

École polytechnique de Louvain

Spin-dependent thermoelectric phenomena in 3D interconnected nanowire networks

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Academic year 2018–2019

Master [120] in Physical Engineering

Abstract

This Master thesis investigates the spin-dependent thermoelectric properties of three-dimensional interconnected nanowire networks made of nickel-iron (Ni-Fe) alloys. Homogeneous and multilayered nanowires have been studied. Track-etched polymer membrane were used as template, allowing the filling of the crossed nanopores by electrodeposition from a single electrolyte bath. The connectivity between the nanowires allows the system to be self-supported and mechanically stable after the polymer template dissolution. Moreover, transport and magnetotransport measurements are easily performed in current-perpendicular-to-plane (CPP) configuration.

High values of giant magnetoresistance (GMR) of 20% at room temperature and 60% at 15 K for multilayered permalloy/copper (Py/Cu) crossed nanowires were measured, comparable with the values obtained on arrays of parallel nanowires. Furthermore, spin-dependent Seebeck coefficients have been determined based on magneto-Seebeck measurements on multilayered Py/Cu crossed nanowires, leading to a difference $S_{\uparrow} - S_{\downarrow}$ of $-12 \mu\text{V/K}$. Finally, the control of the Ni-Fe alloy composition allows to measure Seebeck coefficients up to $-46 \mu\text{V/K}$.

Keywords: Spin-dependent Seebeck, permalloy, giant magnetoresistance, nanowires

Acknowledgements

I would like to thank my supervisor, Professor Luc Piraux, for the opportunity to work on this interesting topic. He was always available when I needed advice and he showed strong considerations about this work. This was really motivating and helped developing my knowledges.

I am also extremely grateful to Tristan da Câmara Santa Clara Gomes for his time consideration and guidance in this work. His deep knowledge in the field, along with his perpetual desire to help in all considerations regarding this project, were immensely helpful to reach the objectives. The quality of this Master thesis would not have been the same without his precious help.

I want to warmly thank Flavio Abreu Araujo for his availability, support and advice. His experience in research significantly helps improving this Master thesis through several valuable discussions. I am grateful to Delphine Magnin for the training and support regarding SEM. I also want to thank Pascal Van Velthem for his assistance and availability. In a more general way, I want to warmly thank all the people involved in the lab for their kindness and considerations. This created a nice atmosphere during this Master thesis. It was a real pleasure to work in this lab and to know everyone.

Finally, I am grateful to my family and friends for their support during my studies. Notably, to my parents who gave me the opportunity to follow these studies and were always supporting and motivating me. I want to warmly thank my teammates at the lab, Shana Massar and Lancelot de Halleux, for their kindness and the great support we gave each other during this Master thesis.

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List of symbols

α	Spin asymmetry coefficient
β	Bulk spin asymmetry coefficient
Δ	Difference operator
δ	Domain wall thickness
θ	Angle between the magnetisation direction and the current flow
ϵ	Energy
ϵ_F	Fermi energy
Γ	Volume of matter
κ	Thermal conductivity
κ_{Cu}	Thermal conductivity of copper
κ_{Py}	Thermal conductivity of permalloy
λ	Ratio of the thicknesses of the multilayered stack
ϕ	Angle between two electrons' spin
Π	Peltier coefficient
ρ	Electrical resistivity
ρ_{av}	Average resistivity
ρ_{AP}	Electrical resistivity in antiparallel configuration
ρ_{Cu}	Electrical resistivity of copper
ρ_{Cu}^{RT}	Ideal resistivity of copper at room temperature
ρ_{IP}^{sat}	Electrical resistivity at saturated external field along in-plane direction
ρ_{OOP}^{sat}	Electrical resistivity at saturated external field along out-of-plane direction
ρ_P	Electrical resistivity in parallel configuration
ρ_P^0	Residual resistivity in parallel configuration
ρ_P^{RT}	Electrical resistivity in parallel configuration at room temperature
ρ_{Py}	Electrical resistivity of permalloy
ρ_{Py}^{RT}	Ideal resistivity of permalloy at room temperature
ρ_i	Ideal resistivity
ρ_{res}	Residual resistivity
$\rho_{ }$	Electrical resistivity when the magnetisation is parallel to the current
$\rho_{\perp}$	Electrical resistivity when the magnetisation is perpendicular to the current
$\rho_{\uparrow}$	Electrical resistivity contribution of majority electrons
$\rho_{\downarrow}$	Electrical resistivity contribution of minority electrons
ρ_0	Electrical resistivity of the demagnetised sample
σ	Electrical conductivity
$\sigma_{\uparrow}$	Electrical conductivity contribution of majority electrons
$\sigma_{\downarrow}$	Electrical conductivity contribution of minority electrons
μ_0	Vacuum permeability
μ_B	Bohr magneton
χ	Magnetic susceptibility

a	Lattice parameter
$\mathbf{B}$	Magnetic induction
d	Derivative operator
d	Pores diameter
E	Deposition potential
E_{ex}	Exchange energy
E_{a}	Anisotropy energy
E_{Z}	Zeeman energy
e	Electron charge
GMR^{IP}	Giant magnetoresistance with the external field applied in the in-plane direction
GMR^{OOP}	Giant magnetoresistance with the external field applied in the out-of-plane direction
$\mathbf{H}$	Magnetic field
H_{IP}	External field applied in the in-plane direction
H_{OOP}	External field applied in the out-of-plane direction
$H_{\text{max}}^{\text{IP}}$	External field applied in the in-plane direction at which the resistance is maximal
$H_{\text{max}}^{\text{OOP}}$	External field applied in the out-of-plane direction at which the resistance is maximal
H_{c}	Coercive field
$\mathbf{H}_{\text{d}}$	Demagnetising field
H_{eff}	Effective anisotropy field
$\mathbf{H}_{\text{i}}$	Internal magnetic field
$\hbar$	Reduced Planck constant
J	Exchange integral
K_{a}	Uniaxial anisotropy constant
L_0	Lorentz number
l_{sf}	Spin diffusion length
$\mathbf{M}$	Magnetisation
M^{n+}	Metallic ion with n electrons missing
M_{r}	Remanence magnetisation
M_{S}	Spontaneous magnetisation
M_{s}	Saturation magnetisation
$\mathbf{m}$	Magnetic moment
m_{e}	Electron mass
n_{w}	Weiss constant
$n_{\uparrow}$	Density of majority electrons
$n_{\downarrow}$	Density of minority electrons
$\mathcal{N}$	Demagnetising tensor
$\mathcal{N}_x, \mathcal{N}_y, \mathcal{N}_z$	Demagnetising factors
P	Porosity
PF_{AP}	Power factor in antiparallel configuration
PF_{P}	Power factor in parallel configuration
R	Resistance
R_0	Resistance in absence of external field
R_{AP}	Resistance in antiparallel configuration
R_{P}	Resistance in parallel configuration
R_{sat}	Resistance at saturated external field
S	Seebeck coefficient
S_{AP}	Seebeck coefficient in antiparallel configuration
S_{CIP}	Seebeck coefficient in current-in-plane measurement configuration

S_{CPP}	Seebeck coefficient in current-perpendicular-to-plane measurement configuration
S_{Cu}	Seebeck coefficient of copper
S_{P}	Seebeck coefficient in parallel configuration
S_{Py}	Seebeck coefficient of permalloy
$S_{\uparrow}$	Seebeck coefficient for majority electrons
$S_{\downarrow}$	Seebeck coefficient for minority electrons
T	Temperature
T_{C}	Curie temperature
t	Deposition time
t_{Cu}	Thickness of the copper layer
t_{FM}	Thickness of the ferromagnetic material layer
t_{NM}	Thickness of the normal metal material layer
t_{Py}	Thickness of the permalloy layer
V	Electrical potential
ZT	Thermoelectric figure of merit

List of acronyms

2D	Two-dimensional
3D	Three-dimensional
$\mu\Omega$	Micro Ohm (unit)
μm	Micrometer (unit)
μV	Micro Volt (unit)
Ω	Ohm (unit)
AGFM	Alternating gradient field magnetometer
AMR	Anisotropic magnetoresistance
AP	Antiparallel configuration of the multilayered stack
Ag	Silver
Ar	Argon
Au	Gold
bcc	Body centered cubic
BiTe	Bismuth telluride
CGS	"Centimeter, gramme, second" unit system
CIP	Current-in-plane
CNWs	Crossed nanowires
CPP	Current-perpendicular-to-plane
Co	Cobalt
cos	Cosine
Cr	Chromium
Cu	Copper
cm	Centimeter
DOS	Density of states
EDX	Energy-dispersive X-rays spectroscopy analysis system
FE-SEM	Field-emission scanning electron microscopy
Fe	Iron
FM	Ferromagnetic
fcc	face centered cubic
G	Gauss (unit)
hcp	Hexagonal close-packed
K	Kelvin (unit)
$\text{k}\Omega$	Kilo Ohm (unit)
kG	Kilo Gauss (unit)
kOe	Kilo Oersted (unit)
kV	Kilo Volt (unit)
IP	In-Plane
GMR	Giant magnetoresistance
ln	Natural logarithm

MR	Magnetoresistance
MPF	Magneto-power factor
MTP	Magnetothermopower
m	Meter (unit)
m Ω	Milli Ohm (unit)
mK	Milli Kelvin (unit)
mm	Millimeter (unit)
NaOH	Sodium hydroxide
Ni	Nickel
NM	Normal metal
NW	Nanowire
NWs	Nanowires
nm	Nanometer (unit)
nV	Nano Volt (unit)
Oe	Oersted (unit)
OOP	Out-Of-Plane
P	Parallel configuration of the multilayered stack
PC	Polycarbonate
PF	Power factor
PID	Proportional-integral-derivative
Py	Permalloy
pH	"Potentiel hydrogène" measuring the acidity
RRR	Residual resistivity ratio
RT	Room temperature
SI	International unit system
T	Tesla (unit)
UCLouvain	Université catholique de Louvain
V	Volt (unit)
W	Watt (unit)

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Introduction

This Master thesis lies in the field of nanoscience, more specifically in the study of complex three-dimensional crossed nanowires (CNWs). This system has recently led to exciting results at the Université catholique de Louvain (UCLouvain) in recent years [1–6]. At UCLouvain, the group of Pr. Luc Piraux is a pioneer in the fabrication and characterisation of various systems made of nanowires (NWs). The versatile "bottom-up" approach by electrodeposition grants access to a wide window of complex nanostructures. The control of the NWs morphology, composition and structural properties is easily done thanks to the different parameters of the fabrication process, namely the deposition potential or the angle of exposure of the membrane for nanopores creation. Moreover, the synthesis of such systems is cheap and easy to perform.

The control of the exposure angle of the membrane allows to vary the nanofibres orientation with respect to the normal of the polycarbonate (PC) membrane. This track-etched PC membrane offers high quality crossed nanopores with diameter of a few tens of nanometers. The growth from electrolyte baths containing the metallic ions allows to reach homogeneous NWs as well as multilayered ones [2, 7]. This "bottom-up" approach has been widely used by the group of Prof. Luc Piraux at UCLouvain, highlighting the interesting versatility of this method as well as the magnetic, magnetotransport and magnetothermoelectric properties of various systems [2, 4, 7, 8].

This thesis focuses on the fabrication and characterisation of nickel-iron (Ni-Fe) alloy NWs electrodeposited in the porous PC template. The work described here is in direct continuation of research performed in the group on magnetoresistance and magnetothermoelectric properties of magnetic NWs [4, 6, 7]. Indeed, the high interconnectivity of the CNWs is of great interest regarding electrical characterisation, namely compared to arrays of parallel NWs which require a small overfilling for the connections. Moreover, this interconnectivity makes the structure mechanically stable and easy to manipulate using a tweezer. On the other hand, multilayered electrodeposited CNWs can easily be characterised by current-perpendicular-to-plane (CPP) measurement configuration. This is of great interest regarding the magnetoresistance and magnetothermoelectric characterisations.

The objective of this thesis is to determine key spin-dependent thermoelectric properties of Ni-Fe alloys using the interconnected NW networks. Ni-Fe alloys exhibit interesting magnetoresistance [9] and thermoelectric [10] properties. The use of the interconnected system allows to measure them, confirming the interest of the CNWs. The experimental work of this thesis was split in two parts. The first one consists of the sample fabrication by growing high aspect-ratio NWs inside the porous PC template by electrodeposition. The second part includes both magnetoresistance and magnetothermoelectric characterisations of the samples. Only a small window of the possible structures achievable with

this approach have been investigated, with a limited range of material: various Ni-Fe homogeneous CNWs and multilayered permalloy/copper (Py/Cu) CNWs. In this thesis, the notation permalloy (Py) refers to Ni-Fe alloy with a Ni content around 85%. Other compositions of the alloy are explicitly specified.

This report displays a review of the work done during this Master thesis, the results obtained and their discussions. The first section is dedicated to the presentation of theoretical bases of magnetism, magnetotransport and spin-dependent thermoelectric properties of ferromagnetic (FM) materials. The impact of the nanoscale of the structure as well as the layering of the NWs is also shown. Then, an experimental part devoted to the manufacturing and characterisation of the interconnected NW networks is presented in the second section. The sample synthesis and morphologic characterisation followed by the magnetotransport and magnetothermoelectric characterisation techniques are also described. Finally, the results are presented, along with their analysis and discussions. This last section aims to prove the interest of the set-up used for spin-dependent thermoelectric properties determination, as well as for magnetoresistance measurements. To conclude, the main results are summarised and future perspectives for the CNWs system are outlined.

1 State of the art

This section is dedicated to the presentation of the theoretical background of the study. This Master thesis focuses on ferromagnetic materials. Therefore, general considerations about their magnetic properties will be provided, going from bulk materials to the case of three dimensional (3D) interconnected multilayered nanowire networks. Then, it will introduce the spintronics field through the different magnetotransport properties, namely in nanowire structures. Finally, the field of spin caloritronics will be outlined, emphasizing spin-dependent thermoelectric properties and the interest of 3D interconnected nanowire networks for their determination.

1.1 Magnetic properties

1.1.1 Bulk ferromagnetic materials

Each material exhibits a response under a magnetic field. This response is related to the magnetic moment $\mathbf{m}$. Some materials displayed such response even in absence of external magnetic field. This magnetic moment is given by [11]:

$$\mathbf{m} = \mathbf{M} \Gamma \quad [\text{A m}^2], \quad (1)$$

with Γ being the volume of matter by which the magnetic moment is carried and $\mathbf{M}$ the magnetisation. The latter is a mesoscopic average of the magnetic moment carried by the volume Γ . It arises from the combination of magnetic moments generated by electrons' spin and their orbital motion. The expression of the magnetisation is given by:

$$\mathbf{M} = \frac{d\mathbf{m}}{d\Gamma} \quad [\text{A m}^{-1}]. \quad (2)$$

A wide range of materials exhibits a random distribution of their magnetic moments in absence of external magnetic field, leading to no global magnetisation. On the other hand, some materials show a spontaneous magnetisation in absence of external magnetic field under a specific temperature: the Curie temperature T_C . Above this, the distribution of magnetic moments is randomised by thermal agitations. When a magnetic field, noted $\mathbf{H}$ is applied, the magnetic moments of the material will align with it and strengthen it.

The magnetic induction $\mathbf{B}$ is related to the external magnetic field $\mathbf{H}$ and the material magnetisation $\mathbf{M}$:

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) \quad [\text{T}], \quad (3)$$

with μ_0 being the vacuum permeability equal to $4\pi \cdot 10^{-7}$ [J A⁻² m⁻¹]. This holds using the international unit system (SI). Using the CGS (centimetre, gramme, second) unit system, Equation 3 reduces to:

$$\mathbf{B} = \mathbf{H} + 4\pi \mathbf{M} \quad [\text{G}]. \quad (4)$$

The conversion between the two systems is presented in Table 1. In this study, both systems will be used.

	SI system	CGS system	Conversion
H	A m ⁻¹	Oersted (Oe)	1 Oe = $\frac{10^3}{4\pi}$ Am ⁻¹
M	A m ⁻¹	emu cm ⁻³	1 emu cm ⁻³ = 10 ³ Am ⁻¹
B	Tesla (T)	Gauss (G)	1 G = 10 ⁻⁴ T

Table 1: Conversion between SI and CGS unit systems for the magnetic field, the magnetisation and the magnetic induction.

The enhancement of the magnetic field by a material is depicted by the magnetic susceptibility χ defined as:

$$\chi = \frac{M}{H} \quad [-]. \quad (5)$$

Ferromagnetic (FM) materials exhibit a high value of χ (up to 10⁴), while paramagnetic materials exhibit a low one (around 10⁻³). A negative value for the magnetic susceptibility means that the magnetic moments of the material align in the opposite direction of the external field. This is called diamagnetism. Typical FM materials are transition metals like nickel (Ni), iron (Fe) and cobalt (Co) as well as their alloys.

The alignment of the intrinsic magnetic moments in a FM material is related to the minimisation of the exchange energy. Assuming two atoms with their spin being S_i and S_j making an angle ϕ together, the exchange energy E_{ex} between these atoms is given by:

$$E_{\text{ex}} = -2JS_i \cdot S_j = -2JS^2 \cos(\phi) \quad [\text{J}], \quad (6)$$

with J being the exchange integral. If J is positive, the system tends to align its intrinsic magnetic moments and behaves thus like a FM material. Considering a solid with n atoms per unit cell with a lattice parameter a , the continuous expression of the exchange energy in the x direction is:

$$E_{\text{ex}} = -2\frac{n}{a}JS^2\frac{d\phi}{dx} \quad [\text{J}]. \quad (7)$$

The alignment of the spin magnetic moments minimises the global energy of the system. For FM materials, this behaviour depends on temperature. Indeed, above the Curie temperature T_C , the thermal agitations randomise the distribution of magnetic moments, leading to a paramagnetic behaviour of the system. Different values of T_C are given in

Table 2 for different FM materials. This research focuses mainly on Ni-Fe alloys presenting a high Curie temperature [12].

Material	T_C [K]
Fe	1044
Co	1388
Ni	628
Ni ₈₅ Fe ₁₅	816
Ni ₈₀ Fe ₂₀	872
Ni ₅₀ Fe ₅₀	816

Table 2: Curie temperatures of different transition metals and Ni-Fe alloys. Data from [11, 12].

This transition between the FM and the paramagnetic behaviour is also represented by the spontaneous magnetisation M_S falling to zero at the Curie temperature. The typical evolution of M_S with temperature is represented at Figure 1 for Ni.

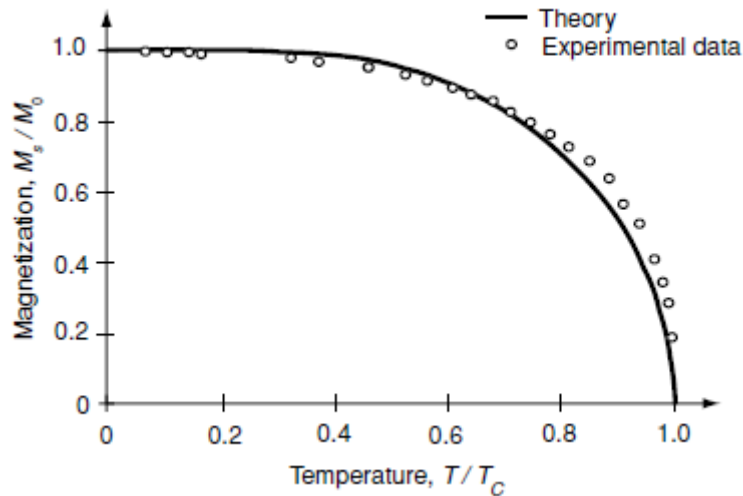


Figure 1: Evolution of the spontaneous magnetisation with temperature for Ni. The spontaneous magnetisation is normalised with respect to the one at 0 K, while temperature is normalised with respect to the Curie temperature. At $T = T_C$, M_S falls to zero and the system behaves like a paramagnetic material, showing no global alignment of its intrinsic magnetic moments due to thermal agitations. Figure from [11].

The FM behaviour originates from the density of states (DOS) and the imbalance in spin up and spin down electrons. Figure 2 represents the DOS of a typical transition metal and the one for a FM material. There is an overlap between the 4s band allowed to host 2 electrons on a large energy range, and the 3d band populated by at the most 10 electrons on a narrower energy range. For transition metals, the Fermi energy ϵ_F crosses the energy bands at the level of the peak of the 3d band. Thus, these materials exhibit a high DOS at the Fermi level [11].

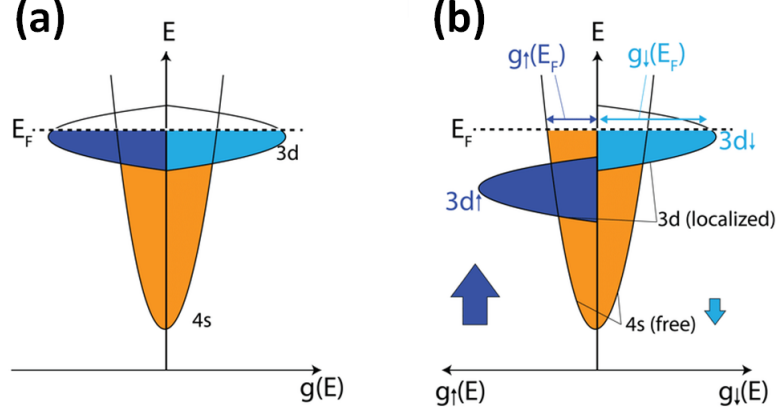


Figure 2: Schematic representation of the density of states for **(a)** a typical transition metal **(b)** a FM transition metal. Only the $3d$ and $4s$ bands are represented for simplicity. Both systems exhibits a high DOS at the Fermi level. The imbalance for the FM material is represented by a DOS for spin down electrons $g_\downarrow(E_F)$ higher than the one for spin up electrons $g_\uparrow(E_F)$. Figure from [13].

