phase image (b). (e) Magnetostatic simulation of the induction vector map of a CoFeB/Cu (8 / 12 nm) NW, corresponding to the measured layer thicknesses, with axially magnetized magnetic layers.

Figure 5.13. CoFeB/Cu (9 / 15 nm) NW for an applied magnetic field perpendicular to the axis: (a) Hologram image (acquired at 200 keV) and (b) magnetic contour map (no magnetic contours are observed).

5.4. Trilayer NW (40 nm diameter)

5.4.1. Structural and morphological characterizations

The detection of a magnetic signal, if present, is limited by the resolution of the electron holography technique used to acquire the holograms. In this case, two microscopes with different resolutions were used. Figure 5.14 (a) and (b) show STEM and BF images of a typical CoFeB/Cu/CoFeB/Cu (nominally 9/3/9/50 nm) NW, extracted
from the alumina membrane. As was found in the case of the other NWs with the same method of preparation, NaOH could not always remove all of the alumina.

Figure 5.14 (c) and (d) show HRTEM images of the regions selected in box 1 and 2 in Figure 5.14 (b). They confirm that the alumina debris had a thickness comparable to that of the NW itself. The areas at the edge with no alumina debris have a thin amorphous layer with an average thickness of 3 nm to 5 nm. The average diameter of this NW was 40 ± 5 nm.

The two regions indicated by white boxes in Figure 5.14 (c) show areas with lattice fringes, parallel to the axis of the NW. Their spacing, 0.2 nm, is consistent with (110) CoFe alloy planes. The magnified view of area 2, Figure 5.14 (e), also clearly shows lattice fringes, 0.2 nm, in an area 10 nm × 7 nm. The region in the black square, Figure 5.14 (c), is magnified in the insert image shown in the corner. It shows Moiré fringes in an area belonging to the Cu layer. Similar to the previous NWs, randomly oriented grains with different sizes were observed in the Cu layers.

The two selected areas in Figure 5.14 (d), show fringes also with the same spacing (0.2 nm) either in one direction but not parallel to the axis of the NW (the black box is blown up at the corner) or existing in multiple randomly oriented directions (white box). The dominant type of lattice fringe observed for the magnetic layer was (110) CoFe alloy planes.

The SADP of the NW, after filtering the ring pattern, is shown in Figure 5.14 (f). The indexed spots are consistent with a (111) electron beam direction for a BBC structure. Therefore, [112] and [110] directions, perpendicular to the [111] direction, are in the plane of the NW. As a result, those areas with (110) lattice fringes along the axis of NW indicate that the (112) crystallographic orientation is predominantly along the axis of this NW.

It was difficult to observe contrast between CoFeB and Cu layers with STEM imaging perhaps due to presence of alumina debris and also the small thickness of the magnetic layers (Figure 5.14 (a)). Nevertheless, EDS mapping along the axis of NW was
carried out on several NWs and the presence of a tri-layer CoFeB/Cu/CoFeB was confirmed for some of them, as can be seen in Figures 5.15 (a - d).

Figure 5.15 (a) shows a STEM image of a NW with a clear contrast showing three layers on the top part of the wire. It can be seen that most of the contrast in the STEM image is coming from different thicknesses of the alumina debris around the nanowire. An EDS line scan was done along the red line and the corresponding profiles are shown in Figure 5.15 (b). These profiles indicate that there was an average tri-layer (CoFeB/Cu/CoFeB) thickness of $22 \pm 3$ nm, close to the predicted thickness of the tri-layer ($9+3+9 = 21$ nm). The layer interfaces are almost perpendicular to the axis of the NW and the average thickness of the magnetic layers within the tri-layer was $8 \pm 2$ nm.

A STEM image of another wire with clearer tri-layers is shown in Figure 5.15 (c). One sees that the tri-layers are not along the NW but make small angles to its axis. The EDS profiles of a line scan along the red line shows different tri-layer peak widths (Figure 5.15 (d)) compared to the NW of Figure 5.15 (b). The average peak width of the tri-layer was $30 \pm 3$ nm with larger thicknesses for both magnetic and nonmagnetic layers (for CoFeB layer the average thickness was $12 \pm 2$ nm).