Moreover, considering a FM material, the DOS at the Fermi level exhibits an imbalance for spin down and spin up electrons in the $3d$ band. Below T_C , the $3d$ band splits spontaneously into a $3d_\uparrow$ band, populated by spin up electrons, and a $3d_\downarrow$ band populated by spin down electrons [11]. By convention, majority electrons are the spin up electrons, as depicted at Figure 2. The magnetisation of a FM material can be formulated thanks to density of majority (resp. minority) electrons $n_\uparrow$ (resp. $n_\downarrow$):

$$M = (n_\uparrow - n_\downarrow) \mu_B \quad [\text{emu cm}^{-3}], \quad (8)$$

with μ_B being the Bohr magneton that represents the intrinsic magnetic moment generated by the spin of the electron. The value of μ_B is given by:

$$\mu_B = \frac{e\hbar}{2m_e} \approx 9.274 \cdot 10^{-24} \quad [\text{A m}^2], \quad (9)$$

with e the charge of the electron, m_e the electron mass and $\hbar$ the reduced Planck constant.

The appearance of the imbalance between the spin up and spin down density of states occurs only if the Stoner criterion is respected. This is expressed as:

$$\mu_0 \mu_B^2 n_w g(\epsilon_F) > 1 \quad [-], \quad (10)$$

with $g(\epsilon_F)$ being the DOS at the Fermi level and n_w the Weiss constant that connects the

internal magnetic field $\mathbf{H}_i$ to the external field $\mathbf{H}$ and the magnetisation $\mathbf{M}$ by:

$$\mathbf{H}_i = n_w \mathbf{M} + \mathbf{H} \quad [\text{A m}^{-1}]. \quad (11)$$

The Stoner criterion is based on the divergence of the susceptibility χ of a metal, leading to the high value of χ for FM materials compared to paramagnetic ones [11]. Based on Equation 10, the behaviour of some transition metals can be understood. Indeed, a high DOS at the Fermi level is required to meet the Stoner criterion. Some transition metals, like Fe or Ni, exhibits a high DOS at the Fermi level thanks to the broad $3d$ band as depicted at Figure 2. The imbalance for transition metals are represented on Figure 3.

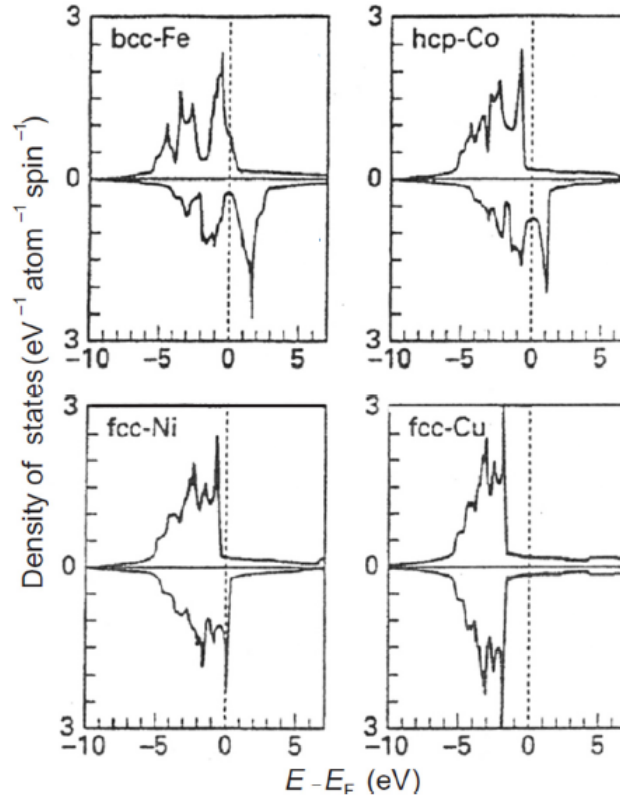


Figure 3: DOS of transition metals Fe, Co, Ni and Cu at their close packing that is stable at room temperature. The dashed line represents the Fermi level, highlighting the imbalance between spin up and spin down DOS for Fe, Co and Ni. The case of Cu exhibits no imbalance, explaining that copper is not FM. Figure adapted from [14].

Usually, FM materials exhibit anisotropic magnetic properties, meaning that there are preferred orientations for the magnetisation, called easy axis of magnetisation. At the contrary, hard axis correspond to orientations that are less favoured. The energy associated to a deviation θ of the magnetisation from the easy axis, considering that there is only one, is given by:

$$E_a = K_a \sin^2(\theta) \quad [\text{J m}^{-3}], \quad (12)$$

with K_a being the uniaxial anisotropy constant. The term uniaxial relates the existence

of only one easy axis.

Different origins can explain the global magnetic anisotropy of a material. A first contribution to anisotropy comes from the geometry, called the shape anisotropy. The impact of geometry on the internal magnetic field is related to the demagnetising field $\mathbf{H}_d$ and the external field $\mathbf{H}$ by:

$$\mathbf{H}_i = \mathbf{H} + \mathbf{H}_d \quad [\text{A m}^{-1}]. \quad (13)$$

In the general case, the demagnetising field is expressed as a function of the magnetisation of the material:

$$\mathbf{H}_d = -\mathcal{N} \mathbf{M} \quad [\text{A m}^{-1}], \quad (14)$$

with $\mathcal{N}$ a tensor linking the demagnetising field to the magnetisation. Written in the principal axes of the system, this tensor reduces to a diagonal one, whose values can be written as $\mathcal{N}_x$, $\mathcal{N}_y$ and $\mathcal{N}_z$ [11]. These coefficients are called demagnetising factors with unitary summation:

$$\mathcal{N}_x + \mathcal{N}_y + \mathcal{N}_z = 1 \quad [-]. \quad (15)$$

Typical values of $\mathcal{N}$ for different systems are represented at Table 3.

Geometry	Direction	$\mathcal{N}$
Sphere	All directions	1/3
Long wire	Along the wire	0
	Perpendicular to the wire	1/2
Thin film	Perpendicular to the plane	1
	Parallel to the plane	0

Table 3: Demagnetising factors of typical geometries. Data from [11].

To alter the magnetisation, the applied magnetic field must exceed the demagnetising field, meaning that the higher the demagnetising factor, the harder the axis.

Another contribution to the anisotropy comes from the crystal structure, called the magnetocrystalline anisotropy. Depending on the crystalline structure, the anisotropy is more pronounced. Figure 4 represents the magnetisation of single crystals of Fe, Ni and Co.

As explained earlier, this study focuses on Ni-Fe alloys, both components presenting cubic structure with low magnetocrystalline anisotropy, compared to the shape anisotropy due to the wire shape. Investigations of magnetic properties of Ni-Fe alloys show the vanishing magnetocrystalline anisotropy in a significant range of composition in the alloy, confirming the negligible contribution of this anisotropy [15]

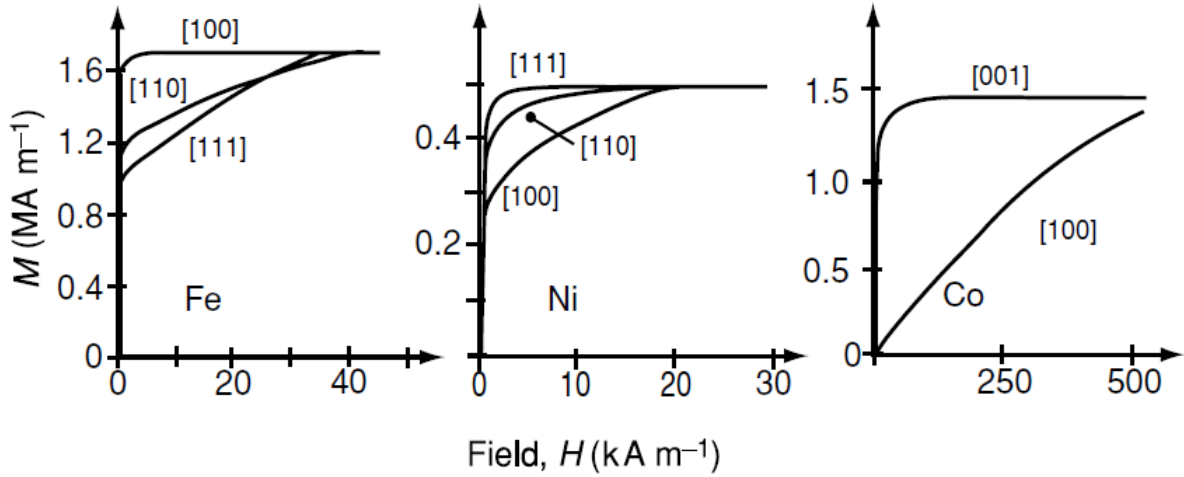


Figure 4: Magnetisation curves of single crystals of bcc-Fe, fcc-Ni and hcp-Co, highlighting the impact of the crystalline directions on the magnetisation. The hcp crystalline structure exhibits a higher magnetocrystalline anisotropy than the cubic structures. Figure from [11].

Several FM materials exhibit a global magnetic moment even in absence of external magnetic field. They are called permanent magnets presenting a "+" pole and a "-" pole. When magnets are interacting together, they tend to conciliate the "+" pole of one to the "-" pole of the other, decreasing the global energy. This is called the dipolar interaction as each permanent magnet can be seen as a dipole. The magnetostatic energy incorporates the dipolar interaction, the exchange energy and the shape anisotropy energy.

On the other hand, some FM materials are not permanent magnets. They are more stable without exhibiting any dipolar behaviour. Domain theory allows to understand how the magnetisation of these materials evolves. By dividing the material into several domains and assuming that each domain has its own magnetisation, it is possible to represent a global material presenting no dipolar configuration. This situation is schematically represented at Figure 5.

The interface between two magnetic domains are called domain walls. Neighbouring domains can have their magnetisations oriented in the opposite direction. This inversion takes place on a certain distance, called the domain wall thickness δ . It arises from the compromise between the exchange energy, tending the system to align its intrinsic magnetic moments, and the anisotropy, tending the magnetisation inside the material to follow the orientation of an easy axis. The representation of the rotation of the magnetisation along the domain wall thickness is depicted at Figure 6.

The rotation of the magnetisation can be in the plane, as represented at Figure 6, or within the plane of the domain wall. In the first case, domain walls are called Bloch walls, while the latter ones are called Néel walls. Bloch walls are the most common ones while Néel walls are only stable in films thinner than the wall width. Typical values of δ for FM materials stand in the nanometer range, but some materials exhibit orders of magnitude higher domain wall thickness (the value of δ for $\text{Ni}_{80}\text{Fe}_{20}$ is around $2 \mu\text{m}$) [11].

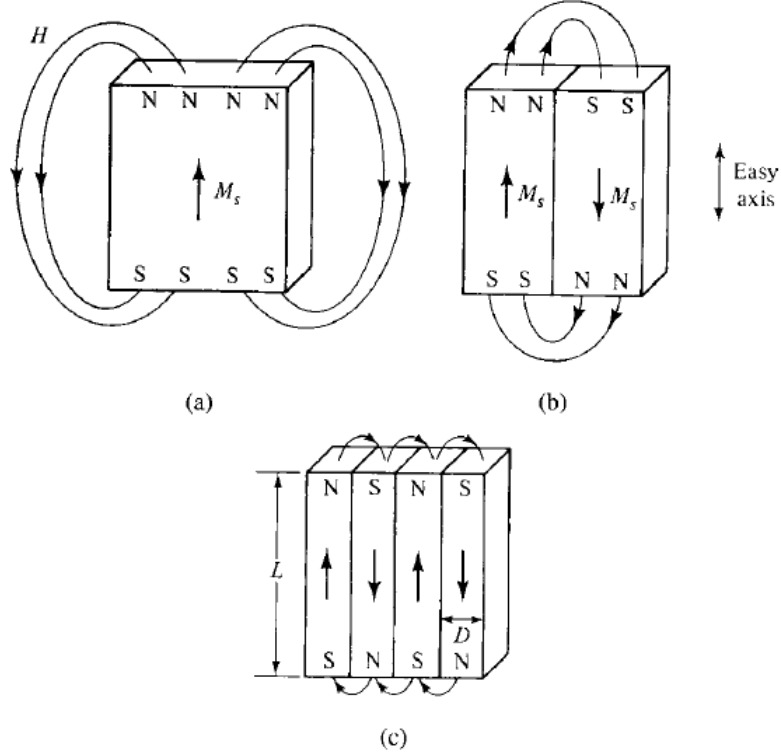


Figure 5: Schematic representation of the magnetisation for **(a)** a permanent magnet **(b)** a material with two magnetic domains, vanishing the global magnetisation and **(c)** a material with several magnetic domains, also vanishing the global magnetisation. Each magnetic domain is assumed to have its own magnetisation, allowing the system to exhibit no global magnetisation. Indeed, the magnetisation of the first domain $\mathbf{M}_1$ is oriented in the opposite direction of the one of the second domain $\mathbf{M}_2$, while exhibiting the same value of magnetisation. Figure from [16].

Considering a FM material divided in domains exhibiting no global magnetisation, the application of an external field $\mathbf{H}$ will force the magnetisation $\mathbf{M}$ to align with the external field. This is related to the minimisation of the Zeeman energy that is expressed by:

$$E_Z = -\mu_0 \mathbf{H} \cdot \mathbf{M} \quad [\text{J m}^{-3}], \quad (16)$$

which becomes for multidomain materials:

$$E_Z = -\mu_0 \int \mathbf{H} \cdot \mathbf{M} \quad [\text{J m}^{-3}], \quad (17)$$

with the integration made in all magnetisation directions inside the material. Domains tend to vanish when increasing the external magnetic field $\mathbf{H}$.

Let us consider a multidomain FM material exhibiting no global magnetisation in absence of external magnetic field. As $\mathbf{H}$ increases, the magnetic moments of each domain will progressively align with the external field, until the global magnetisation reaches a saturation M_s . When the external field disappears, the magnetisation does not fall down to zero but reaches a value called the remanence magnetisation M_r . This is due to the comeback

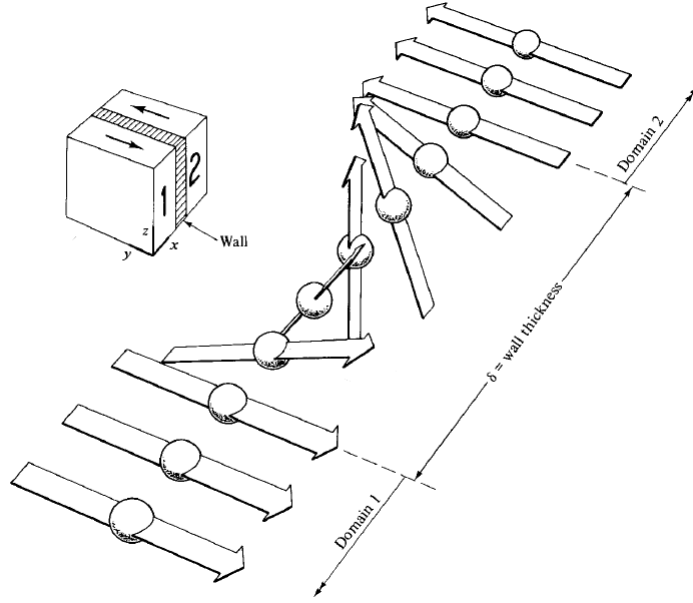


Figure 6: Schematic representation of the rotation of the magnetisation in a Bloch wall between anti-parallel domains. The rotation of the magnetic moment is in plane of the domain wall. Figure adapted from [16].

of the domains that keep in memory the impact of the previously applied external field. Their magnetisation directions preserve a part of the direction imposed by $\mathbf{H}$. To make the global magnetisation come back to zero, a field in the opposite direction, called the coercive field H_c , is required. Then, increasing the external field in this direction leads to a new saturation. Then, relaxing the applied field will again lead to a remanence before going back to zero. This is called the hysteresis loop and is depicted at Figure 7.

Looking more carefully at the phenomenon, when the external field increases, the domains with their magnetisation oriented in the easy axis the more opposed to $\mathbf{H}$ disappear the first. Indeed, the easy axis required less energy to modify the magnetisation in this direction compared to hard axis. Then, the material becomes monodomain with its magnetisation along the easy axis that is the closest to the direction of $\mathbf{H}$. At high external field, the global magnetisation rotates to finally align with $\mathbf{H}$. The behaviour described by Figure 7 can be separated in two cases: hard ferromagnet and soft one. The first type of FM materials exhibits a high remanence and requires a large coercive field to vanish the global magnetisation, leading to a square shaped hysteresis loop. The soft ferromagnets exhibit on the contrary low remanence and coercive field, leading to a thin hysteresis loop. Ni and Fe based alloys are soft ferromagnets, meaning that inverting their global magnetisation requires less energy [16].

1.1.2 Single nanowire system

This study is based on systems of crossed magnetic nanowires as the one represented in Figure 10. To understand the behaviour of such system, the first step is to understand the magnetic properties of different nanowire systems, increasing the complexity and interactions between the nanowires.

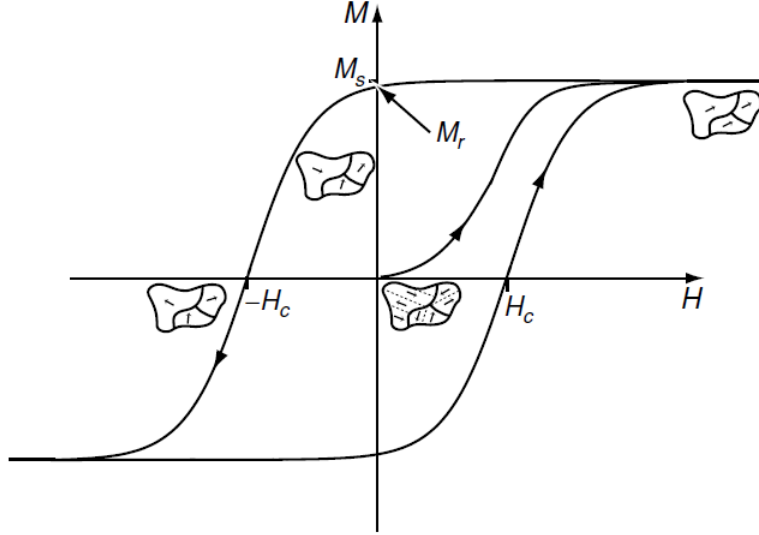


Figure 7: Hysteresis loop of an initially unmagnetised multidomain FM material. The first magnetisation step, going from zero magnetisation to saturation, is followed by the loop going from saturation in one direction to saturation in the opposite direction. When the magnetisation at saturation M_s is reached, the material is monodomain with the magnetisation oriented in the same direction as $\mathbf{H}$. When relaxing the external field, multidomain behaviour appears but the magnetic moments still keep in memory the previous saturation orientation, leading to remanence M_r . Figure from [11].

An important parameter that modifies the behaviour of such system is the nanometer scale of the dimensions. Indeed, decreasing the size of the system also reduces the number of magnetic domains. At a certain limit, the system can be considered as monodomain: one dimension of the system being at the same order as the domain wall size, the single domain state becomes the most stable. Due to the nanometer size of the diameter of the NWs, the structure can be seen as monodomain. On the other hand, magnetic domains can appear along the wire. Shape anisotropy allows to have the magnetisation of the FM NWs aligned with their axis in absence of magnetic field. In terms of energy, as monodomain means uniform magnetisation, only two terms enter the game: the Zeeman energy, aligning the magnetisation with the external field, and the uniaxial anisotropy energy arising mainly from shape anisotropy, but other contributions as magnetocrystalline anisotropy could influence. Equations 16 and 12 of Subsection 1.1.1 respectively represent the Zeeman energy and the uniaxial anisotropy energy.

The first case to analyse is the single FM NW. As explained in the Subsection 1.1.1, the shape of the NW induces shape anisotropy, with the easy axis oriented along the wire (see Table 3 for values of demagnetising factors of the long wire shape). Considering a single FM monodomain NW in absence of external magnetic field, the magnetisation is oriented along the NW axis direction. If the external field is applied along the NW, the magnetisation is not affected as all domains have their magnetic moment already oriented in the NW axis. When the external field is reversed in direction, nothing happens until a sufficiently high field is applied to allow the Zeeman energy to exceed the anisotropy energy. The magnetisation is oriented in the opposite direction from the original state.

Therefore, the hysteresis loop of a single monodomain FM NW will be a perfect square. If the external field is applied in a perpendicular direction to the NW axis, the story changes: the required external magnetic field to align the magnetic moments perpendicular to the NW axis is higher. Moreover, when the external magnetic field is relaxed, the magnetisation aligns with the NW axis, being the easy axis due to shape anisotropy. The behaviour of the NW in this direction exhibits no hysteresis loop [17].

1.1.3 Array of parallel nanowires system

One step further towards the system represented in Figure 8 is to consider an array of parallel magnetic nanowires. The comparison of the hysteresis loop for a single NW and an array of parallel NWs is depicted at Figure 8.

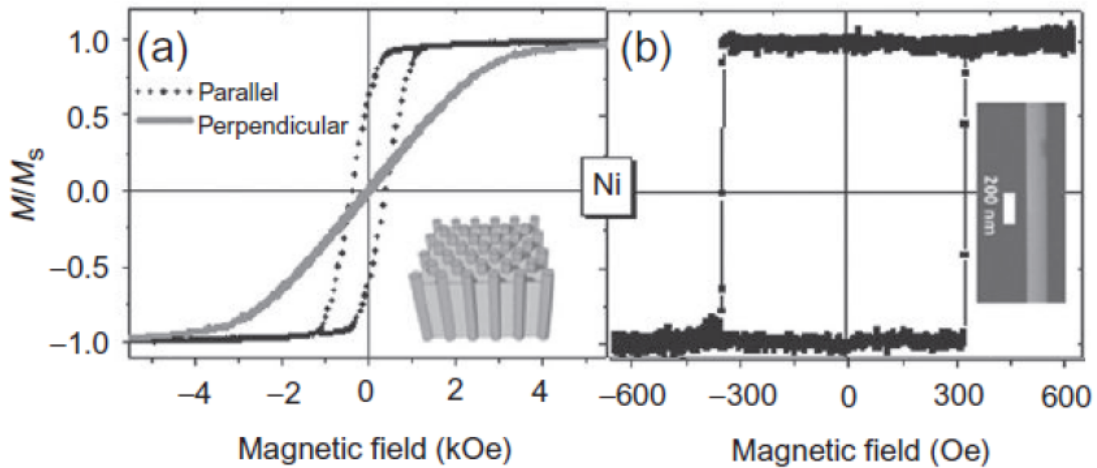


Figure 8: Comparison between the hysteresis loop for (a) an array of parallel Ni nanowires and (b) a single Ni nanowire. The square shape for the single nanowire is "softened" in an array of parallel nanowires, due to dipolar interaction between them. Figure from [17].

The transition from the saturated state in one direction to the opposite direction is less abrupt for the array of parallel nanowires. All NWs do not reverse their magnetisation at the same time and they interact with each other. Indeed, each of them can be seen as a dipole interacting with other neighbouring dipoles. When the external field is relaxed, the remanence is reduced compared to the single magnetic nanowire. In absence of external magnetic field, each dipole will tend to promote an anti-parallel configuration with neighbouring dipoles. Therefore, the remanence is smaller than the magnetisation at saturation because some NWs will flip their magnetic moments when the external field goes to zero.

The dipolar interaction between neighbouring NWs can be represented by a dipolar interaction field H_d . Its direction is perpendicular to the NWs axis, opposed to the demagnetising field of the NWs. If the interaction between NWs is sufficiently high, the magnetisation can exhibit a component perpendicular to the NW axis, namely due to the precession of

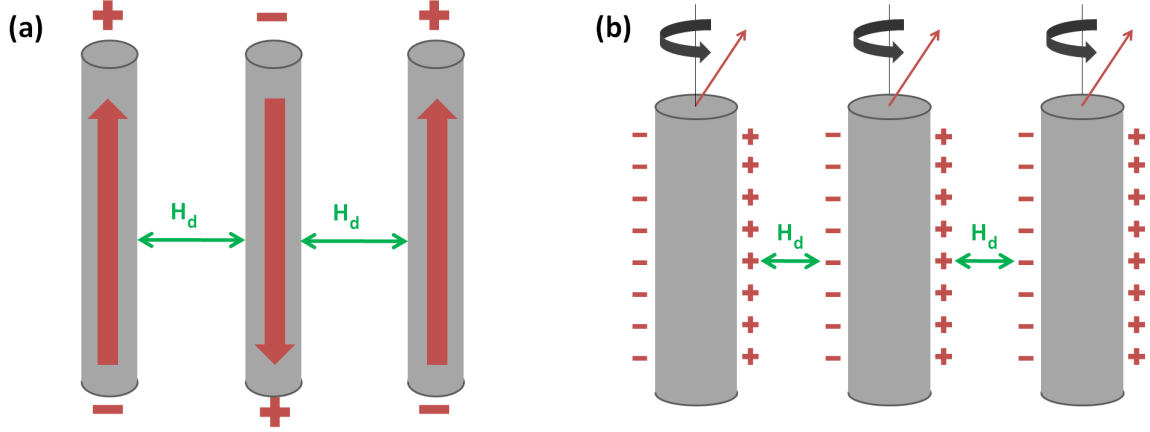


Figure 9: Schematic representation of the dipolar coupling for **a)** an array of elongated parallel magnetic NWs with their magnetisation oriented along the wire axis and **b)** an array of thicker parallel magnetic NWs. The aspect ratio of the NWs influences the behaviour of the magnetisation that can precess around the easy axis, leading to a component of the magnetisation perpendicular to the NW axis.

the magnetisation around the easy axis. The impact of the aspect ratio on the interaction and magnetisation is represented in Figure 9 .

To estimate the impact of the different anisotropies of a system on its free energy, the effective anisotropy field H_{eff} is used. It contains, in the most general case for isolated particles, contributions from magnetocrystalline, shape and/or other possible anisotropy(ies). Considering an array of parallel magnetic NWs with negligible magnetocrystalline anisotropy, the main contribution to H_{eff} is shape anisotropy at room temperature [9]. Therefore, the effective field is purely magnetostatic and can be expressed as a function of the saturation magnetisation M_s of and the porosity P of the system [18]:

$$H_{\text{eff}} = 2\pi M_s(1 - 3P) \quad [\text{A m}^{-1}]. \quad (18)$$

The impact of porosity reduces the effective field due to the increasing dipolar interaction between the NWs. Indeed, increasing porosity reduces the distance between the nanowires which improves their interaction. Two limiting cases can be observed: when $P \rightarrow 0$, the system tends to a single nanowire while $P \rightarrow 1$ leads to a system similar to a film.

1.1.4 Interconnected nanowire network

The system studied in this thesis is represented in Figure 10. It consists in an interconnected NW network forming a macroscopic film. Such systems are fabricated by electrodeposition into polycarbonate (PC) template exhibiting crossed nanochannels (see Subsection 2.1.2 for details).

In comparison with the previous case, the NWs exhibit an angle of 25° with respect to the normal of the template, along four azimuthal angles of 90° (see Subsection 2.1.1 for

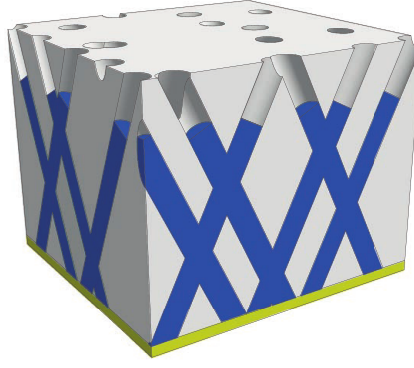


Figure 10: Schematic representation of the 3D interconnected NW network filling the PC template. The grey part represents the porous PC template, while the blue part represent the electrodeposited NWs filling the pores. The metallic cathode from which the NWs were grown is also depicted by the green part at the bottom of the structure. Image from [5].

details). Shape anisotropy forces the NWs to have their magnetisation oriented along their axis. Therefore, the easy axis of each NW is oriented with an angle of 25° with respect to the normal of the template. On the other hand, the hysteresis loop of homogeneous crossed nanowires (CNWs) of Ni and Fe were investigated [19]. The global behaviour of the hysteresis loop exhibits an easy axis in the out-of-plane (OOP) direction, when the external field is applied in the NWs axis direction.

The interconnections increase the complexity of the analysis of the magnetic behaviour. Indeed, the shape and volume is different for each connection inside the CNWs network. Therefore, there is a distribution of shape and volume for the interconnections which makes the modelling of their magnetic behaviour really hard. Some can act like domain walls while others can exhibit a rotation of the magnetisation. On the other hand, the small volume fraction of these interconnections reduces their contribution to the magnetic behaviour compared to the NWs, as highlighted by static magnetic characterisation of Ni and Fe CNWs [19]. The domain walls on a single NW have already been found to exhibit complex magnetic structures [20–22].

1.1.5 Multilayered nanowire network

In addition to the system represented in Figure 10, multilayered nanowires were investigated. To ease the analysis, only the magnetic behaviour of single multilayered nanowire will be presented. The schematic representation of the multilayered CNWS is depicted at Figure 11.

The stack consists in a succession of FM material layers followed by normal metal (NM) layers. The NM exhibits no FM behaviour when a magnetic field is applied. Therefore, compared to the systems previously presented, other considerations must be taken into account. These are based on the thickness of the FM layers and also the one of the NM layers. A schematic representation of a multilayered NW is depicted at Figure 12.

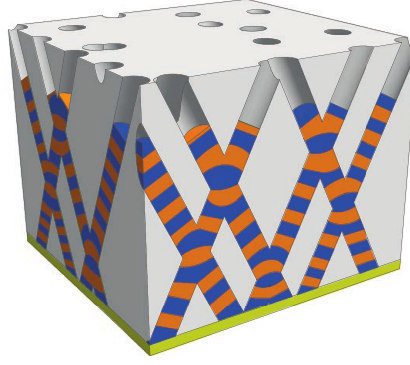


Figure 11: Schematic representation of the 3D PC with crossed nanochannels template filled with interconnected multilayered NWs. Figure from [4].

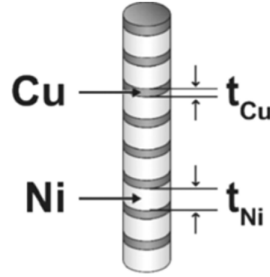


Figure 12: Schematic representation a multilayered NW made of a stack of Ni and Cu layers. The Ni (resp. Cu) layers thickness is noted t_{Ni} (resp. t_{Cu}). Image from [23].

Considering only one layer made of a FM material, the easy axis for each layer can be different depending on its thickness. Indeed, considering large value of the FM thickness t_{FM} , compared to the layer diameter, the layer can be seen as cylinder. Therefore, the easy axis of the layer is oriented along the wire axis. On the other hand, a low value of t_{FM} leads to a thin disk whose diameter is higher than its height. In this case, the easy axis is perpendicular to the NW axis.

Considering now a multilayered NW as the one depicted in Figure 12, the FM layers magnetisation is also influenced by the NM layer thickness. Indeed, the FM layers can interact by dipolar coupling, as presented for the arrays of parallel NWs (see Subsection 1.1.3). This interaction is controlled by the NM layer thickness t_{NM} . Indeed, large values of t_{NM} allows to considered the FM layers as decoupled. Their magnetisation is therefore mainly influenced by the aspect ratio of the FM layers. At lower NM layer thickness, the dipolar interaction between successive FM layers tends to lower the rate at which the FM layer aspect ratio dictates the easy axis of magnetisation [18]. Hence, even if the FM layers exhibit a geometry close to the one of thin disks, the easy axis can be oriented in the direction perpendicular to the layers stack if the NM layer thickness is small. Figure 13 represents hysteresis loops for different multilayered nanowire system made of CoCu/Cu

stack [18].

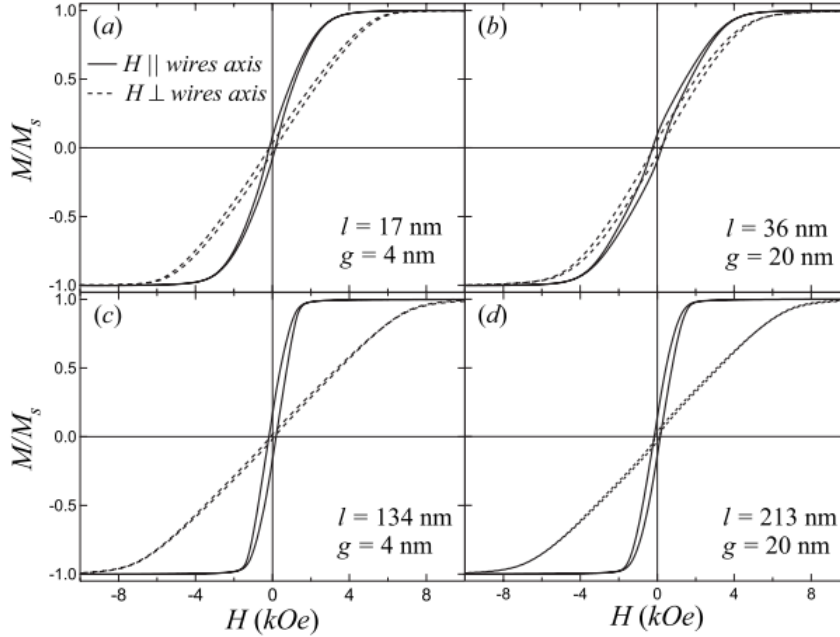


Figure 13: Hysteresis loops of multilayered CoCu/Cu systems with different thicknesses for the layers **(a)** CoCu(17 nm)/Cu(4nm), **(b)** CoCu(36 nm)/Cu(20nm), **(c)** CoCu(134 nm)/Cu(4nm) and **(d)** CoCu(213 nm)/Cu(20nm). The diameter of the pores are 140 nm. The thickness of CoCu (resp. Cu) layers is depicted by the notation l (resp. g). Image from [18].

Comparing Figures 13 (a) and (c), or (b) and (d) together, the impact of the thickness of the FM layer on the magnetisation curve appears. When the field is applied in the direction of the NW axis, the saturation magnetisation is reached a lower field for the system with larger FM layers. This confirms the enhancement of the easy axis of the NW by the cylinder shape of the FM layers. On the other hand, the direction perpendicular to the NW axis becomes harder for the larger FM layers, confirming the ease of the direction perpendicular to the NW axis for thinner FM layers.

Moreover, the curves presented in Figure 13 allow also to see the impact of the NM layer thickness. Indeed, Figure 13(a) exhibits an easy direction oriented along the NWs axis, even though the geometry of the FM layers is close to the one of thin disk. The diameter of the NWs is almost 10 times larger than the FM layer thickness. This arises from the dipolar coupling between adjacent FM layers, forcing the successive magnetisations to follow a head-to-tail configuration, leading to an easy axis oriented along the NW axis. This can be understood by the evolution of the effective anisotropy field with respect to the NM and FM layers aspect ratios. This is depicted in Figure 14.

The smaller the aspect ratio of the NM layer, the smaller the aspect ratio of the FM layer must be to make the transition between an easy direction along the NW axis and perpendicular to it. This explains this lower rate of transition between the easy directions

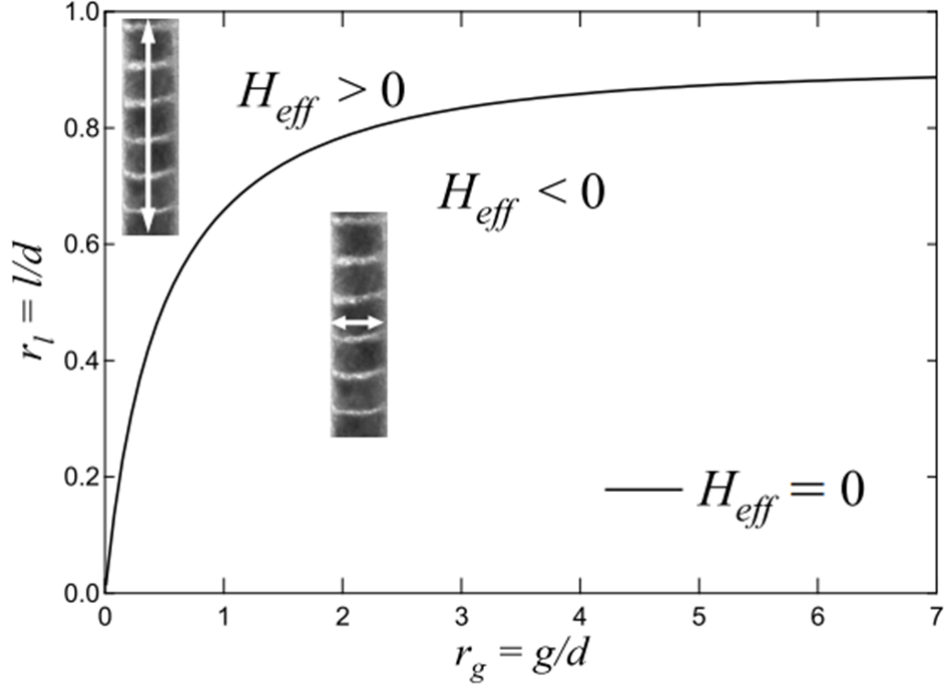


Figure 14: Anisotropy diagram as a function of the aspect ratio of the FM ($r_l = l/d$) and the NM layer ($r_g = g/d$) aspect ratios, d being the diameter of the NWs. The continuous line represents the values of r_l and r_g for which the effective anisotropy field H_{eff} is zero. The magnetisation direction depending on the sign of H_{eff} is provided. Figure from [18].

for the multilayered structure when the NM layers thickness decreases. The systems studied in this thesis exhibit a low aspect ratio as the one presented in Figure 13.

1.2 Magnetotransport properties

The transport of electrical charge is influenced by the presence of external magnetic field. This is called the magnetoresistance (MR) effect. Different sources of MR exist, depending on the system through which the current flows. Two different effects are presented in this section, spotlighting the case of NWs systems.

1.2.1 Anisotropic magnetoresistance effect

Considering a bulk ferromagnetic material carrying an electrical current, its resistivity is influenced by the relative orientation between its magnetisation and the current flow direction. This relative orientation is represented by the angle θ . Assuming the magnetisation to be saturated, $\rho_{\parallel}$ (resp. $\rho_{\perp}$) denotes the resistivity state corresponding to $\mathbf{M} \parallel$ (resp. $\perp$) to the current flow. In general cases, $\rho_{\parallel}$ corresponds to the highest resistivity state, while $\rho_{\perp}$ corresponds to the lowest one. The resistivity can be expressed as a function of these two states and the angle θ as :

$$\rho(\theta) = \rho_{\perp} + (\rho_{\parallel} - \rho_{\perp}) \cos^2 \theta \quad [\Omega\text{m}]. \quad (19)$$

The oscillating behaviour of ρ is represented in Figure 15, with a schematic representation of the two limiting cases when $\theta = 0^\circ$ and $\theta = 90^\circ$.

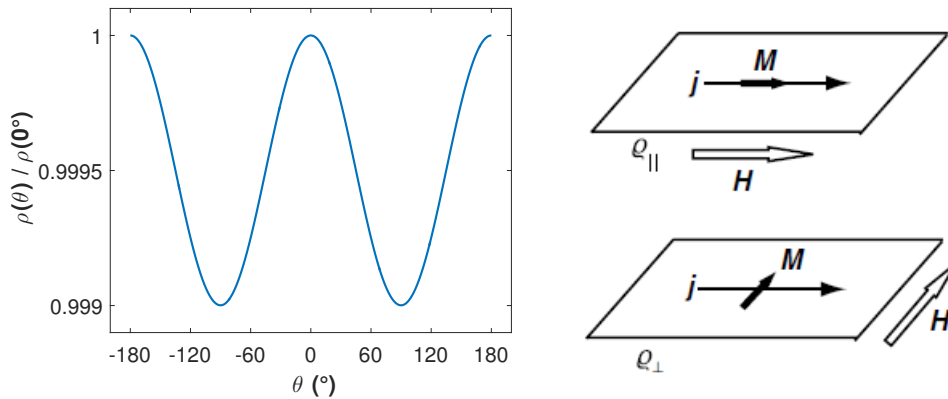


Figure 15: Dependence of the resistivity on the relative orientation between the magnetisation and the current flow. This evolution follows a squared cosine of the angle θ , oscillating between the high resistivity state $\rho_{\parallel}$ and the low resistivity state $\rho_{\perp}$. Right figure from [11].

This effect is due to a higher scattering probability of the electrons from 4s to 3d band when the magnetisation is parallel to the current flow. Considering a bulk material in absence of external magnetic field, the sample is broken into multiple domains, each exhibiting a specific angle with the current flow. Therefore, the global resistivity state stands between $\rho_{\parallel}$ and $\rho_{\perp}$, as depicted in Figure 16.

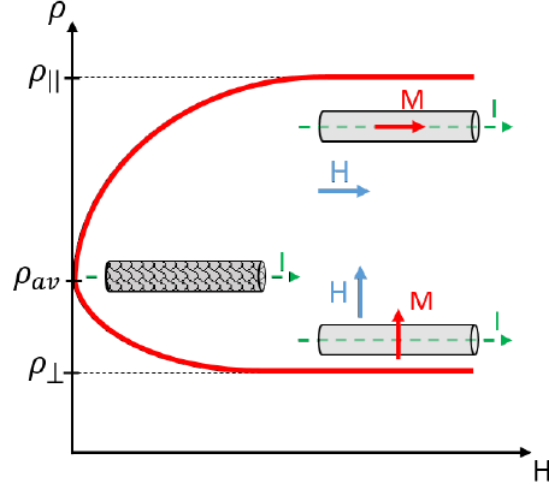


Figure 16: Representation of the different resistivity states of a bulk FM material. The higher resistivity $\rho_{||}$ is reached when the magnetisation and the current flow are parallel, while the lower resistivity $\rho_{\perp}$ is reached when these are perpendicular. The resistivity of the demagnetised sample is approximated by ρ_{av} . Figure adapted from [24].

When the sample is demagnetised, the resistivity is denoted by ρ_0 . The usual approximation is to average the two limiting cases $\rho_{||}$ and $\rho_{\perp}$, denoted ρ_{av} :

$$\rho_{av} = \frac{1}{3}\rho_{||} + \frac{2}{3}\rho_{\perp} \quad [\Omega\text{m}]. \quad (20)$$

This definition of ρ_{av} corresponds to an average taken by the number of possible directions in space for the parallel (only one direction) and the perpendicular (two possible directions) state for the resistivity. The AMR ratio is defined as [25]:

$$\text{AMR} = 100 \frac{\rho_{||} - \rho_{\perp}}{\rho_{av}} \quad [\%]. \quad (21)$$

This ratio may depend on temperature, typically increasing when temperature is decreased [25]. Generally, the AMR ratio is positive and at the order of 1% for pure ferromagnetic metals as Ni, Fe or Co. However, some alloys even reach values of 20% for binary alloys at 14 K [25]. Note that some diluted FM alloys exhibit slightly negative values of the AMR ratio [26]. Values of AMR ratio for different materials are presented in Table 4.

Nanowire systems exhibit some interest regarding the AMR effect, as the current direction is imposed by the geometry of the system. Therefore, in absence of external field, an array of parallel NWs exhibits a resistivity equal to $\rho_{||}$ as both magnetisation and current flow are oriented along the NWs axis. Applying a magnetic field in the direction perpendicular to the NWs axis pushes their magnetisation to be perpendicular to the current flow. This leads to the lower resistivity state $\rho_{\perp}$ when all the NWs have reached their saturation magnetisation in the direction of the external field. This is depicted in Figure 17.

The impact of forcing the magnetisation to be perpendicular to the NWs axis is observable thanks to the decrease of resistance when $\mathbf{H}$ is increased. The resistance seems unchanged when the external field is applied along the NWs axis, but a small decrease can be observed

Material	Temperature [K]	AMR ratio [%]	Reference
Ni	RT	2.02	[27]
	77	3.25	[27]
Fe	RT	0.2	[28]
	77	0.3	[29]
Ni ₈₃ Fe ₁₇	RT	4.3	[25]
	77	14.4	[25]
	4.2	16.4	[25]
Ni ₇₀ Fe ₃₀	RT	2.5	[30]
	20	14.5	[30]
Ni ₅₅ Fe ₄₅	20	3	[30]

Table 4: Anisotropic magnetoresistance ratio values of bulk ferromagnetic metals and alloys.