Figure 5.15 (b) and (d) show the most commonly observed profiles for the tri-layers. However, there were cases with the same average thickness ($30 \pm 3$ nm) but different thicknesses for the magnetic layers.
Figure 5.14. (a) STEM image and (b) BF TEM image (acquired at 200 keV) of a CoFeB/Cu (nominally 9/3/9/50 nm) NW. (c) and (d) show HRTEM images of the regions of box 1 and 2 in (b), respectively. At the corner of (c) is a magnified view of the black box area. (e) shows (110) lattice fringes for a CoFe alloy with an average lattice constant of 0.28 nm (the 2 nm line shows 10 CoFe lattice fringes). The region of the black square is shown magnified in the insert image at the corner in (e). The same lattice fringes were observed in both selected regions in (d). (f) Selected area diffraction pattern of the same wire with the ring pattern filtered.
Figure 5.15. (a) and (c) are STEM images (acquired at 200 keV) of CoFeB / Cu NWs with average tri-layer thicknesses of $22 \pm 3$ nm (a) and $30 \pm 3$ nm (c). (b) and (d) are plots of the integrated peak counts from EDS along the axis of the same NW in (a) and (b) (red line) from Co, Fe, and Cu spectra.
5.4.2. Magnetic characterization

Several holograms of this NW type were acquired for both perpendicular and parallel applied magnetic fields. The magnetic phase images of most of the reconstructed holograms did not show any strong detectable magnetic signal. As confirmed by EDS profiles Figure 5.15 (b) and (c)), two types of the CoFeB (9 nm)/Cu (3 nm)/CoFeB (9 nm) tri-layers with average period of either 22 ± 3 nm or 30 ± 3 nm were observed. In both cases, magnetic interactions between the magnetic layers produced an overall in-plane magnetization that could be seen in the magnetic phase contribution.

A hologram of a portion of the NW in Figure 5.14 (b), the related MIP and magnetic phase contributions with its magnetic induction contour maps for an applied magnetic field parallel to the axis of NW, are shown in Figure 5.16 (a)-(d), respectively. There should be a remnant magnetization with random directions in each magnetic layer, when the parallel applied field is off, but this is not detected. Note that most of the $B_{\perp}$ contour lines in Figure 5.16 (d) are false due to reconstruction artifacts. The $B_{\perp}$ contour lines in the chosen area (black box), on the other hand, show a real magnetic signal and Figure 5.16 (c) shows its corresponding profile of phase change. The observed magnetic signal is related to a typical tri-layer (22 ± 3 nm), with a remnant magnetization at the same angle to the axis of the NW in both layers. The magnetostatic simulation of the induction $B_{\perp}$ vector map, Figure 5.16 (e), shows a CoFeB/Cu/CoFeB/Cu (8/6/8/50 nm) nanowire, with anti-parallel alignment for each set of tri-layers. The magnetization of both magnetic layers of the middle tri-layer is oriented at 30° relative to the wire axis.

Figure 5.17 (a) and (b) show a hologram (120 keV) and associated $B_{\perp}$ contour map from another NW of the same kind, in a perpendicular applied field. Note that there is no magnetic signal detection in Figure 5.17 (b). The visible $B_{\perp}$ contour lines are again reconstruction artifacts, except for a weak signal in the form of a magnetic vortex (in the boxed region). But one would expect to see opposing magnetization in the neighbouring magnetic layers because of the dipolar interactions. Based on the detection and size of the observed vortex (22 nm), the same as the typical thicknesses observed via EDS profiles), it can be concluded that this is in fact an opposing magnetization of the
neighbouring layers that looks like a vortex due to the limited spatial resolution of the microscope (7.5 nm). The profile of the magnetic phase variation of the observed vortex along the axis of the NW (Figure 5.17 (b)) confirms the opposing magnetization directions through the phase changes in the layers. The magnetostatic simulation of the induction vector map Figure 5.17 (c), shows a CoFeB/Cu/CoFeB/Cu (8/6/8/50 nm) NW, with the magnetizations of the two magnetic layers in a tri-layer anti-parallel, as expected for the strong dipolar coupling between these layers.
Figure 5.16. CoFeB/Cu/CoFeB/Cu multilayer NW (22 nm tri-layer thick) for a magnetic field applied parallel to the axis of the NW: (a) Hologram image (acquired at 200 keV) with the insert showing a magnified view of the holographic fringes, (b) MIP phase contribution with a line profile across the NW along the white line. This phase image with the associated profile shows the actual shape of the wire. (c) Magnetic phase contribution with a line profile of the same line as for the MIP phase contribution. This profile shows the total phase shift across the NW. (d) Contours of equal phase showing the associated $B_\perp$ contour map (magnetic flux line) (contour spacings 0.05 T). (e) Magnetostatic simulation of the induction vector map of a CoFeB/Cu/CoFeB/Cu (8/6/8/50 nm) NW. The magnetization of each set of tri-layers is anti-parallel, with an arbitrary azimuthal alignment.
Figure 5.17. CoFeB/Cu/CoFeB/Cu multilayer NW (22 nm tri-layer thick): (a) Hologram image (acquired at 120 keV) and (b) associated $B_{\perp}$ contour map for a perpendicular applied magnetic field with a phase profile related to the white box along the axis of the NW. The white box area shows an opposite orientation of magnetization in the neighbouring layers (an apparent magnetic vortex). (c) Magnetostatic simulation of the $B_{\perp}$ vector map of a CoFeB/Cu/CoFeB/Cu (8/6/8/50 nm) NW, with anti-parallel alignment for each set of tri-layers. The magnetization of both magnetic layers of the middle tri-layer is oriented at $30^\circ$ relative to the wire axis.