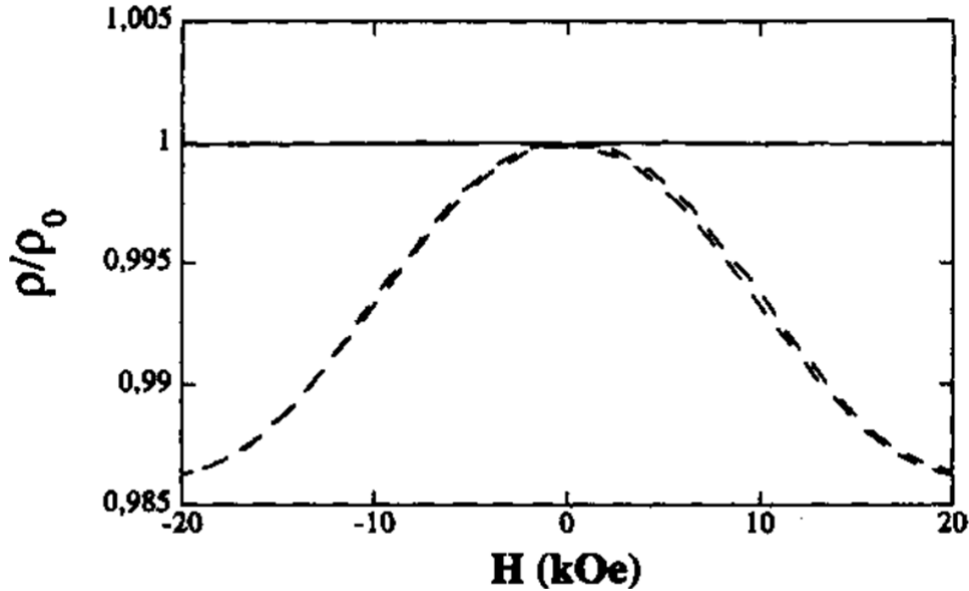


Figure 17: Normalised magnetoresistance curve of an array of parallel Ni NWs performed at 4.2K. The full line corresponds to the case of the external field applied along the NWs direction. The dashed line depicts the case of the external field applied in the direction perpendicular to the NWs axis. Figure from [31].

at low field. Indeed, the magnetisation reversal is not abrupt in nanowires system and different mechanisms can dominate the magnetisation reversal [32]. A possible mechanism consists of the nucleation of a domain wall at the edge of the NW, moving along the NW when the external field is further increased in the opposite direction of the initial magnetisation. The current flow can locally be perpendicular to the magnetisation in the domain wall, reducing the resistivity. In single NW, this propagation of a domain wall is quite fast [33] and the decrease in resistivity is almost not observable. However, for arrays of parallel NWs, this effect is stronger as the magnetisation reversal is less abrupt in such system (see Figure 8).

Note that the computation of the AMR for NWs system is based on Equation 21 with the expression of ρ_{av} defined in Equation 20. Nevertheless, for a NW in absence of external field, the magnetisation is oriented along the NW axis due to shape anisotropy. The nanometric scale allows to consider the whole system as monodomain. Hence, the resistivity state in absence of external field is $\rho_{\parallel}$ and not ρ_{av} , which arise from the macroscopic scale of the bulk material broken into several domains with their own magnetisation direction.

1.2.2 Giant magnetoresistance effect

As mentioned in Subsection 1.1.1, the imbalance in the DOS for spin up and spin down allows to understand the spontaneous magnetisation of ferromagnetic materials. Other properties also depend on the spin of the electrons, leading to the birth to different fields studying the impact of the spin on different transport properties. The discovery of the Giant Magnetoresistance (GMR) effect in 1988 was a breakthrough in the understanding of the impact on electrical charge transport [34]. This opens the way to new application as spin-logic devices based on spin current generation/detection or spin transfer torque for data writing devices. The spintronics field is often related to ferromagnetic materials as the spin of the electrons can be easily collectively controlled, but non-ferromagnetic materials can also be used [35, 36].

The behaviour of the electrons must be different depending on their spin degree of freedom. This is the required condition to observe the impact of the spin on different properties. As electrical current are limited by the electron's mean free path, the spin current is limited by the distance on which the electrons encounter a spin-flip mechanism. This distance is called the spin diffusion length l_{sf} . It is defined as the mean distance between two spin-flip scattering events. Typical values for different ferromagnetic materials are presented in Table 5.

Material	Spin diffusion length [nm]	Temperature [K]	Reference
Py	4.3 ± 1	77	[8]
Cu	36 ± 14	300	[37]
	140 ± 15	77	[38]
Co	38 ± 12	300	[39]
	59 ± 18	77	[39]

Table 5: Spin diffusion lengths of some metallic materials. Values found in [40].

These spin diffusion lengths were determined by CPP-GMR measurements on electrodeposited NWs in porous template. This set-up is similar to the one used in this thesis (see Section 2.1). Other methods were used to determine l_{sf} , leading to different values than the one presented in Table 5 (see [40] for more details). The spin diffusion length decreases as temperature is increased. This is namely due to the higher probability of "spin-flip" scattering by magnons at higher temperature [41].

Considering the impact of spin dependence on the electrical conductivity σ , it can be decomposed as the sum of majority and minority electrons contributions. This is known as the two current model, widely used at room temperature. The conductivity can be written:

$$\sigma = \sigma_{\uparrow} + \sigma_{\downarrow} \quad [(\Omega\text{m})^{-1}], \quad (22)$$

with $\sigma_{\uparrow}$ and $\sigma_{\downarrow}$ being respectively the conductivity contributions of respectively majority and minority electrons. The electrical resistivity is given by:

$$\rho = \frac{\rho_{\uparrow} \rho_{\downarrow}}{\rho_{\uparrow} + \rho_{\downarrow}} \quad [\Omega\text{m}], \quad (23)$$

with $\rho_{\uparrow}$ and $\rho_{\downarrow}$ being respectively the resistivity contributions of respectively majority and minority electrons.

As already mentioned in Subsection 1.1.1, the DOS of a ferromagnetic material depends on the spin degree of freedom, splitting its $3d$ band. The electrons mainly responsible for electrical transport stand in the $4s$ band, typical said to contain free electrons. The electrons lying in the $3d$ exhibit a higher effective mass, leading to a slower motion than the others. Considering the schematic band structure represented in Figure 18, minority electrons have more states for scattering than majority ones. Empty states are available in the $3d$ band overlapping the $4s$ band. Majority electrons can only scatter inside the $4s$ band, while minority electrons can be also scattered from the $4s$ band to the $3d$ band. The scattering probability depends on the DOS at the Fermi level, which is high for the $3d$ band. So, the probability for minority electrons to scatter from the $4s$ band (mainly responsible of the electrical transport) to the $3d$ band (negligible impact on the electrical transport compared to the other one) is high.

The resistivity contribution of the minority electrons $\rho_{\downarrow}$ is therefore different from the one of majority electrons $\rho_{\uparrow}$. This imbalance is represented by the spin asymmetry coefficient defined as:

$$\alpha = \frac{\rho_{\downarrow}}{\rho_{\uparrow}} \quad [-]. \quad (24)$$

Another widely used coefficient relating the spin asymmetry in resistivity is defined as:

$$\beta = \frac{\rho_{\downarrow} - \rho_{\uparrow}}{\rho_{\downarrow} + \rho_{\uparrow}} = \frac{\alpha - 1}{\alpha + 1} \quad [-]. \quad (25)$$

Let us consider a system made of a stack of FM and NM layers crossed by a current flowing in the direction perpendicular to the stack (CPP measurement). Such systems are of great interest regarding the magnetoresistance effect that can rise up to tens of percent. This phenomena is known as the GMR effect. When electrons flow through a ferromagnetic material, the conductivity is influenced by the relative orientation between the magnetisation of the FM layer and their spin degree of freedom. Electrons with their spin aligned with the magnetisation of the FM will be transmitted easily. On the contrary, electrons with their spin oriented in the opposite direction will be preferentially reflected.

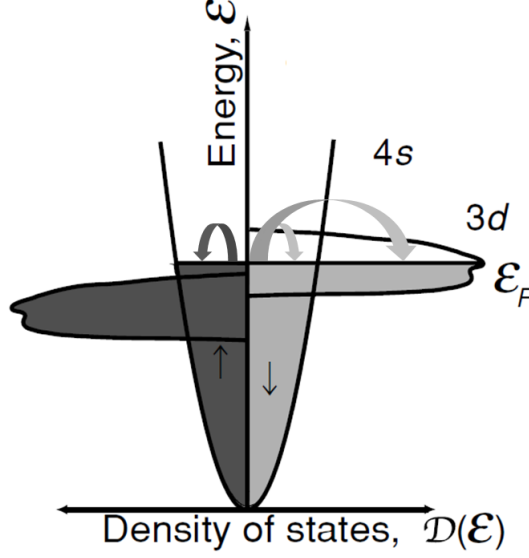


Figure 18: Schematic representation of the band structure for a ferromagnetic transition metal. Majority electrons can scatter from $4s$ to $4s$, while minority electrons can scatter to $4s$ or $3d$, with a high probability for the latter. This explains why the resistivity contribution of majority and minority electrons are different. Figure adapted from [11].

To ensure the electron to keep its spin while crossing the FM layer, the thickness of the NM layer must be smaller its spin diffusion length l_{sf} .

Let us assume the two-current model and neglect possible spin-flip events at FM/NM interface. Depending on the relative orientations of the FM layers, the resistivity of the stacked system is modified. Indeed, if the FM layers exhibit magnetisations oriented in the same direction, called parallel (P) configuration, the resistivity will be low thanks to the transmission of the same spin through the two layers. On the other, if their magnetisations are oriented in opposite directions, called anti-parallel (AP) configuration, the resistivity will be higher. Indeed, if the electron is transmitted through the first FM layer, it will be reflected by the second FM layer. These configurations are schematically represented in Figure 19.

Based on the two-current model depicted in Figure 19, the resistivity in P configuration ρ_P is given by:

$$\rho_P = \frac{\rho_{\uparrow} \rho_{\downarrow}}{\rho_{\uparrow} + \rho_{\downarrow}} \quad [\Omega\text{m}]. \quad (26)$$

The resistivity in AP configuration is given by:

$$\rho_{AP} = \frac{\rho_{\uparrow} + \rho_{\downarrow}}{4} \quad [\Omega\text{m}]. \quad (27)$$

Considering a ferromagnetic material, $\rho_{\uparrow}$ and $\rho_{\downarrow}$ are different (see Figure 18), meaning $\alpha \neq 1$ following Equation 24 and $\rho_P < \rho_{AP}$. The GMR ratio is defined as:

$$\text{GMR} = 100 \frac{\rho_{AP} - \rho_P}{\rho_P} \quad [\%]. \quad (28)$$

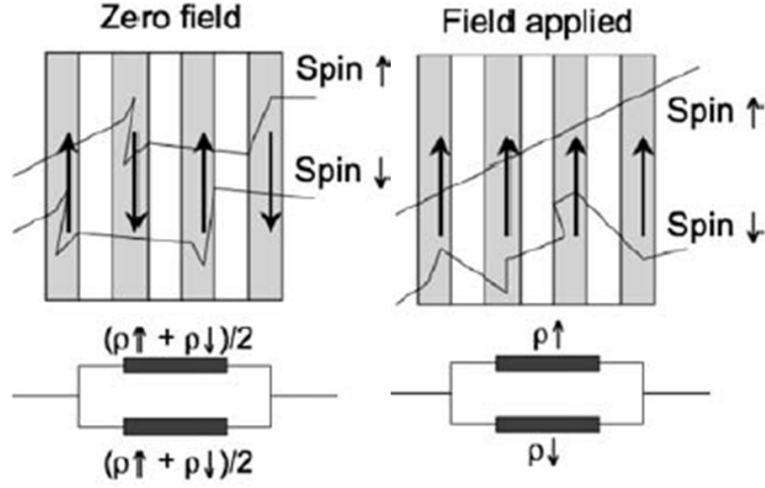


Figure 19: Schematic representation of CPP-GMR measurement with the P and AP configurations of the multilayered stack. The equivalent two-current model is represented for both AP and P configurations, highlighting the lower resistive state for P configuration. Figure from [11].

This ratio increases when temperature is decreased. Indeed, at lower temperature, the probability for the electrons to encounter "spin-flip" events are reduced. The spin diffusion length l_{sf} is therefore higher, as CPP-GMR measurements on Co/Cu multilayered NWs show [39].

The observation of the GMR effect requires an AP, or at least random, configuration for the successive FM layers magnetisation. If the configuration in absence of external field is P, applying $\mathbf{H}$ will not allow to reach the AP configuration. The NM layer plays an important role in the configuration in absence of external field. Depending of its thickness, the NM layer induces either a ferromagnetic or antiferromagnetic coupling between the FM layers. The exchange coupling is therefore influenced by the NM layer thickness. An oscillating behaviour between ferromagnetic and antiferromagnetic coupling was observed in Co/Cu multilayered systems [42]. This is depicted in Figure 20.

The coupling between successive FM layers is quite sensitive to a change in NM layer thickness. Considering really thin NM layers, some Ångströms can change the coupling from ferromagnetic to antiferromagnetic. The oscillating behaviour disappears when the NM layer thickness is further increased. Using sufficiently thick NM layers allows to suppress the exchange coupling, leading to a random configuration for successive FM layers. This leads to a higher resistivity state than the one reached when all FM layers exhibit their magnetisation in the same direction, typical the one imposed by the external field. GMR effect observations are represented in Figure 21.

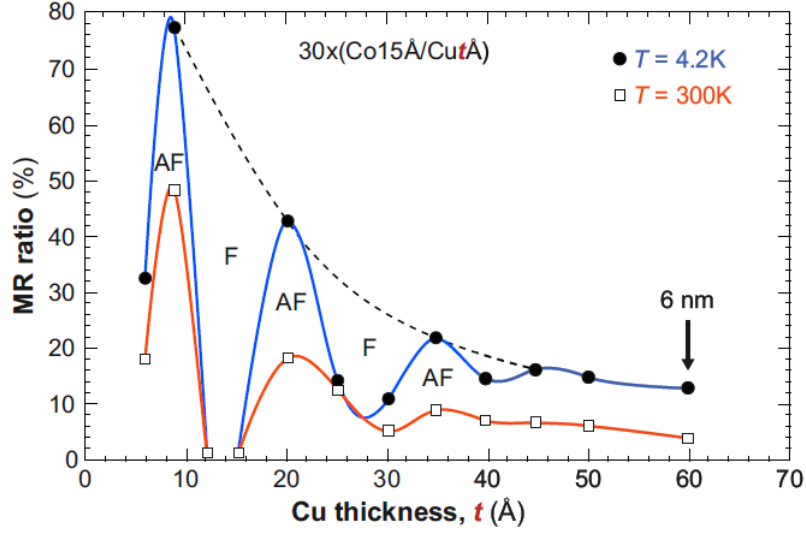


Figure 20: Oscillating behaviour of the MR ratio with the Cu thickness in Co/Cu multilayered systems. Depending on the NM layer thickness, the coupling between successive FM layers can be either ferromagnetic (P configuration) or antiferromagnetic (AP configuration). Figure from [43], adapted from [42].

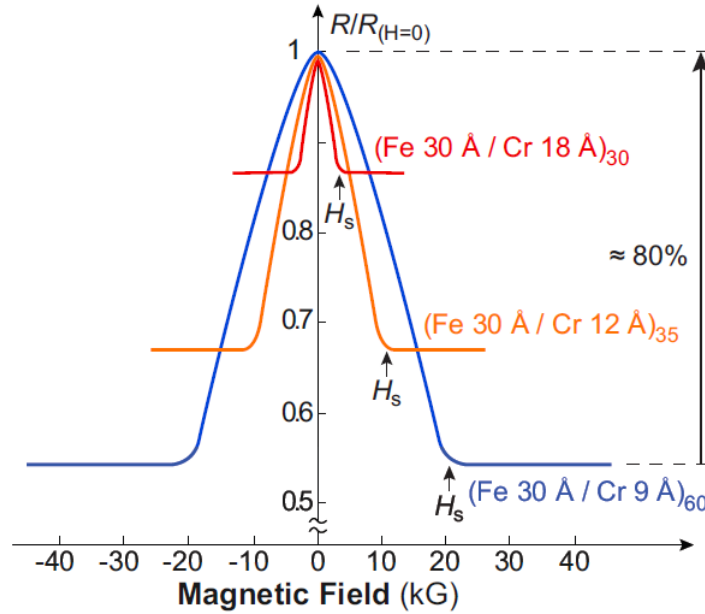


Figure 21: GMR measurements of Fe/Cr multilayered systems in 1988. The thickness of the Cr layer is modified, highlighting the impact on the exchange coupling between the Fe layers and the GMR signal obtained. The GMR ratio was around 80% for small Cr spacer layers. Figure taken from [43], adapted from [34].

Other structures allow to reach AP configuration in absence of external field. For instance, a stack made of a FM/NM/FM trilayer can be used with one of the two FM layers being blocked regarding its magnetisation, the other layer being free. Such pinning of the FM layer magnetisation can be achieved by fixing an antiferromagnetic material to FM layer, leading to a spin-valve system or by using a hard FM material for the first layer and a soft FM materials for the other, called a pseudo spin-valve.

Multilayered NWs are of great interest regarding CPP-GMR measurements. Indeed, these systems were useful to study the regime where the thickness of the layers is larger than the spin diffusion length. It also allows to determine high l_{sf} values in copper for instance [38]. Figure 22 represents CPP-GMR measurements on two different multilayered NWs systems. At $H = 0$ G, the higher resistivity state is the starting point (see inset in Figure 22), with a random configuration for the successive FM layers in the NWs. Then, when the external field is increased in the direction perpendicular to the NWs axis, the magnetisation of all FM layers align more and more with $\mathbf{H}$. This decreases the resistivity, until reaching the fully P configuration with all FM layers magnetisation oriented in the same direction. When the external field is relaxed, AP configuration becomes more and more favourable due to dipolar interaction between the FM layers. However, at $H = 0$ G, the higher resistivity state is not reached. The system exhibits more parallel magnetisations than the starting point, due to a hysteresis effect of the FM layers (see Figure 8 for the hysteresis loop of an array of parallel NWs). Then, the external field increases in the other direction. The resistivity increases a little before reaching a peak. This arises from the Zeeman energy that adds up to the dipolar interaction. After this peak in resistivity, the magnetisations of the FM layers tend more and more to align with $\mathbf{H}$, decreasing again the resistivity. It reaches saturation in resistivity when all the magnetisations are parallel. When the external field is again relaxed, the behaviour is similar to the one presented previously. The curve presents a symmetric behaviour as depicted in Figure 22. The GMR effect was also observed on CNWs system, reaching similar values than the ones found on arrays of parallel NWs [4, 7].

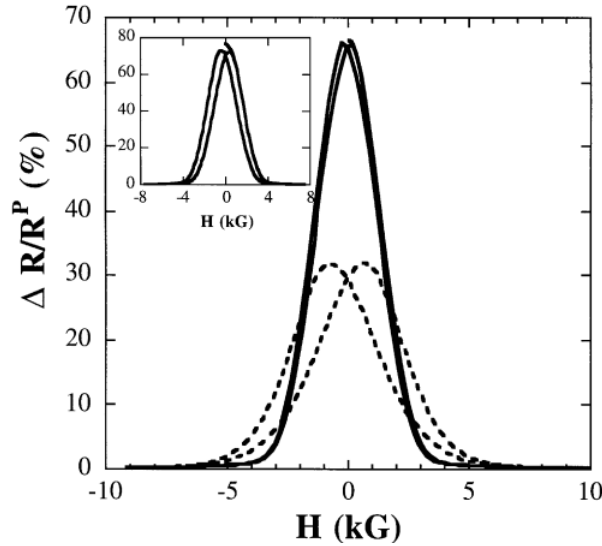


Figure 22: CPP-GMR measurements of Py/Cu (full line) and Co/Cu (dashed line) multilayered NWs systems at 77 K. The inset shows the measurement of the Py/Cu system at 4.2 K. The GMR effect is enhanced when temperature drops. Figure from [9].

1.3 Spin-dependent thermoelectric properties of ferromagnetic materials

The influence of magnetic fields on an electrical current leads to the field of spintronics, with some of its well-known effects presented in Section 1.2. The electrical properties are influenced by the spin degree of freedom of the electrons. On the other hand, as a direct consequence of this impact on electrical current, the spin of the electrons also influences heat current that are, among others, carried by electrons. This connection between spin and heat leads to the emerging field called spin caloritronics. This section will first briefly introduce the field of thermoelectricity, relating heat to electricity conversion. Then, spin caloritronics will be presented through the spin-dependent Seebeck effect, which was investigated in this thesis. Finally, the interest of the interconnected nanowire networks will be presented regarding spin caloritronics measurements.

1.3.1 Thermoelectricity

The first of the thermoelectric effects was discovered by T.J. Seebeck in 1821. He proved the existence of an electromotive force when the junction between two electrical conductors is heated. This opened the way to the fabrication of thermocouples, allowing to convert a temperature difference into a measurable electrical potential. This conversion is the core of the field of thermoelectricity and leads to several research to improve its efficiency [44,45].

The Seebeck effect relates this appearance of an electrical potential when a material is subject to a thermal gradient. The conversion is given by the Seebeck coefficient S , defined as:

$$S = \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T} \quad [\text{V/K}], \quad (29)$$

ΔT being the temperature difference arising from the thermal gradient and ΔV the resulting electrical potential measured. Typical values for metallic materials are given in Table 6. The Seebeck coefficient is, by convention, negative when the cold side is the lower part regarding the electrical potential.

Material	Seebeck coefficient [$\mu\text{V/K}$]
Ni	-19.5
Fe	15
Cu	1.83

Table 6: Seebeck coefficient of some metallic materials at 300K. Values found in [46].

Different contributions influence the generated electrical potential from the applied thermal gradient, as depicted in Figure 23. The first one is called the diffusion regime. Considering a bar of an electrical conductor subject to a temperature difference ΔT , a gradient of electronic density is created between the hot and the cold sides. Indeed, the hot side will be depleted in electrons due to their higher kinetic energy, leading to a flow of electrons from the hot side to the cold side. This flow is counterbalanced by the generated electric field arising from the gradient of electronic density, the cold side exhibiting a higher

concentration of electrons. The appearance of this thermally induced electric field is the relates the thermoelectric behaviour of the sample. The Seebeck coefficient in the diffusion regime is given by Mott's formula:

$$S = -eL_0T\left(\frac{d\ln(\sigma(\epsilon))}{d\epsilon}\right)\bigg|_{\epsilon=\epsilon_F} \quad [\text{V/K}], \quad (30)$$

e being the electron electrical charge (taken as positive value), L_0 the Lorentz number equal to $2.44 \cdot 10^{-8} \text{ V}^2 \text{ K}^{-2}$, σ the electrical conductivity of the material and ϵ_F the Fermi energy. Most metals exhibit a low derivative of σ with respect to the energy at the Fermi level, leading to lower values of S . However, $3d$ ferromagnetic materials show a high derivative at the Fermi level due to the $3d$ band, leading to higher absolute value of the Seebeck coefficient (see Table 6 the value of Fe compared to Cu).

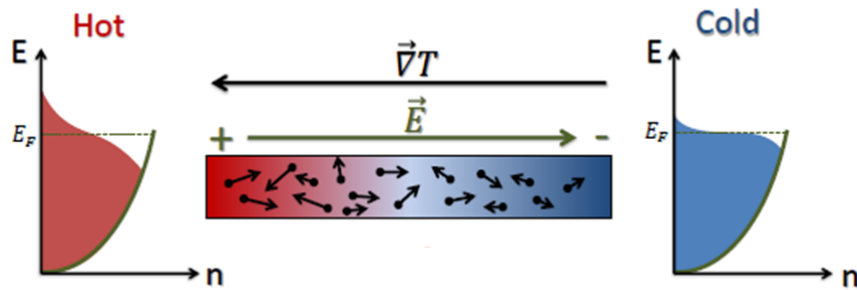


Figure 23: Schematic representation of the diffusion regime of the Seebeck effect. The thermal gradient $\vec{\nabla}T$ induces an electric field $\vec{E}$ that drives the charge carrier in the direction of the thermal gradient. Schematic DOS at the hot and cold sides are represented to highlight the difference of charge carriers concentration between the two ends. Figure adapted from [47].

Another contribution to the Seebeck effect arises from phonons. Indeed, thermoelectric powers of semiconductors exhibit higher values than expected from the diffusion regime at specific temperature [48]. This unexpected high value is explained by the drag of the charge carriers by the stream of phonons from the hot side to the cold side of the sample. This contribution is significantly influenced by the electronic density of the material [49]. Moreover, considering nanostructures, size effects limit the phonon mean free path. This vanishes the phonon drag contribution in nanostructures [50].

The efficiency of the thermoelectric generation is represented by the dimensionless figure of merit ZT given by:

$$ZT = \frac{S^2\sigma T}{\kappa} \quad [-], \quad (31)$$

κ being the thermal conductivity. From this definition, the impact of each property on ZT can be understood. Indeed, a high electrical conductivity is required to allow the charge carriers to flow from the hot side to the cold side, generating the electric field due to charge accumulation. On the contrary, the thermal conductivity must be low to keep the applied thermal gradient: thermal conduction may lead to a vanishing thermal gradient as heat could spread inside the material. The temperature is added to

reach a dimensionless efficiency gauge. The figure of merit for metallic materials can be reduced considering Wiedemann-Franz relation, which related the electrical and thermal conductivities through the Lorentz number. The figure of merit reduces to S^2/L_0 , allowing to evaluate the efficiency of thermoelectric generation for metallic systems only through the Seebeck coefficient value. The figure of merit of typical materials used for thermoelectric applications are provided in Table 7.

Material	ZT [-]	Temperature [K]	Reference
p-doped BiTe	1.4	308	[51]
n-doped BiTe	1.1	308	[51]
Constantan	0.06	300	[4]
Chromel	0.014	300	[4]

Table 7: Figure of merit of typical materials used for thermoelectric applications.

Research have been done on optimising this figure of merit but values higher than unity were hardly reached [51]. This limitation is due to the interconnection between the material properties: reducing the thermal conductivity of a metallic material also reduces its electrical conductivity as both are carried by electrons for metallic materials. Heat is also carried by phonons for semiconductors, insulating materials and metallic alloys. Nevertheless, nanostructures show interest in increasing this figure of merit, as shown for silicon nanowires [52]. On the other hand, the output power density of a thermoelectric material is defined by the power factor PF:

$$PF = \frac{S^2}{\rho} \quad [\text{W K}^2 \text{ m}]. \quad (32)$$

Typical values of the PF scales in mWK^2m for most materials, namely for the widely used bismuth telluride that show values at RT in the range of 1 to 5 mWK^2m [51].

The reciprocal side of the Seebeck effect is known as the Peltier effect. It relates the presence of heating or cooling at the junction between two electrical conductors. Depending the current direction, the heating and cooling points can be inverted. This effect is quantified by the Peltier coefficient Π , which can be related to the Seebeck coefficient thanks to the Onsager relation:

$$\Pi = ST \quad [\text{V}]. \quad (33)$$

1.3.2 Spin-dependent Seebeck effect

The spin dependence of electrical transport has been investigated in the field of spintronics (see Section 1.2). The DOS at the Fermi level is not the same for both spin electrons populations. Following Equation 29, this would leads to different Seebeck coefficients for majority ($S_{\uparrow}$) and minority ($S_{\downarrow}$) electrons. This means that when a thermal gradient is applied to a ferromagnetic material, the electrical current that is generated in a closed

circuit is accompanied by a net spin current, arising from the band split at the Fermi level. In open circuit conditions, this would result in a spin accumulation in both ends of the sample. Such accumulation vanishes inside the sample in distance equal to the spin diffusion length. The polarisation at the hot side is opposite to the one at cold side. This is the spin-dependent Seebeck effect [53].

Again, different contributions may give rise to the spin-dependent Seebeck effect. The diffusion regime and phonon drag contribution play a role as the creation of a charge current or electrons flow is accompanied by a net spin current in a ferromagnetic materials. On the other hand, spin current may be carried by magnons, the spin "twin" of phonons. Indeed, considering the total exchange energy in the ferromagnetic ground state, the cost related to the reversal of the spin of one site is expensive. Therefore, all sites will share the spin reversal through periodic oscillations of their spin orientation as depicted in Figure 24. Such oscillations spread through the whole lattice in spin waves [11].

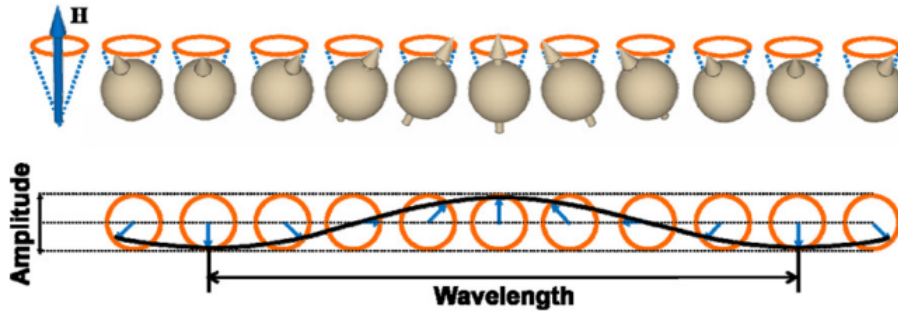


Figure 24: Schematic representation of a spin wave. The top picture is a side view highlighting the global direction of all spin aligned (oriented upward). The bottom picture exhibits a top view of the spin oscillations showing the spin wave amplitude and wavelength. Figure from [54].

Similarly to the case of charge carriers, the magnons density is different at the hot and cold sides due to the temperature difference. Therefore, the gradient in magnons concentration induces a magnons flux accompanied with a spin current. The magnon drag contribution to the spin dependent Seebeck effect adds to the diffusion regime contribution. The temperature dependence of the magnon drag contribution to the Seebeck coefficient follows a $T^{3/2}$ law and has a significant impact on some pure transition metals in a wide range of temperature [50].

As for the Seebeck effect, Peltier effect also exhibits a dependence on the spin leading to the spin dependent Peltier effect. The Onsager relation still holds, allowing to connect the two spin-dependent thermoelectric coefficients as shown in Equation 30. It relates the generation of heating/cooling when a spin current is injected through the interface between two different materials. Its observation and determination of spin dependent Peltier coefficients open the way for magnetic control of cooling systems in nanoscale devices [4,55].

Considering a multilayered structure as those used to emphasise the GMR effect, the Seebeck coefficient will be different in the P configuration compared to the AP configu-

ration, depicted by the notation S_P and S_{AP} respectively. Assuming the thermoelectric power being dominated by the diffusion regime contribution, the difference in Seebeck coefficients can be understood from the link between S and ρ described in Equation 30. The deviation of the Seebeck coefficient, as a function of the external magnetic, from the Seebeck coefficient in absence of external field $\Delta S = S(H) - S_{AP}$ can be expressed as a linear function of the difference between the inverse of the resistance at a certain external field and the inverse of the resistance in absence of external field $\Delta(1/\rho) = 1/\rho(H) - 1/\rho_{AP}$. This link also arises from Mott's formula for the Seebeck coefficient in diffusion regime (see Equation 30). This evolution is given by:

$$\begin{aligned} S(H) &= \frac{S_P \rho_P - S_{AP} \rho_{AP}}{\rho_P - \rho_{AP}} + \rho_P \rho_{AP} \frac{S_{AP} - S_P}{\rho_P - \rho_{AP}} \frac{1}{\rho(H)} \\ &= A + \frac{B}{\rho(H)} \\ \Rightarrow \Delta S(H) &= B \left(\frac{1}{\rho(H)} - \frac{1}{\rho_{AP}} \right) = B \Delta \left(\frac{1}{\rho(H)} \right) = \chi B \Delta \left(\frac{1}{R(H)} \right) \end{aligned} \quad [\text{V/K}], \quad (34)$$

χ being a constant linking the electrical resistivity ρ to the electrical resistance R of the sample.

The diffusion regime is characterised by a linear relation between ΔS and $\Delta(1/R)$. Previous studies on the interconnected nanowire networks show the dominance of the diffusion regime by the linear dependence of the Seebeck coefficient with temperature as well as the confirmation of the linear relation depicted at Equation 34 [4].

Similarly to the case of the resistance, the impact of the magnetic field on the interconnected multilayered nanowire network can be expressed by a dimensionless ratio. This is called the magnetothermopower (MTP) ratio that is given by:

$$\text{MTP} = 100 \frac{S_{AP} - S_P}{S_{AP}} \quad [\%], \quad (35)$$

allowing to quantify the impact of the magnetic field on the Seebeck coefficient, exactly as it influences the resistance of the sample. A value of -29.3% has been determined at RT for interconnected CoNi/Cu NW network, highlighting the significant impact of the external field on the Seebeck coefficient [4]. This impact is emphasised also by the definition of the magneto-power factor (MPF) that represents the relative change in power factor between the P and AP configuration. This ratio is given by:

$$\text{MPF} = \frac{PF_P - PF_{AP}}{PF_{AP}} \quad [-], \quad (36)$$

PF_P and PF_{AP} being the PF in the P and AP configurations. CoNi/Cu exhibits a MPF ratio of around 135% at RT, showing the possible magnetic modulation of the output power density of interconnected nanowire networks.

Regarding the interconnected NWs networks, the determination of the spin dependent Seebeck coefficients $S_\uparrow$ and $S_\downarrow$ in the diffusion regime is based on Seebeck coefficients in AP and P configurations [4]. Neglecting the effect of FM/NM interface resistances, assuming that no spin-flip events occurs in the FM layers and considering the resistivity of the NM negligible compared to the resistivity of the FM material, the resistivities in the P

and AP configurations can be expressed thanks to the two currents model (See Equations 26 and 27 for the expressions). Applying the same reasoning for the Seebeck coefficients leads to the following expressions (see Supplementary information of [4]):

$$\begin{aligned} S_P &= \frac{S_{\uparrow}\rho_{\downarrow} + S_{\downarrow}\rho_{\uparrow}}{\rho_{\uparrow} + \rho_{\downarrow}} \\ S_{AP} &= \frac{S_{\uparrow}\rho_{\uparrow} + S_{\downarrow}\rho_{\downarrow}}{\rho_{\uparrow} + \rho_{\downarrow}} \end{aligned} \quad [\text{V/K}]. \quad (37)$$

Solving this system of two equations for $S_{\uparrow}$ and $S_{\downarrow}$ gives the following expressions for the spin dependent Seebeck coefficients:

$$\begin{aligned} S_{\uparrow} &= \frac{1}{2}[S_{AP}(1 - \beta^{-1}) + S_P(1 + \beta^{-1})] \\ S_{\downarrow} &= \frac{1}{2}[S_{AP}(1 + \beta^{-1}) + S_P(1 - \beta^{-1})] \end{aligned} \quad [\text{V/K}]. \quad (38)$$

The spin asymmetry coefficient β can be determined by MR measurements, leading to the following expression assuming two currents model:

$$\beta = \sqrt{\frac{R_{AP} - R_P}{R_{AP}}} = \sqrt{\text{MR}} \quad [-]. \quad (39)$$

Therefore, spin dependent Seebeck coefficients can be determined by MR and magneto-Seebeck measurements of interconnected multilayered nanowire networks.

1.3.3 Interest of interconnected nanowire networks

As mentioned in Subsection 1.2.2, nanostructures are of great interest regarding the amplitude of the MR signal. On the other hand, such structures lead to low thermoelectric efficiency. Indeed, the Seebeck coefficient being an intrinsic property of the material, it does not alter due to the reduction of the size of the sample. However, the nanoscale of the sample limits the electrical signal generated or the thermal gradient that can be applied. Moreover, contact thermal resistance become hard to determine and/or eliminate. These are an important error source regarding temperature difference measurement, which are essential for thermoelectric properties determination. Simulations were often used to determine the temperature gradient over multilayered stacks [56, 57].

The interconnected nanowire network offers a real solution to observe the magnetic control of thermoelectric properties in multilayered stacks. Indeed, the connectivity between the NWs ensures a sufficient electrical conductivity. Moreover, the configuration of the multilayer stack (see Figure 11) allows CPP-GMR measurement, which is easier to interpret than CIP-GMR measurement and exhibits higher and cleaner signals. The PC template exhibits a low thermal conductivity that stabilises the applied thermal gradient. The flexibility and lightness of the sample is also interesting regarding possible future applications, enhanced by the cheap and easy-to-convert for higher scale manufacturing process.

This network allows reliable determination of key spin-dependent materials properties over a wide range of temperature [4]. The goal of this thesis is to determine these parameters for Py/Cu multilayered and homogeneous Py NWs. This material is of great interest regarding GMR effect [58] and also thermoelectric properties [10]. This thesis tries to reach the recommended Seebeck coefficient of Py [10] and highlights the significant influence of the magnetic field on thermoelectric properties. Spin-dependent Seebeck coefficients will also be determined.

2 3D interconnected magnetic nanowires manufacturing and characterisation techniques

This section is dedicated to the fabrication and characterisation of the 3D interconnected nanowire networks easily filled with homogeneous or multilayered magnetic nanowires by electrodeposition. The different characterisation techniques used are split in two categories: morphology characterisation and magnetic/magnetotransport characterisations.

2.1 Sample synthesis

The synthesis of the sample is based on a "bottom up" approach which is well-known and widely used at UCLouvain for 3 decades. The procedure is based on electrodeposition of metallic elements inside a porous membrane. This technique is cheap, easy to use and allows to fabricate different structures such as interconnected NWs, nanotubes or nanocables [19]. The template fabrication defines the nanopores diameter, distribution and density. This opens the door to a wide range of possible structures.

This thesis focuses on homogeneous and multilayered interconnected NWs made of Ni-Fe alloys electrodeposited in porous PC template. The sample fabrication procedure is divided in two steps: the template fabrication, responsible for the global morphology of the sample, and the electrodeposition defining the material composition and the NWs type (homogeneous or multilayered).

2.1.1 Template fabrication

"Track-etched" polymer membranes are of great interest regarding the manufacturing of 3D crossed porous templates. Indeed, the successive bombardments steps allow to vary the angle orientation of the nanopores. The PC membrane is hit by a flux of heavy ions at an angle of $\pm 25^\circ$ with respect to the normal axis of the template surface. Then, the membrane is rotated by 90° in the plane followed by a new bombardment step at $\pm 25^\circ$. This step is depicted in Figure 25(a). The orientation of the nanopores as well as their density are controlled by this bombardment step. To ensure the template not to be fragile, the maximum porosity of the template is limited at 30%. The versatility of the pores diameter ranges from 10nm to few hundreds of nm while density ranges from $6 \cdot 10^6$ to $6 \cdot 10^9 \text{ cm}^{-2}$ [59]. The bombarded areas are etched by sodium hydroxide (NaOH) solution defining the final diameter of the pores. The final porous template is represented in Figure 25.

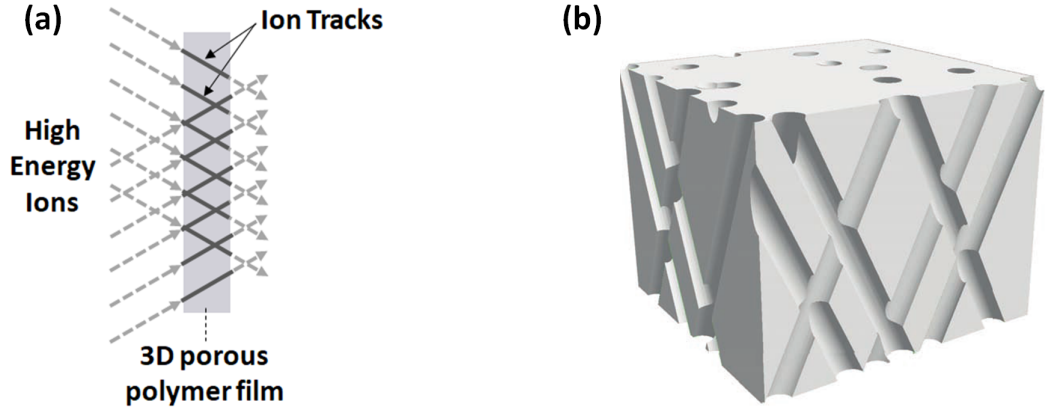


Figure 25: Schematic representation of the bombardment of the template by heavy ions. **(a)** Bombardment step with an angle of $\pm 25^\circ$ with respect to the normal axis of the template surface. Then, the membrane is subject to a rotation in the plane of the template, followed by another bombardment at $\pm 25^\circ$. **(b)** Porous template after the chemical etching by NaOH. A metallic cathode must be sputtered before growing the NWs inside the nanopores. Image **(b)** from [5].

The main disadvantage lies in the random distribution of the pores compared to other porous templates like Alumina templates [17]. The standard angle deviation was maximum $\pm 5^\circ$ with respect to the target angle [2]. The diameter dispersion was 5%. The templates exhibit a thickness of $20\ \mu\text{m}$ and are supplied by the company *it4ip* implanted in Louvain-la-Neuve.

To allow the filling of the pores, a metallic cathode is deposited on one side of the template, clogging one end of the nanopores [59]. A piece of metal is heated by an electron beam, creating a metallic cloud that sputters on the template when the temperature is sufficiently high. Gold (Au) and Cu are typical sputtered cathode used as background for the NWs growth. The sputtered layers were few tens of nm thick to ensure the full cover of the pores while ensuring easy removal. This is essential to allow the growth of the NWs. A 10 nm thick layer of Cr was first sputtered before the Au layer to ensure good adhesion to the template.

2.1.2 Electrodeposition

The second step is the filling of the pores by electrodeposition. This technique is based on the reduction of metallic ions at the working electrode under a certain potential. Considering a bath containing the ions of a metallic material M^{n+} , the chemical reaction allowing to reduce the metal on the working electrode is given by:



Depending on the potential applied, the equilibrium is pushed towards the formation

of solid metal on the working electrode or its dissolution inside the bath. Usually, the electrodeposition is potentiostatic, meaning the electrical potential is kept constant by a reference electrode and the electrical current is allowed to vary. The inverse configuration is also possible and is called galvanostatic electrodeposition. The schematic representation of the experimental set-up used is depicted at Figure 26.

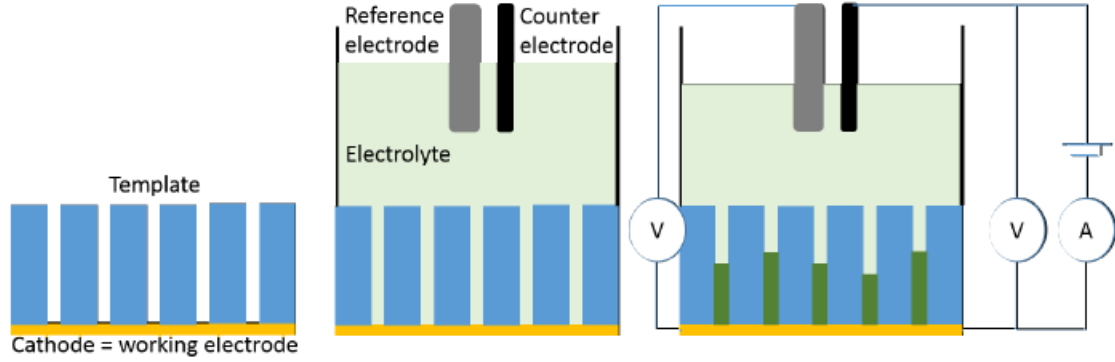


Figure 26: Schematic representation of the nanopores filling by potentiostatic electrodeposition. Three electrodes are required: reference electrode to keep the electrical potential constant, the working electrode at which the reduction reaction occurs (starting point of the NWs growth) and the counter electrode closing the electrical circuit through which the current is flowing. The porous template represented here depicts an array of parallel nanopores. The process for crossed nanopores filling is identical. Image from [19].

The electrolyte bath contains the different metallic elements required for the NWs. In this study, the metallic materials used are Ni, Fe and Cu. By applying a constant potential, homogeneous Py NWs were grown with few Cu impurities inside. Multilayered structures can be reached using a single electrolyte bath as shown in previous study [60]. Indeed, using a pulsed signal allows to control the rate at which each metallic element reduces at the working electrode. At higher potential in absolute value, Ni and Fe are preferentially reduced even if a small fraction of Cu can reduce also, while at low potential only Cu reduces at the working electrode. This is depicted at Figure 27.

To reduce the Cu impurities inside the Py layers, the concentration of Cu must be much lower than the concentration of Ni or Fe [61]. The speed of reduction being larger at higher potential, deposition times for Py and Cu are different as depicted in Figure 27. The control of layers thickness is mainly possible through the deposition times or the deposited charge [9].