5.5. Discussion

In this Chapter, crystallographic and magnetic properties of isolated electrodeposited ferromagnetic multilayer NWs (CoFeB/Cu) were investigated, using off-axis EH and analytical STEM techniques. Based on selected area diffraction patterns,
both the Cu and CoFeB layers were nanocrystalline (FCC and BCC, respectively). There was no evidence that the CoFeB was amorphous as reported for Co$_{94}$Fe$_{5}$B$_{1}$ thin films and single composition NW arrays in [67]. The apparent contradiction between these results may be due to nucleation of crystalline magnetic alloy on the Cu layers, which are always crystalline, but nanocrystalline NWs were also seen for the single phase NWs made under similar conditions.

The thickness of individual layers in all of the NWs investigated by STEM and EH was often greater than what was estimated from the electrodeposition experimental conditions. In particular, when the layers were thinner than the NW diameter (45 nm), both Cu and CoFeB tended to be thicker than expected. For layer thicknesses larger than the diameter, the CoFeB layers tended to be thicker, while Cu grew at the expected rate. The NW surfaces were rougher and there was more evidence of alumina debris present when the template was dissolved in NaOH, than with phosphochromic acid.

Discrepancies between the measured and anticipated thicknesses are not too surprising considering that thickness predictions were based on a somewhat rough estimation assuming an electrodeposition efficiency of 70% for the magnetic metal and 100% for the non-magnetic metal, with an effective surface area of 10% of the membrane surface area. Such an approach had provided relatively good estimates on 170 nm (much larger than 40) pore diameter, but it might not be reliable for 40 nm pore diameter [67]. As shown in Ref. [67] the alloy grown with the same electrolyte in current-controlled electrodeposition yields a typical composition of Co$_{94}$Fe$_{5}$B$_{1}$, with a Co/Fe atomic ratio of 94/5 = 20. In pulse-potential electrodeposition, as used in this work (-1 V for CoFeB and -0.56 V for Cu), this ratio can change, notably because the current is not controlled.

The contribution of the dipolar interaction to the effective magnetic anisotropy of an individual multilayered NW can be quantified with a constant (the effective dipolar anisotropy constant, $K_{\text{eff}}$) as described by Eq. (1.2). The anisotropy constant can then be associated with an effective anisotropy field, $B_{\text{eff}} = 2K_{\text{eff}}/M_s$, Eq. (1.2) provides a general description of the effect of the saturation magnetization, $\mu_0M_s$, and of the thickness ratio of non-magnetic to magnetic layers, $t_N/t_{FM}$, on the effective dipolar anisotropy field in a
NW. For a small $t_N/t_{FM}$ ratio, the effective shape anisotropy is given by the shape of the entire NW, and therefore the NW tends to behave as a long cylindrical granular magnet with the parallel anisotropy of a long cylinder (shape of the nanowire). On the other end, for a large $t_N/t_{FM}$ ratio, the anisotropy is dominated by the shape of the individual magnets.

When magnetic structure in a magnetically isolated cylindrical magnet is dominated by shape anisotropy, different magnetization states could exist depending on the length/diameter ratio of the magnet. For a large length/diameter ratio, the magnetization tends to be parallel to the symmetry axis of the magnet. If this ratio is small (the case of a flat disk), the magnetization tends to be perpendicular to the symmetry axis. There is a crossover between these two trends where the shape anisotropy vanishes (a ratio on the order of 1) and the magnetization tends to be randomly oriented [36].

The off-axis EH technique was able to resolve magnetic volumes as small as $(10 \text{ nm})^3$ using a single biprism in a field-emission electron column at 120 keV. The measured magnetic induction of individual CoFeB layers ranged between 1.5 T and 0.5 T depending upon the thickness of the layer, which ranged between 250 nm and 50 nm. While a thin film of Co$_{94}$Fe$_5$B$_1$ electrodeposited in similar conditions on a gold-coated substrate has yielded a magnetization of 1.7 T [67], the magnetic layers here incorporated far less Co and a significant amount of Cu. The Co/Fe ratio from EDS analysis was 3/1.