Table 8 shows the different samples that were deposited and further characterised. The sputtered cathode and deposition times are also given. The acidity of the solution is represented by the value of pH of the solution. This influences significantly the lifetime of the electrolyte solution, which degrades due to the oxidation of the metallic elements. Reducing the pH to 2.05 allows to increase significantly the electrolyte lifetime. Both homogeneous and multilayered samples are presented. All samples were electrodeposited at RT.

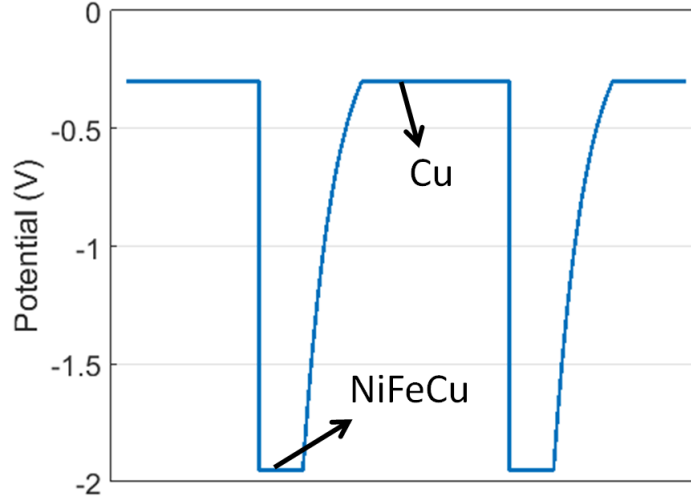


Figure 27: Schematic pulsed potential signal used during the electrodeposition of multilayered Py/Cu NWs in the porous PC template. During the step at high potential, Py is deposited with some Cu impurities. This is denoted by the notation NiFeCu. During the lower potential step, only Cu is able to deposit.

Sample label	P [%]	d [nm]	Cr/Au [nm]	Potential(s) [V]	t [s]	pH
PyCu	3	80	4.7(Cr)/400	-1.95	3000	3.85
Ni ₈₂ Fe ₁₈ Cu	3	80	4.7(Cr)/400	-1.6	800	2.05
Ni ₇₀ Fe ₃₀ Cu	3	80	4.7(Cr)/400	-1.1	1500	2.05
Ni ₆₀ Fe ₄₀ Cu	3	80	4.7(Cr)/400	-1.05	1500	2.05
Ni ₅₀ Fe ₅₀ Cu	3	80	4.7(Cr)/400	-1	5000	2.05
Py/Cu	3	80	4.7(Cr)/400	Py: -1.95 Cu: -0.3	0.3 120	2.05

Table 8: Electrodeposition parameters for each sample: Porosity P , diameter d , template cathode, deposition potentials, deposition times t and pH of the electrolyte. The multilayered Py/Cu samples is made of 400 bilayers.

No overflowing was observed for any sample, ensuring the NWs structure without connection between them at the surface of the template. Table 8 also exhibits the possible control of the alloy composition by the applied potential. Indeed, decreasing the potential reduces the deposition rate of all elements but not in the same way for each. Decreasing the deposition potential increases the Fe content of the alloy. The Ni content in the alloy influences significantly the AMR ratio of the alloy [25].

2.2 Morphologic characterisation by scanning electron microscopy and X-rays spectroscopy analysis

This section is devoted to the characterisation of samples morphology by field-emission scanning electron microscopy (FE-SEM). Moreover, chemical composition determinations have been performed thanks to energy-dispersive X-rays spectroscopy analysis system (EDX). SEM and EDX characterisations were performed with the collaboration of Tristan da Câmara Santa Clara Gomes.

The device used was a JEOL FEG SEM 7600F equipped with an EDX system which was a JEOL JSM2300 with a resolution < 129 eV. Electron-matter interactions are the core of these characterisations. The SEM has a resolution around 10 nm. Figure 28 represents a schematic view of the microscope.

Electrons are emitted from the electron gun and accelerated by a high electrical potential. Magnetic lenses allow to focus the beam on the sample. The magnification is controlled by the beam width. Astigmatism is handled by another magnetic coil called the stigmator. The topography information are related to secondary electrons arising from the atoms of the sample. These electrons are ejected from the sample by inelastic scattering. Backscattered electrons, arising from elastic scattering with the sample, give information about mass variations. X-rays emitted by electrons excitation of the sample allow to get information about chemical composition. This last information is provided by the EDX system.

The electron-matter interaction volume is depicted at Figure 29. After the primary electron beam hits the sample surface, several information can be obtained from different depth. Typically, secondary and backscattered electrons come from a depth of few nm and tens to hundred nm, respectively. Characteristic X-rays arise from deeper in the matter, typically between 1 and 3 μm . A high vacuum inside the chamber is required to avoid collisions between the electrons and other particles that may be present inside.

Only the low porosity (3%) samples were analysed by SEM and EDX. They did not require any preparation as polishing or specific coating. Small parts of the electrodeposited sample were cut using a scalpel blade. Then, the PC template was dissolved using dichloromethane solution. The metallic cathode was kept to ensure a sufficient stability for the sample. Non-conductive parts in the sample lead to charge accumulation on the sample. Therefore, the PC template has to be completely removed. Thanks to the metallic cathode and their morphology, CNWs networks can be manipulated by a tweezer after the template dissolution. The sample is fixed on a metallic holder by adhesive carbon fibre film. The applied acceleration tension was 15 kV with a working distance of 8 mm.

Quantitative chemical composition analysis was performed by the integrated Analysis Station software. Two steps were applied in order to obtain reliable quantitative results on chemical composition over the analysed section:

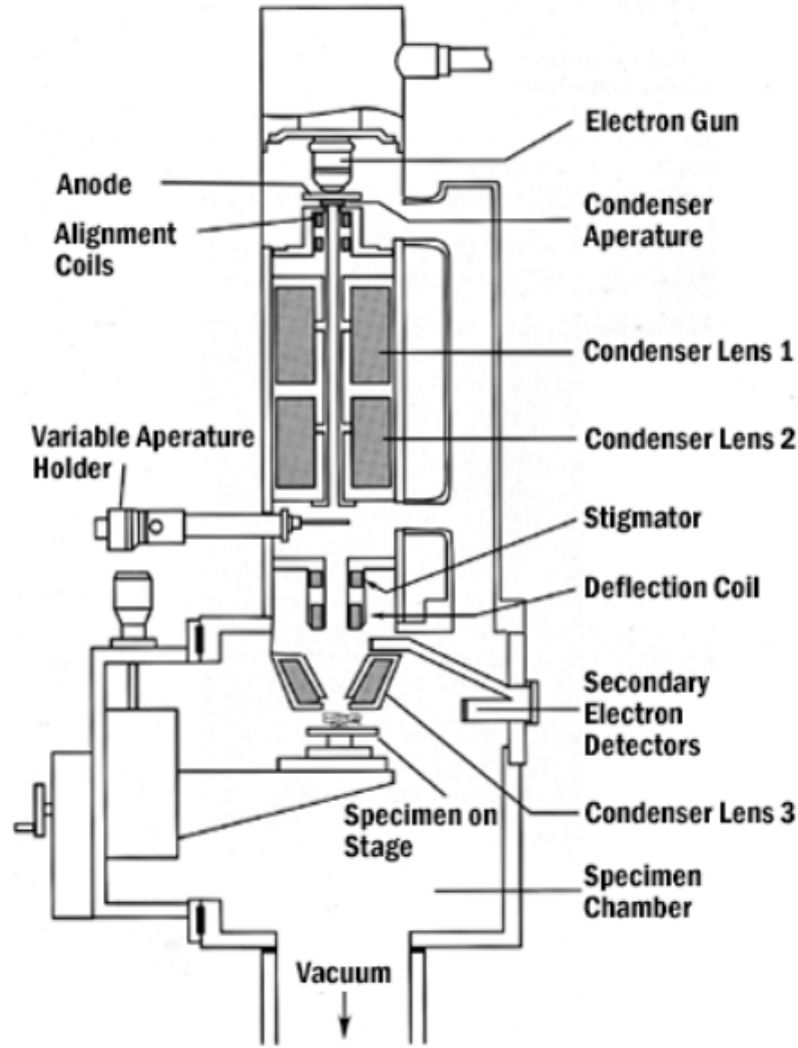


Figure 28: Schematic representation of a field-emission scanning electron microscope (FE-SEM). The emitted electrons are first accelerated by a high electrical potential before being focused on the sample by magnetic condenser lenses. Other magnetic lenses are used to vanish astigmatism. The X-rays, backscattered and secondary electrons are collected by different detectors for characterisation. The chamber must be under high vacuum to avoid collisions between electrons and particles. Figure from [62]

- Bremsstrahlung subtraction by classical "Top Hat Filter" method [64,65].
- Atomic peak area quantification by ZAF model. "Z" stands for atomic number of the element, "A" for the absorbance and "F" for fluorescence. The atomic and weight percentages are calculated from the ZAF model [64].

Figure 30 provides SEM images of the 3D interconnected NWs network. The interconnections between the NWs and the complexity of the structure are highlighted. This structure arises from the porous PC template that has been filled by electrodeposition. The interconnections are of great interest for electrical conductivity as well as for robustness (even if for low porosity samples, the metallic cathode was kept to ensure mechanical stability).

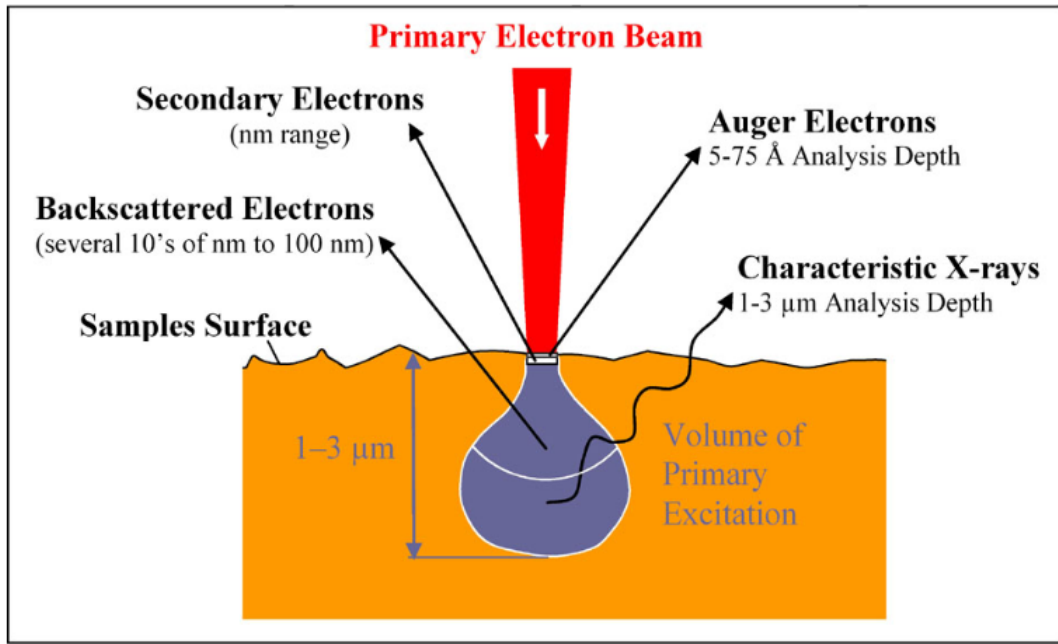


Figure 29: Electrons-matter interaction volume. Secondary electrons arise from nm range depth, backscattered electrons from tens up to hundred nm and X-rays arise from few μm . Image from [63].

As depicted in Figure 30, the volume fraction of the interconnections is much lower than the volume fraction of NWs. Therefore, phenomenon related to volume effects will be dominated by the monodomain NWs rather than the small interconnections. Furthermore, Figure 30 depicts the macroscopic film shape of the system after dissolution of the PC template, highlighting the ease of manipulation by tweezers.

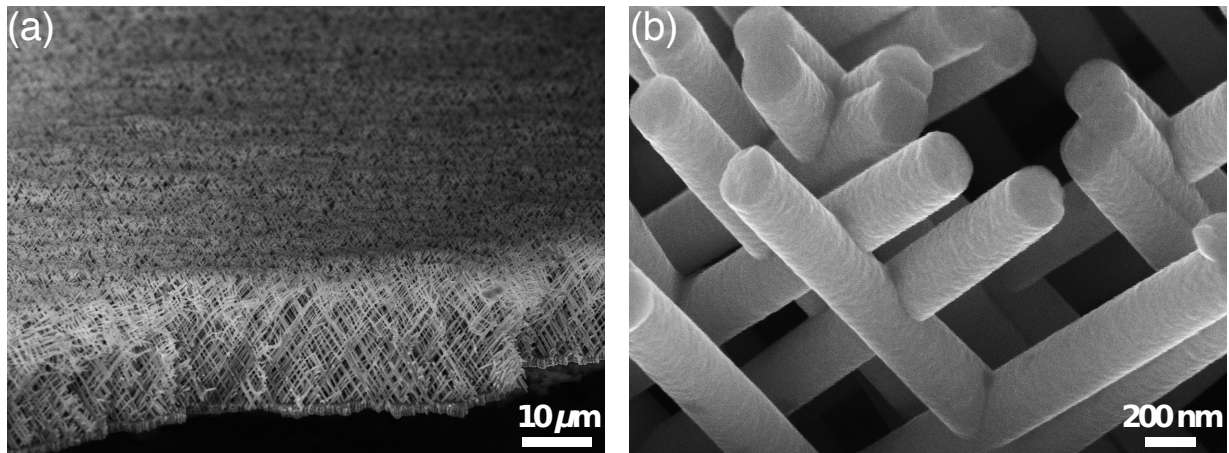


Figure 30: SEM images of the interconnected nanowire network when the PC template has been dissolved. Different magnifications are presented to show the self-supported behaviour of the sample and the interconnections between the NWs. Figure from [66].

Table 9 provides the chemical composition of the low porosity homogeneous samples. The values were determined by analysing different points on each sample. Decreasing the

deposition potential reduces the Ni content of the alloy. As the electrolyte solution also contains Cu, the nickel-iron alloys are contaminated by Cu impurities. The concentration of Cu is less than 10% for all samples.

Sample label	Ni content in NiFe [%]	Cu content [%]
PyCu	87 ± 4	1
Ni ₈₃ Fe ₁₇ Cu	83 ± 5	3
Ni ₇₀ Fe ₃₀ Cu	73 ± 4	2
Ni ₇₀ Fe ₃₀ Cu	60 ± 4	1
Ni ₇₀ Fe ₃₀ Cu	51 ± 3	7

Table 9: Atomic composition of the different low porosity homogeneous samples. The Ni content values corresponds to the fraction of Ni in the sample, the Cu content being removed. The uncertainty on Cu content is around 5%.

The different elements atomic composition are evaluated thanks the K_α peak. The typical EDX spectrum of the homogeneous sample is provided in Figure 31. Other elements as carbon, oxygen or even the metallic cathode could appear in the spectrum. These were taken into account when the atomic compositions were evaluated.

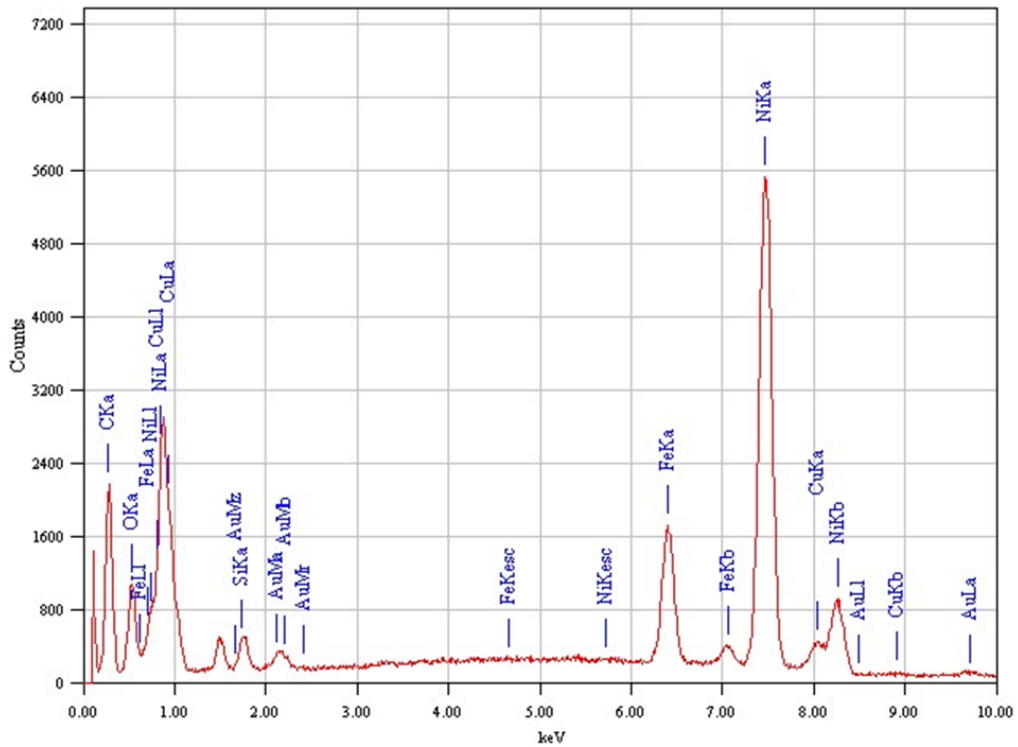


Figure 31: EDX spectrum of one homogeneous sample electrodeposited inside the porous PC template. The computation of the atomic content of the sample are based on K_α peaks of the spectrum.

2.3 Magnetic and magnetotransport characterisation techniques

Three different material properties under an external magnetic field have been investigated: the magnetic moment, the resistance and the Seebeck coefficient. The experimental set-up for each type of measurements are presented in this section. The results will be presented and discussed in Section 3. The notations IP and OOP relate the direction in the plane of the sample and the direction along the normal of the sample surface. Therefore, the OOP direction exhibits an angle of 25° with the NWs, while the IP direction is harder to define with respect to the NWs (see Figure 10 in Subsection 1.1.4). Indeed, due to the in-plane rotation of the sample between the two bombardment steps, the IP direction exhibits a distribution of angles with respect to the NWs axis. Therefore, the normal to the macroscopic film plane is taken as the reference to define both OOP and IP directions.

2.3.1 Static magnetic properties

The characterisation of static magnetic properties was performed by an alternating gradient field magnetometer (AGFM-LakeShore). This device provides the magnetisation in the IP and OOP directions. The characterisations were done at RT. The AGFM used in this thesis is represented in Figure 32. This device allows to apply a maximum magnetic field 14 kOe. This limits the possible determination of magnetisation at saturation. Indeed, if the calibration steps were well followed, the magnetisation at saturation could be reached if a field of 14 kOe is sufficient. As sample size may influence the magnetic moment, all curves are normalised by their magnetisation when the external field is maximal ($H = 14$ kOe). Remanent magnetisation is determined as a fraction of the saturation magnetisation. Coercive fields are also provided thanks to the AGM measurements.

The magnetometer creates a static magnetic field that can rise up to 14 kOe. A small magnetic field gradient $d\mathbf{h}_x/dx$ is superimposed on this static field, typically of 40 Oe/cm [69,70]. The sample is fixed on a piezoelectric tip, as depicted on Figure 32(b). Tip displacements are then detected through electrical signals. The small magnetic field gradient, applied in the x direction, induces a force in the same direction on the sample volume Γ . This force is given by [11,68–70]:

$$\mathbf{F}_x = m_x \frac{d\mathbf{h}_x}{dx} = -\mu_0 \Gamma M_x(H_x) \frac{d\mathbf{h}_x}{dx} \quad [\text{N}]. \quad (41)$$

The gradient field being applying by the system and the force being measured, the only unknown parameters are the sample volume Γ and the sample magnetisation evolving with the static external magnetic field $M_x(H_x)$. To suppress the unknown Γ , the magnetisation is normalised by the magnetisation at saturating external field. The gradient field being small, the magnetisation of the sample is mainly influenced by H_x , allowing to determine the hysteresis loop of the magnetisation with respect to the static external field $M_x(H_x)$.

To fix the sample, two different piezoelectric tips were used, each one allowing to measure

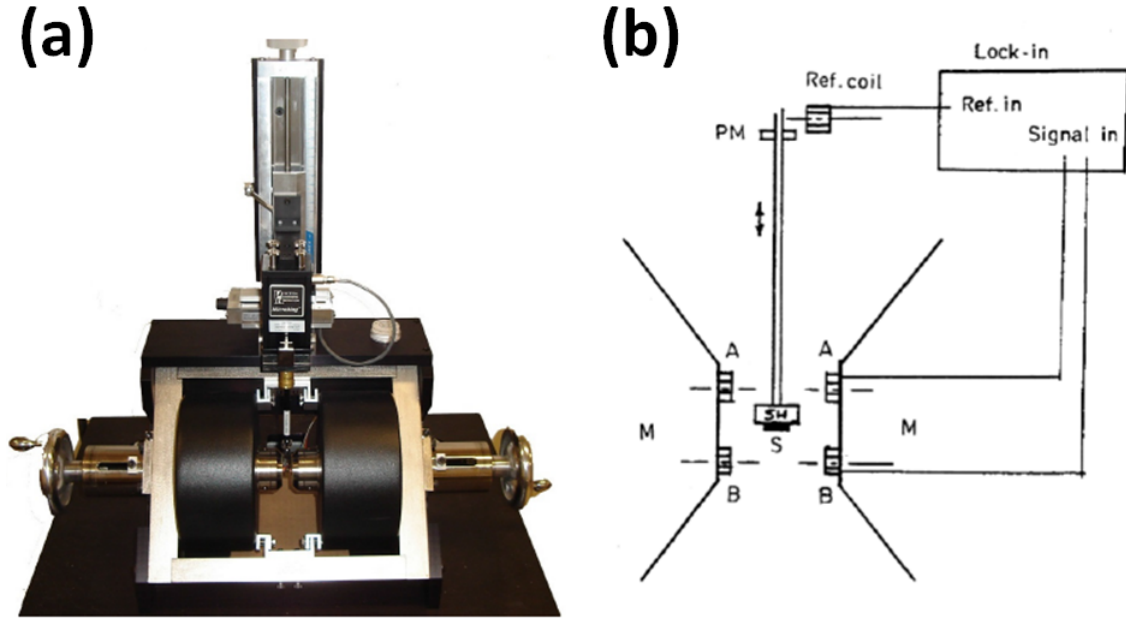


Figure 32: Alternating gradient field magnetometer similar to the one used in this thesis. Images from [67,68].

the magnetisation in a different direction (OOP or IP). A small piece of the sample is cut and deposited on a glass plate by silicon grease. Neither the PC template nor the metallic cathode were dissolved. The software allows to remove the paramagnetic and diamagnetic effect arising from the metallic cathode and/or the PC template. Therefore, only the ferromagnetic effect of the sample is measured. The AGM measurements have been made by Tristan da Câmara Santa Clara Gomes.