For relatively thick magnetic layers compared with those of the Cu layers, the $B_{\perp}$ contour lines followed the shape of the NWs parallel to the axis of the NW with small demagnetization effects clearly evident in the Cu layers (75 nm). From Eq. (1.2), the threshold above, which an FM layer starts to be dominated by its self-demagnetizing field, is $t_{FM}/t_N < 2$. That is, in samples other than the second (CoFeB/Cu = 200/75), the FM layers are to be expected to experience stronger self-demagnetization fields than the “re-magnetizing” dipolar fields of the other layers.

For thinner layers, a deviation in the direction of the average magnetic induction of individual magnetic layers, away from exactly parallel to the axis, was indeed
observed. This is attributed to demagnetizing effects within the layers and due to the influence of magnetic neighbours. While the magnetic anisotropy appears to be dominated by the dipolar interaction, one cannot rule out other contributions. Notably, the observation of the off-axis remanence in the contour lines of the NWs magnetized by perpendicular fields, suggests a contribution to the total anisotropy from magnetocrystalline anisotropy.

Finally, it is important to emphasize that Eq. (1.2), which assumes a uniform magnetization in each layer, neglects the possibility of vortex or flower states in individual layers, as discussed in the introduction. In fact, it may come as a surprise to some that the effective anisotropy, estimated from Eq. (1.2), is independent of the ratio of the thickness to the diameter of each individual layer. That is due to the nature of the dipolar interaction, which is long range, and to the implicit assumption that the multilayered nanowire is significantly longer than it is wide (regardless of the ratio of individual layers). For the tri-layered samples, however, the situation is different. There, the strong dipolar coupling between the neighbouring magnetic layers leads to an antiparallel configuration of the pairs within a trilayer, effectively screening the long range dipolar field for the other sets of trilayers. For the smallest thickness layers (8/6/8 nm or 8/12 nm), magnetic signals associated with the interaction of neighbouring layers were detected.
Chapter 6.

Summary and future plans

6.1. Summary

6.1.1. Single layer CoFeB Nanowires

In Chapter 4, STEM, SAED, EDS, EFTEM and EH techniques were used to analyze the morphology and magnetic properties of individual CoFeB NWs with different diameters. The diffraction patterns obtained from the largest (170 nm) NWs indicated that these NWs were random nanocrystalline (FCC) rather than amorphous. The observed nanocrystallinity justified the assumption [7-8] that the magnetic anisotropy in macroscopic NW arrays was dominated by inter-wire dipolar interactions as well as shape anisotropy macroscopic NW arrays.

The efficiency of alumina removal by NaOH and phophochromic acid was also studied through STEM and EDS analysis. This showed that phophochromic acid can attack and further oxidize the NWs, while NaOH is less violent but also did not remove all of the alumina. Elemental mapping indicated that the Co and Fe were uniformly distributed in the wire, whereas O and Al were present on the surfaces of the wires. In addition, around the end of the wires, Co and O were observed together. The presence of O is mostly due to residual Al₂O₃ covering the wires but was also correlated with Co oxides.

Electron holograms acquired from individual NWs showed that the magnetization inside NWs with diameters from 20 nm to 200 nm was uniform over most of their length, except at their edges. Since the NWs consisted of soft magnetic nanocrystals, the magnetic anisotropy was likely dominated by the shape anisotropy. Numerical
simulations suggested that the stray fields at the top of the NWs were well reproduced by a truncated cone model, rather than a cylinder. The measured magnetic induction of NWs with a range of diameters larger than 30 nm was the same, to within experimental error, equal to \(1.6 \pm 0.3 \text{ T}\). The larger diameter NWs had a high remanence along the NWs axis, while for arrays of such wires, a very small remanence was observed [7-8]. This is in agreement with the assumption that the inter-wire dipolar interactions dominated the anisotropy in the arrays. For isolated wires, calculations [8] suggested that the NWs should be single domain, with magnetization oriented along the wire axis, which is what we observed.

### 6.1.2. CoFeB/Cu multilayer Nanowires

In Chapter 5, analytical STEM techniques and off-axis EH were used to study the morphology and magnetic properties of four types of isolated electrodeposited ferromagnetic multilayer NWs (nominally CoFeB/Cu) with a range of magnetic-nonmagnetic layer thicknesses. Diffraction patterns obtained from the NWs suggested that they were nanocrystalline rather than amorphous. STEM and EDS analysis showed that the CoFeB layer thicknesses were similar to the expected values, except for the one case with an aspect ratio (thickness to radius) larger than one. However, the analysis also showed that the Cu layers were thinner than expected for aspect ratios smaller than one. Overall, the measured average thicknesses of the examined NWs were 50/50 ± 5 nm, 150/75 ± 5 nm, 8/12 ± 3 nm, and 8/6/8/50 ± 3 nm.

The observed magnetization in the wires agreed with our expectations based on the aspect ratios (thickness to radius) of the individual magnetic layers and the dipolar fields of the other layers. The magnetization direction was predominantly parallel to the longer dimension of the magnetic volume, and was relatively uniform throughout the magnetic layer. However, depending upon the thicknesses of the layers, the behavior could differ.

For CoFeB/Cu (50/50 nm) NWs, the observed magnetization by EH was uniform and aligned either along the axis of the wire (when the applied external magnetic field was parallel to the wire axis), or at an angle to the axis (when the applied field had been
perpendicular to the axis). It is probable that a magnetocrystalline anisotropy would play a role in producing these remanent states. The NWs with the largest thicknesses of CoFeB/Cu (200/75 nm) showed a magnetic induction that followed the wire axis, independent of the angle of the external field, indicating that the dipolar field dominated in these circumstances.

Electron holography from thinner multilayers of CoFeB/Cu (8/12 nm) and CoFeB/Cu/CoFeB/Cu (8/6/8/50 nm) in NWs with 40 nm diameters did not provide a detectable magnetic signal. This is because the thickness of these layers was smaller, or of the same order of magnitude, as the spatial resolution of the EH technique. However, for both kinds of NWs, weak magnetic signals, associated with the combination of layers, was observed. For CoFeB/Cu/CoFeB/Cu (8/6/8/50 nm) NWs, a vortex-shaped magnetic signal was observed from a perpendicular applied magnetic field. This could have resulted from an out-of-plane induction at these layers in the NW. Considering that the dipolar effect from the other tri-layers was almost non-existent, the observed vortices should have formed within the tri-layers and from the expected opposing orientations of magnetization in the dipolar-coupled neighbouring layers. Instead, they behaved roughly like quadrupoles, with a much smaller interaction range. For CoFeB/Cu (8/12 nm) NWs, magnetic signal related to uniform magnetization along the axis of the NW was observed when the applied external magnetic field was parallel to the axis.

6.2. Future plans

6.2.1. Remanent hysteresis loop of FMNWs

In this thesis, the magnetic in-plane remanent state of individual magnetic NWs were depicted and calculated by using off-axis EH. However, EH can provide more insight about the interpretation of magnetic behavior of examined NWs through quantitative determination of the entire hysteresis loop for in-plane magnetization. The calculated remanent magnetization in this work was based on fully magnetizing the NWs by applying a large in-plane external magnetic field (objective lens fully on). The applied magnetic field was much larger than the coercive field. But, in order to have a remanent hysteresis loop from the examined NWs, the hologram acquisition method must be
modified. That is, instead of saturating the NW with a large applied magnetic field in both
tilted directions (to be able to subtract the influence of NW thickness, as explained in
chapter 3), it could be fully magnetized in one direction, then in the opposite direction, by
partially turning on the current of the objective lens, and the desired component of the
external magnetic field will be applied to the NW. This can be repeated for different
values of applied field in order to build up a remanent hysteresis loop [92]. From the
depicted hysteresis loop and magnetic induction maps acquired from different holograms
at different external magnetic fields, the mean corecivity of the NWs as well as their
reversal characteristics could be determined.

6.2.2. Electron Holography of arrays of NWs

The examined NWs in this thesis were fabricated initially in array structures so
that any suggested application had to deal with NW arrays. The macroscopic properties
of NW arrays are highly dependent upon the magnetic and morphological properties of
each individual NWs. Indeed, this was the motivation for studying individual NWs in this
thesis. However, the interaction between NWs over an entire array may lead to different
macroscopic magnetic properties of the arrays. By using electron holography on arrays
of NWs, the magnetic interaction between NWs can be shown through magnetic
induction maps of the arrays. Moreover, the final remanant state of the arrays as well as
their mean coercivity could be quantified by EH. While TEM sample preparation of
arrays within the alumina suitable for electron holography is feasible, the volume of
material that can be imaged in one hologram is not large. Therefore, careful overlap of
neighbouring holograms would need to be carried out.

There is also continuing improvements in the capabilities of electron microscopes
including those with aberration correctors. Besides using multiple biprisms to simplify
hologram analysis, using the correctors as a means to compare the phase from different
parts of the sample is beginning to be applied. Comparisons of these approaches with
the conventional biprism approach of this thesis will be an interesting new direction.
References