2.3.2 Magnetoresistance characterisation

The characterisation of the samples magnetoresistance was performed by electrical measurements under a external magnetic field, ranging from -10 kOe to 10 kOe. For homogeneous samples, these measurements allow to approximate the AMR ratio and to investigate the magnetic properties of the interconnected structure, namely the impact of the interconnections. The electrical current flowing only through the NWs, resistance measurements include several local magnetisation contributions, which reduce in this system into the monodomain NWs and the interconnections contribution (which is supposed to be small as depicted by previous studies on CNWs networks [19]). Measurements on multilayered systems allow to measure the GMR effect in CPP configuration: the current is restricted along the NWs segment, i.e. in the direction perpendicular to the successive layers.

As already mentioned, the 3D interconnected nanowire networks are of great interest for electrical measurements due to the interconnectivity between the NWs. The circular electrodeposited sample has a typical diameter of 13 mm. It is cut into mm wide strips, which are locally etched by plasma in their center to create the design schematically represented in Figure 33. The resistance measurements are based on four/two-probe measured. The current is injected from one unetched end of the strip. Then, the current flow through CNWs and reaches the other unetched end. This is also depicted at Figure 33. The different connections to the unetched part of the sample were made by Ag paint.

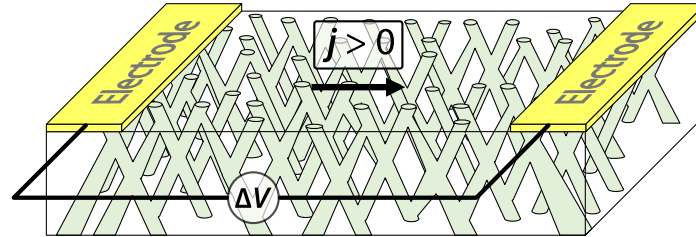


Figure 33: Schematic representation of the set-up used for resistance measurements on the interconnect nanowire networks. The center of the strip is etched to force the electrical current to flow through the NWs. The two unetched ends act as electrodes for current injection and resistance measurements. Image from [5].

An alternating current is used to increase the signal-to-noise ratio. An alternating potential source with a resistance of 10 k Ω , much larger than the resistance of the samples and the contacts, is used. Moreover, the resistance of the samples is higher than the contact resistances and Cu wires used for the connections. Therefore, four- and two-probes measurements should lead to similar results. The holder, with the sample fixed on it, is placed on a rotary cane to modify the direction of the applied magnetic field with respect to the plane of the sample. Figure 34 represents a picture of the etched sample placed on the holder with the connections required for the resistance measurement.

The measurements have been done at RT, but also at 150 K and 15 K. This allows to investigate quickly the behaviour at lower temperature of the system. Helium compressor cryogenic device allows to reach low temperature inside the chamber previously put under vacuum. The temperature could be dropped down to 10 K and the cold finger can be stabilised around 15 K. The cold finger is in contact with the holder. A heating resistance is used to heat the system and a PID controller controls the power injected through the resistance. This allows to stabilise the temperature at the wanted target temperature.

Some notations have to be defined regarding the different external field directions. Considering the interconnected nanowire networks, H_{OOP} and H_{IP} are related to the external field applied in the OOP and IP directions, respectively. On the other hand, $\rho_{\parallel}$ and $\rho_{\perp}$ refer to the resistivity when the sample magnetisation is parallel and perpendicular to the current flow, respectively. Finally, $\rho_{\text{OOP}}^{\text{sat}}$ and $\rho_{\text{IP}}^{\text{sat}}$ define the resistivity when the sample magnetisation is saturated with the external field applied in the OOP and IP directions, respectively.

The removal of the metallic cathode at the center of the strip was performed by plasma etching. The sample was placed on a holder, its ends being protected by a mask. This enables only the center part of the strip to be etched. An argon (Ar) plasma was used under

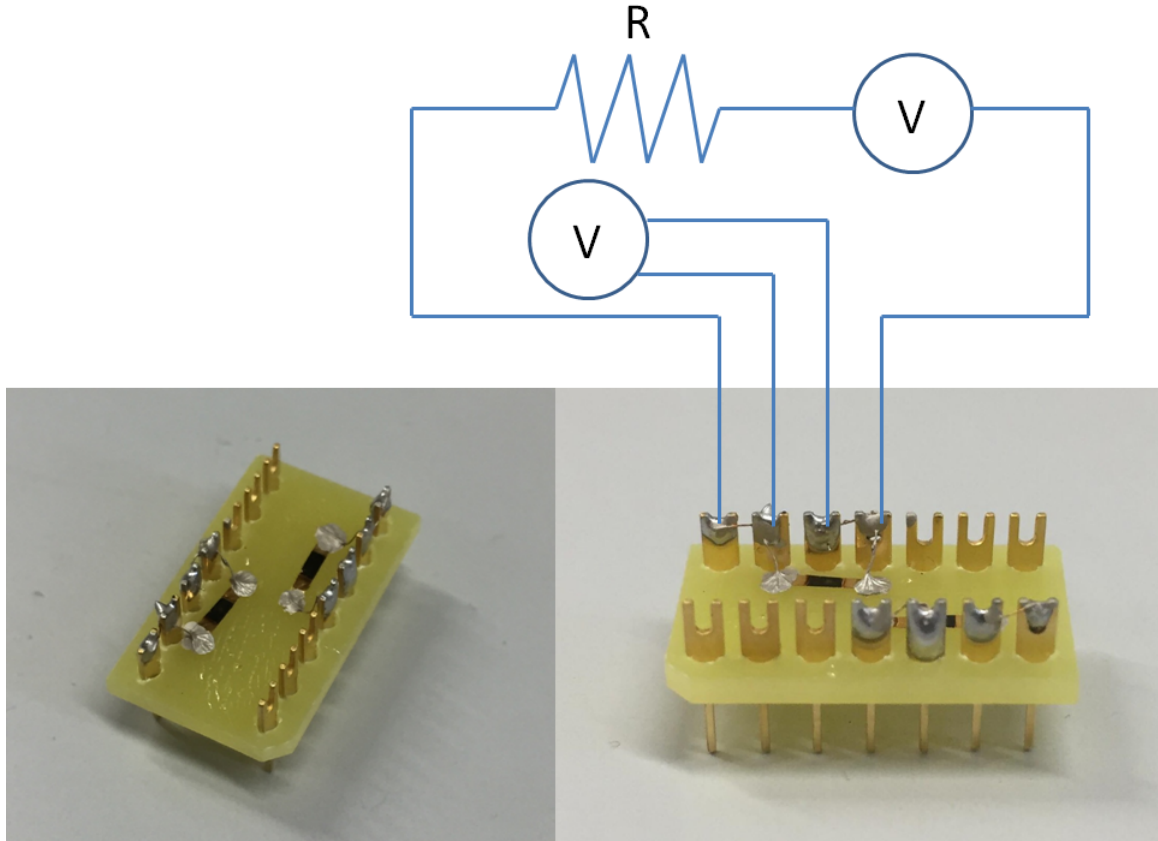


Figure 34: Pictures of the sample preparation for resistance measurements. The strip is etched at its center and the unetched parts are connected by Cu wire to the Au pins of the holder. The wires were connected by Ag paint to the metallic cathode of the sample. The electrical circuit of the four-probes resistance measurement is schematically represented. Figure from [5].

a $5 \cdot 10^{-3}$ Torr pressure and an acceleration power of 80 W. The etching procedure was composed of steps of 5 minutes of etching followed by the 5 minutes at rest inside the chamber at high vacuum. This procedure gives high reproducibility for the Cr(4.7nm)/Au(400nm) metallic cathode removal. The use of other metallic cathode thickness requires another etching procedure that could be obtained by comparing the etching of the sample with one strip of the porous template without any electrodeposited material inside. A too long exposure time to the plasma may damage the sample, leading to NWs disconnection and loss of electrical conductivity.

The system used for magnetoresistance characterisation was used as a first and quick investigation of electrodeposited sample behaviour. Another system allows to obtain magnetoresistance measurements at different temperatures, as well as magneto-Seebeck characterisation. This system is presented in the next section.

2.3.3 Magneto-Seebeck characterisation

The set-up used for magneto-Seebeck characterisation of the samples allows to investigate magneto-resistance and -Seebeck coefficient measurements at different temperatures. The sample preparation is similar to the one presented in Subsection 2.3.2 regarding the etching procedure. However, to allow Seebeck coefficients measurements, a thermal circuit must be considered in parallel to the electrical circuit for resistance measurements. The experimental set-up is schematically represented in Figure 35.

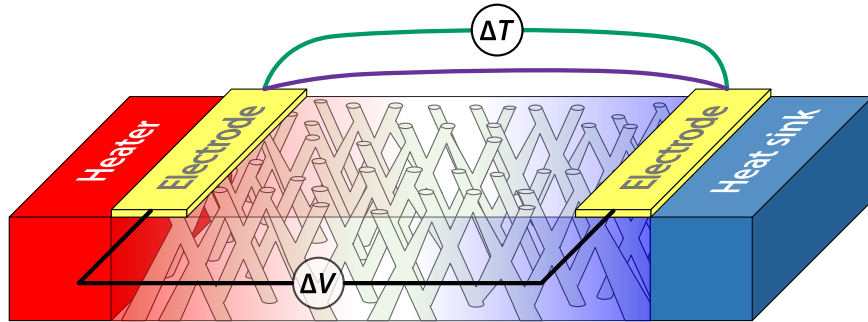


Figure 35: Schematic representation of the experimental set-up used for Seebeck coefficient and magnetothermoelectric effect. The thermal gradient is generated by a resistive element. The temperature difference ΔT and the generated thermoelectric voltage difference ΔV are measured between the metallic electrodes. Figure from [4].

The thermal gradient is generated by injecting a current ranging from 1 mA to 5 mA through a resistive element of $691 \, \Omega$ connected to a piece of Cu. This block corresponds to the heater part represented in Figure 35. One end of the sample is connected to this heater by Ag paint. The other end is connected to another block of Cu which serves as a heat sink. This is the cold point of the system. The two parts must be thermally isolated, heat being allowed to flow only through the interconnected NW network placed in between. Figure 36 depicts the sample connected between the Cu blocks.

A Chromel P/Constantan thermocouple is used to measure the temperature difference between the hot and cold points on the system. The thin voltage leads are made of Chromel P, forcing the subtraction of the contribution of these to the thermoelectric power. This was done by considering the recommended absolute thermopower of Chromel P. The temperature difference was typically between 1 K and 3 K. As for the system described in Subsection 2.3.2, the sample holder was placed on a cane allowing rotation around its axis. The sample was placed in the chamber under vacuum of typically $5 \cdot 10^{-6}$ bar. The temperature inside the chamber was lowered by Helium compressor cryogenic device and a heating resistance allows to impose the global temperature inside the chamber thanks to a PID controller.

Only the PyCu and Py/Cu samples were measured at different temperatures while only RT measurements have been done for the low porosity homogeneous samples. The external magnetic field was raised up to 0.9 T in the IP and OOP directions.

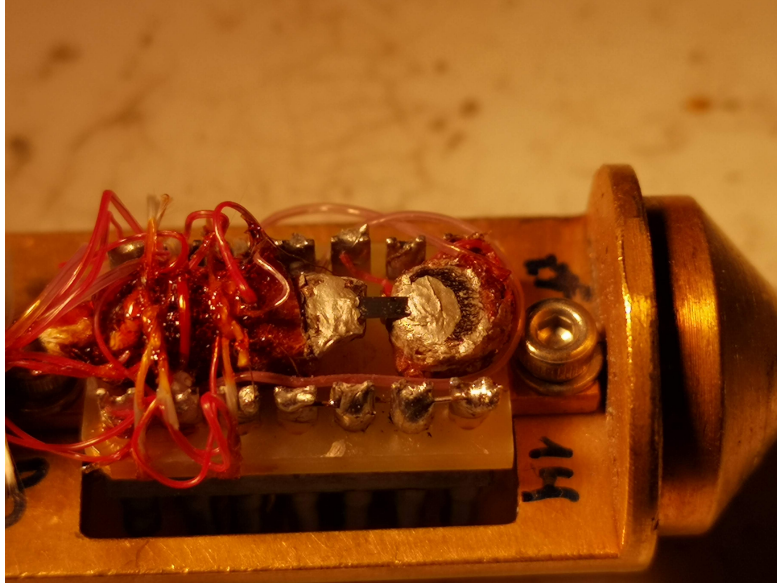


Figure 36: Picture of the experimental set-up for Seebeck coefficient determination. The sample lies between two copper blocks working as heater and heat sink. The heat flow is transferred by the interconnected nanowire network, as well as the generated thermoelectric potential difference. Different connections are required for heating point, temperature difference and electrical measurements.

The set-up depicted at Figure 36 also allows magnetoresistance characterisation in the range of temperatures previously presented. The connections are qualitatively similar to the ones presented in Figure 33: the Cu wires used for electrical potential measurement are connected to the sample by Ag paint on the Cu blocks. On the other, magnetoresistance measurements on this set-up were used using DC current injection, contrarily to the other set-up used (see Subsection 2.3.2). To avoid the self-heating of the Pt while measuring at low temperatures, the injected current is limited to ensure a stable temperature during the measurement. Temperature was varied from 10 K to 320 K.

3 Results and discussion

This section is devoted to the presentation and discussion of magnetic, magnetoresistance and magneto-Seebeck measurements on different samples. First, the characterisation of homogeneous permalloy-copper sample will be discussed, highlighting the interest of this material due to its high Seebeck coefficient (compared to other metallic materials). Then, the multilayered permalloy/copper interconnected NWs case will be presented, proving the high difference of the Seebeck coefficient in the P and AP configurations. Spin-dependent Seebeck coefficients will be extracted from these measurements. Finally, the flexibility of the manufacturing process will be emphasised by the presentation of magnetoresistance measurements for different NiFe alloy compositions, as well as their Seebeck coefficients at room temperature.

The uncertainty bars presented in the different curves correspond to two times the standard deviation, arising from the noise originating from the resistance and temperature measurements. In some case, the signal-to-noise ratio is very high and the uncertainty bars do not or barely appear.

3.1 Homogeneous permalloy-copper sample

The different results of the homogeneous permalloy-copper sample are presented in this section. The static magnetic properties are presented and discussed in Subsection 3.3, along with other compositions for the Ni-Fe alloy.

3.1.1 Magnetoresistance characterisation

Figure 37 provides the magnetoresistance measurement of the PyCu sample in both IP and OOP direction, respectively represented by the blue and red lines. The resistance decreases as the external field increases either in IP or OOP directions. This is due to orientation of the NWs with respect to the normal of the template plane. Indeed, considering the system in absence of external field, both magnetisation and current flow are oriented along the NWs axis. The increase of the external field gives rise to a perpendicular component to the magnetisation with respect to the NWs axis. This angle is higher when the external field is applied in the IP direction. The maximal uncertainty arising from resistance measurements is around 25 m Ω .

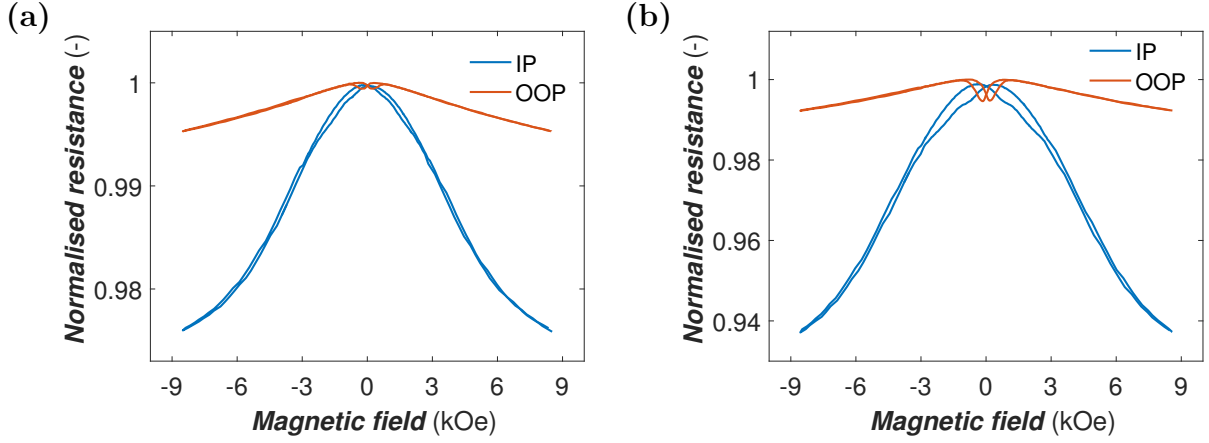


Figure 37: Anisotropic magnetoresistance curve at (a) RT and at (b) 10 K of the PyCu homogeneous sample. The curves with the external field applied in the IP (blue line) and OOP (red line) directions are provided. The uncertainty bars are not shown for clarity.

As mentioned in Subsection 1.2.1, the influence of the interconnections is low compared to the contribution arising from the monodomain NWs. Furthermore, the sample exhibits a porosity of 3%, meaning a small degree of interconnectivity between the NWs. So the magnetoresistance curve presented in Figure 37 exhibits mainly the contribution arising from the monodomain NWs, similar to the behaviour of arrays of parallel NWs depicted at Figure 17. The resistance in the IP direction exhibits a peak around $H = 0$ Oe, due to the magnetisation which is oriented in the direction along the NWs. This corresponds to the $\rho_{\parallel}$ state. As the external field is increased, the magnetisation of the NWs follows more and more the magnetic field direction, leading to a lower resistance state as the angle between the magnetisation and the current flow increases. The evolution of the resistance when the external field is applied in the OOP direction is less pronounced than in the IP direction. Indeed, at saturating magnetic field in the OOP direction, the magnetisation exhibits only an angle of 25° with the current flow, leading to a higher resistance state than at saturating external field in the IP direction. On the other hand, the resistance exhibits a drop at low external fields in the OOP direction. This emphasises the reversal of the magnetisation that dominates in the OOP direction, while the IP direction highlights a magnetisation coherent rotation behaviour. This drop in resistance occurs at higher field when T is low, which is coherent with the temperature dependence of the nucleation field determined for arrays of parallel NWs [71].

Arrays of parallel NWs allow to directly reach the $\rho_{\perp}$ and $\rho_{\parallel}$ states. However, due to the angle of the interconnected NWs and the two steps bombardment, the $\rho_{\perp}$ can not be reached. On the other hand, the $\rho_{\parallel}$ state can be reached as the magnetisation of the NWs is spontaneously oriented along the NWs axis in absence of external field. These limitations force to determine the AMR ratio thanks to IP and OOP magnetoresistance measurements. The model used evaluates $\rho_{\parallel}$ and $\rho_{\perp}$ thanks to the resistivity at saturation in the IP and OOP directions and the angle between the NWs axis and the normal to the template plane (see Supplementary of [3]). The expressions of $\rho_{\parallel}$ and $\rho_{\perp}$ are given by:

$$\begin{aligned}\rho_{\parallel} &= \frac{\rho_{\text{OOP}}^{\text{sat}} K - \rho_{\text{IP}}^{\text{sat}} (1 - K)}{2K - 1} \\ \rho_{\perp} &= \frac{\rho_{\text{IP}}^{\text{sat}} K - \rho_{\text{OOP}}^{\text{sat}} (1 - K)}{2K - 1}\end{aligned}\quad [\Omega\text{m}], \quad (42)$$

$\rho_{\text{OOP}}^{\text{sat}}$ being the resistivity at saturation in the OOP direction, $\rho_{\text{IP}}^{\text{sat}}$ being the resistivity at saturation in the IP direction and $K = \cos^2(\theta)$ with θ the angle between the NWs axis and the normal to the template plane. From these equations, the AMR ratio of the PyCu sample is 3.1% at 300 K, coherent with the values found in literature [2, 25]. The presence of Cu impurities and defects arising from the electrodeposition of the NWs inside the sample reduce the AMR ratio, explaining why the value obtained in this thesis is lower than the one found in the literature [25]. The AMR ratio increases as temperature is decreased, reaching a value of 9% at 10 K, leading to an increase of a factor 3 compared to the AMR ratio at RT. This is coherent with values found in the literature [25].

The evolution of the resistance at saturation (R_{sat}) and the resistance at $H = 0$ Oe (R_0) with temperature are depicted in Figure 38. The behaviour is typical from metallic materials and alloys. The resistance is constant before evolving linearly with temperature. This is due to the vanishing phonon-electron interactions when temperature is sufficiently low. Therefore, the conductivity of the sample is limited by static impurities scattering. The maximal uncertainty for R_0 and R_{sat} are around 26 m Ω and 25 m Ω , respectively.

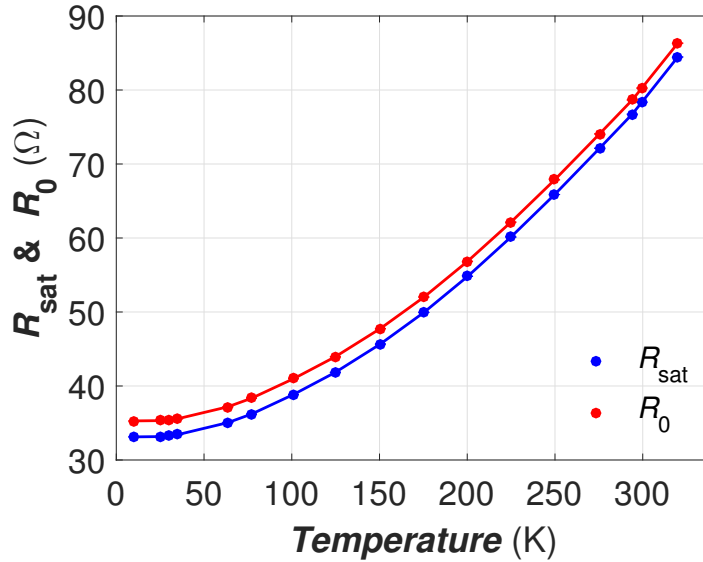


Figure 38: Evolution of the resistance at saturation (R_{sat}) and at $H = 0$ Oe (R_0) with temperature.

From these measurements, the RRR of the electrodeposited PyCu sample can be computed. Assuming the saturation of the resistance at 10 K, the RRR can be evaluated by:

$$\text{RRR} = \frac{R_0^{10\text{K}}}{R_0^{300\text{K}}} \quad [-], \quad (43)$$

R_0^{10K} and R_0^{300K} being the resistance in absence of external field at 10 K and 300 K. This gives a value of 2.27 which is comparable to those already obtained on electrodeposited CNWs made of metallic alloys [4], even though this value is much smaller than what is achievable using pure metallic materials or other fabrication techniques. From the RRR, the residual resistivity ρ_{res} can be approximated. Assuming the ideal resistivity ρ_i of the PyCu sample to be the one of bulk Py at 300 K ρ_i^{300K} , ρ_{res} is given by:

$$\rho_{\text{res}} = \frac{\rho_i}{\text{RRR} - 1} \approx \frac{\rho_i^{300K}}{\text{RRR} - 1} \quad [\Omega\text{m}], \quad (44)$$

leading to a value of $11 \mu\Omega\text{cm}$, assuming $\rho_i^{300K} = 14 \mu\Omega\text{cm}$ [72]. These values of RRR and ρ_{res} justify the lower AMR ratio determined, static impurities increasing the average resistivity ρ_{av} .

Figure 39 provides the evolution of the magnetoresistance (MR) ratio with temperature. The expression of MR considering homogeneous is given by:

$$\text{MR} = 100 \frac{R_0 - R_{\text{sat}}}{R_0} \quad [\%]. \quad (45)$$

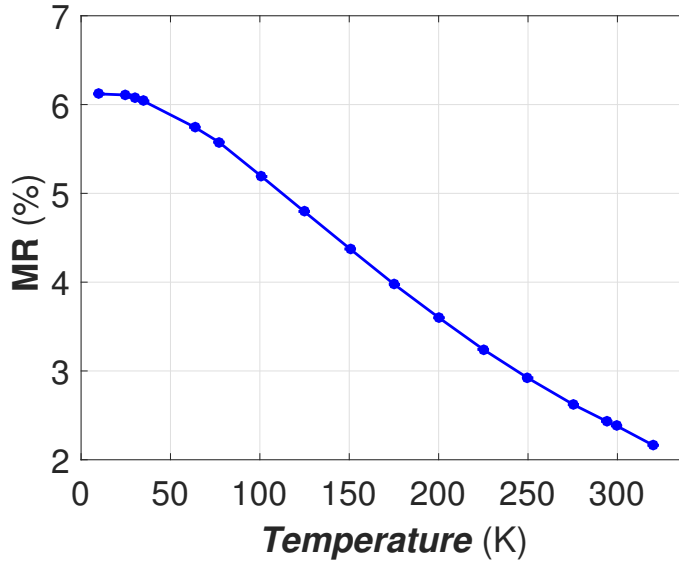


Figure 39: Evolution of the magnetoresistance ratio with temperature for the PyCu sample.

The MR ratio follows a small plateau at low temperatures before decreasing as temperature rises, going from a value of 6.1% at 10 K to a value of 2.4% at 300 K. The plateau is related to the saturation of both resistances at sufficiently low temperatures, as depicted in Figure 38. The MR values are smaller than the AMR ratio values determined previously. This is namely due to the smaller difference $R_0 - R_{\text{sat}}$ compared to $\rho_{\parallel} - \rho_{\perp}$, as the perpendicular resistivity state is not achievable using CNWs.

3.1.2 Magneto-Seebeck characterisation

Figure 40 provides the magneto-Seebeck measurement of the PyCu homogeneous sample. The behaviour is similar to the one presented in Figure 37: the OOP direction shows an almost constant signal while the IP direction shows a higher Seebeck coefficient in absolute value. The similarity between the magnetoresistance curve and the magneto-Seebeck curve is related to Mott's formula (see Equation 30). Indeed, if the diffusion regime dominates, the Seebeck coefficient and the resistivity are linked. Therefore, the evolution of S with the external magnetic field is linked to the magnetoresistance of the sample. The maximal uncertainty on the measured Seebeck coefficient, arising from resistance and temperature difference measurements, is around 80 nV/K.

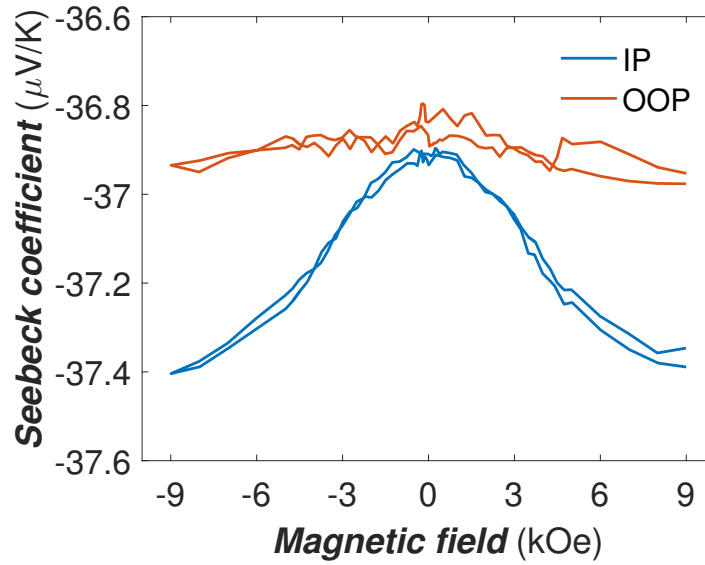


Figure 40: Magneto-Seebeck curve of the PyCu sample at RT. The external field was applied in the IP direction (blue line) and the OOP direction (red line).

The magneto-Seebeck measurement is more noisy than the magnetoresistance measurement. This is due to the challenge of performing accurate thermal measurements, along with the small electrical potential to measure being typically around few tens of $\mu\text{V/K}$. Indeed, the temperature of the sample as well as the temperature difference may vary during the measurement. Therefore, the evaluated Seebeck coefficient is influenced by these temperature fluctuations. The mean temperature of the sample and the temperature difference are provided in Figure 41. The Seebeck coefficient was evaluated before the application of the external magnetic field. This value was around $-36 \mu\text{V/K}$, consistent with the values found in literature [10]. The difference between this computed value and the one measured when $H = 0$ Oe is due to the sample magnetisation influenced by the previous saturation. The sample magnetisation before the measurement and at $H = 0$ Oe during the measurement are slightly different, leading to a small difference in Seebeck coefficient.

Both the mean temperature and temperature difference vary during the measurement,

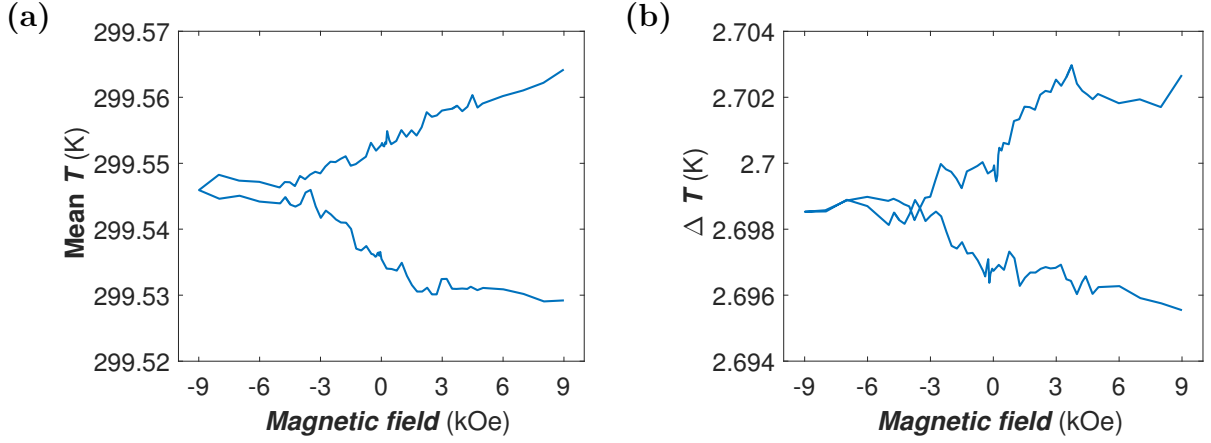


Figure 41: Evolution of (a) the mean temperature and, (b) the temperature difference with the external field for the PyCu homogeneous sample.

explaining the lower signal-to-noise ratio of the Seebeck coefficient compared to the magnetoresistance. Moreover, the need to measure smaller electrical potentials compared to the ones measured during magnetoresistance measurements amplifies this quality difference. However, the thermal variations are quite small: a few tens of mK for the mean temperature and few mK for the temperature difference. This small variations give reliability on the measured Seebeck coefficient, as depicted in Figure 40, where the difference in Seebeck coefficient at saturating positive external field is around $0.05 \mu\text{V/K}$. This difference is related to the gap in temperature difference of 7 mK at saturating positive external field, along with the difference in measured electrical potential.

The evolution of the Seebeck coefficient at the saturation field (S_{sat}) and at $H = 0$ Oe (S_0) are provided in Figure 42. The difference between the S_0 and S_{sat} is quite small and decreases with decreasing temperature. Following Equation 30, both Seebeck coefficients fall down to 0 when $T \rightarrow 0$ K. The maximal uncertainty for S_0 and S_{sat} are around 102 nV/K and 103 nV/K, respectively.

The Seebeck coefficient follows almost a linear relationship in certain temperature range before beginning a saturation. This is coherent considering the diffusion regime dominating the Seebeck effect. The saturating behaviour at high temperatures is coherent with the values given by Ho *et al.* [10]. The curvature appearing may originate from magnon-drag contribution that adds to the diffusion regime contribution.

Figure 43 provides the MR ratio and the magnetothermopower (MTP) as a function of temperature. The definitions used to evaluate these parameters are similar to the ones presented in Equation 28 and Equation 35, but the AP and P configurations are defined for multilayered NWs. Therefore, the determination of MR and MTP for homogeneous samples require resistance values and Seebeck coefficients in other configurations. The P configuration of the multilayered samples can be compared to the homogeneous sample state at saturating external field. Similarly, the AP configuration can be compared to the homogeneous sample state in absence of external field. Therefore, MR and MTP are determined for homogeneous samples using R_0 , R_{sat} , S_0 and S_{sat} (see Equation 45 for MR

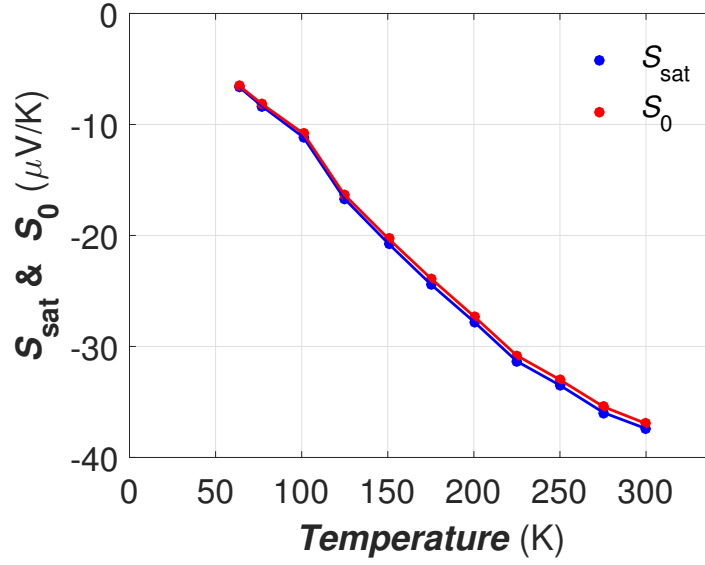


Figure 42: Evolution of Seebeck coefficient at saturation, (S_{sat}) and at $H = 0$ Oe (S_0) with temperature.

expression).

$$\text{MTP} = 100 \frac{S_0 - S_{\text{sat}}}{S_0} [\%]. \quad (46)$$

The maximal uncertainty for the MR and MTP measurements are around 0.08% and 0.8%, respectively.

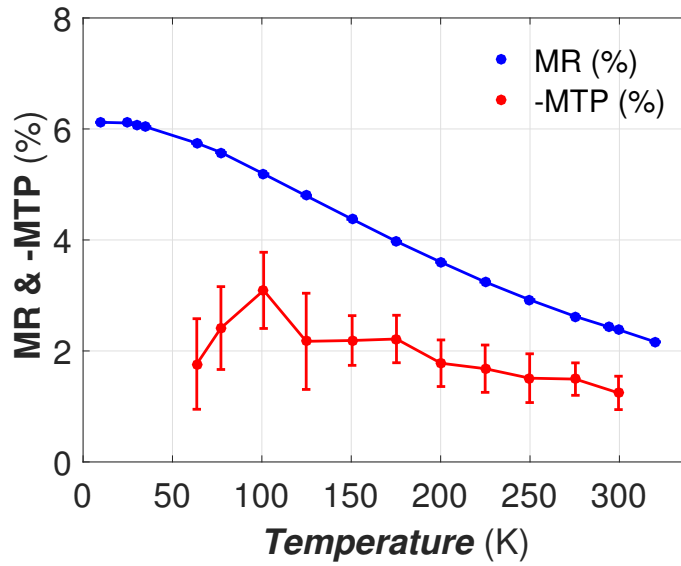


Figure 43: Evolution of the magnetoresistance ratio MR and the magnetothermopower MTP with temperature.

The values of MTP for temperatures under 50 K are not show due very high measurements

uncertainty. The MR ratio saturates at low temperatures due to the behaviour of the resistance depicted in Figure 38. The MTP is lower than the MR ratio and their behaviour are different. This can be understood by considering the linear relationship described in Subsection 1.3.2. The coefficient linking ΔS and $\Delta(1/R)$ depends on temperature meaning that the evolution MTP with temperature is not supposed to be the same as for the MR ratio.

The final characterisation of the thermoelectric properties of the PyCu sample requires the estimation of the the power factor PF and the figure of merit ZT (see Equations 31 and 32 in Subsection 1.3.1 for the expressions of ZT and PF respectively). The resistivity of the PyCu sample is determined thanks to ρ_i and ρ_{res} , the first one taken from the literature [72] and the second one being computed using the RRR. The thermoelectric figure of merit can be approximated assuming the Wiedemann-Franz relation to be suitable for metallic alloys. The different parameters at 300 K are provided in Table 10.

RRR [-]	ρ_i [$\mu\Omega\text{cm}$]	ρ_{res} [$\mu\Omega\text{cm}$]	S [$\mu\text{V/K}$]	PF [$\text{mW/K}^2\text{m}$]	ZT [-]
2.27	14 [72]	11	-37.4	5.6	0.057

Table 10: Data on the RRR, ideal resistivity ρ_i , residual resistivity ρ_{res} , Seebeck coefficient, power factor and thermoelectric figure of merit ZT for the homogeneous PyCu sample at RT. The ideal resistivity at RT was found from [72, 73].

The computed PF value of the PyCu sample is higher than the value for the widely used thermoelectric material bismuth telluride, whose values are ranging from 1 $\text{mW/K}^2\text{m}$ to 5 $\text{mW/K}^2\text{m}$. Moreover, the residual resistivity of the sample may be reduced by optimisation of the electrodeposition process, through the deposition potential, the deposition time, the electrolyte composition, etc. On the other hand, the value of ZT is more than one order of magnitude lower than for bismuth telluride, but is comparable to those of constantan and chromel which are namely used in thermocouples (see Table 7 for the different values of ZT). These evaluated thermoelectric properties of the PyCu sample are based on some approximations, namely for the ZT computation based on the use of Wiedemann-Franz relation. Therefore, these values may not be accurate and the comparison with the typical thermoelectric materials might be slightly modified.

3.2 Multilayered permalloy/copper sample

The different results of the multilayered Py/Cu sample are presented in this section. The static magnetic properties are presented, highlighting the easy direction of magnetisation. This allows to qualitatively know the ratio between the FM layers thickness and the NM layer thickness. The GMR effect is also presented, confirming the results obtained by AGM measurements. Finally, the magnetothermoelectric properties are presented, emphasizing the high difference between the two spin-dependent Seebeck coefficients at RT as well as the significant magnetic control on the thermoelectric properties for the system.

3.2.1 Static magnetic properties

Figure 44 provides the AGM measurement of the Py/Cu multilayered sample in both IP and OOP directions at RT. This measurement depicts the saturation magnetisation easily reach when the external field is oriented in the OOP direction. This arises from the contribution of shape anisotropy of the NWs combined with the dipolar coupling between the FM layers (see Subsection 1.1.5). Therefore, these AGM measurements allows to evaluate the ratio between the Py layers thickness and the Cu layers thickness $t_{\text{Py}}/t_{\text{Cu}}$ to be larger than one. These contributions dominate the magnetic behaviour compared to the contribution arising from the interconnections between the NWs. This is coherent with the SEM images (see Section 2.2) showing the low volume fraction of interconnections compared to NWs segments.

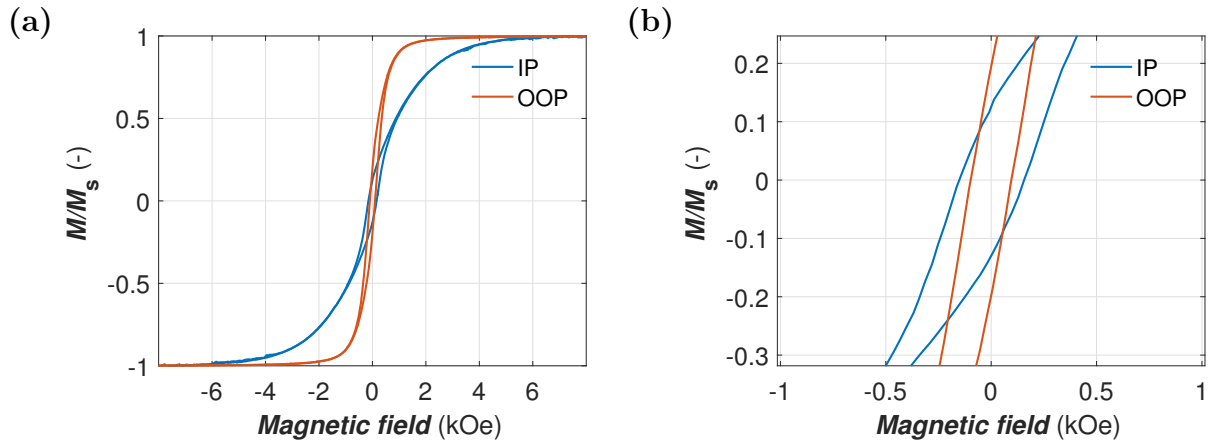


Figure 44: **(a)** AGM measurement of the Py/Cu multilayered sample in both IP (blue line) and OOP (red line) directions. **(b)** Zoom around the origin of the curve in **(a)**.

The coercive field in the OOP direction is lower than the one in the IP direction. The diameter of the nanopores, being of 80 nm, is much larger than the FM layers thickness, which does not exceed much more than two times the spin diffusion length of Py at most. Therefore, the shape anisotropy would force the easy axis to be oriented in the plane of the layers. This is not observed in the AGM measurements, as the easy axis is oriented in the direction perpendicular to the layers. The Cu layers are expected to be very thin,

enhancing the dipolar coupling between successive FM layers. This leads to a head-to-tail configuration the magnetisation inside the FM layers. Therefore, the MR measurements are expected to show a saturation reach easier when the external field is applied in the OOP direction. The remanence, expressed as a fraction of the saturation magnetisation, and the coercive field are given in Table 11 for both IP and OOP directions.

M_r/M_s in OOP [-]	M_r/M_s in IP [-]	H_c in OOP [kOe]	H_c in IP [kOe]
0.2	0.12	0.095	0.156

Table 11: Data of the normalised remanence M_r/M_s and the coercive field H_c in both the IP and the OOP directions.

3.2.2 Magnetoresistance characterisation

Figure 45 depicts the CPP-GMR measurements on the Py/Cu sample in both IP and OOP directions at RT. As presented in Subsection 1.2.2, the resistance in the AP configuration (near $H = 0$ Oe) is higher than the resistance in the P configuration (when H is maximal). The evaluation of the GMR ratio from these measurements are:

$$GMR = 100 \frac{R_{\max} - R_{\text{sat}}}{R_{\text{sat}}} \quad [\%], \quad (47)$$

$R_{\max}$ being the maximal resistance and R_{sat} the resistance when the external field is maximal. These are supposed to correspond to R_{AP} and R_{P} respectively (see Equation 28 in Subsection 1.2.2). Table 12 provides the GMR ratio in the IP (GMR^{IP}) and OOP (GMR^{OOP}) directions at different temperatures. The value of the external field when the resistance was maximal is also provided. These are represented by $H_{\max}^{\text{OOP}}$ for the OOP direction and $H_{\max}^{\text{IP}}$ for the IP direction. The maximal uncertainty for the resistance measurement is around 25 mΩ.

Temperature [K]	GMR^{IP} [%]	GMR^{OOP} [%]	$H_{\max}^{\text{IP}}$ [kOe]	$H_{\max}^{\text{OOP}}$ [kOe]
295	20.4	18.8	-0.3	-0.14
150	40.4	34.8	-0.28	-0.28
15	57.8	48.1	-0.59	-0.29

Table 12: Data on the magnetoresistance properties of PyCu samples: GMR ratio in both IP and OOP directions, external field at maximum resistance in both IP and OOP directions.

This high GMR ratio is coherent with what was found previously on Py/Cu/Py trilayers [8]. The saturation is reached at lower external field in the OOP direction than in the IP direction. This is coherent with the AGM curve obtained (see Figure 44), confirming the combination of shape anisotropy of the NWs and the dipolar coupling between the FM layers dominating the magnetic behaviour. The resistance at saturation is lower when the

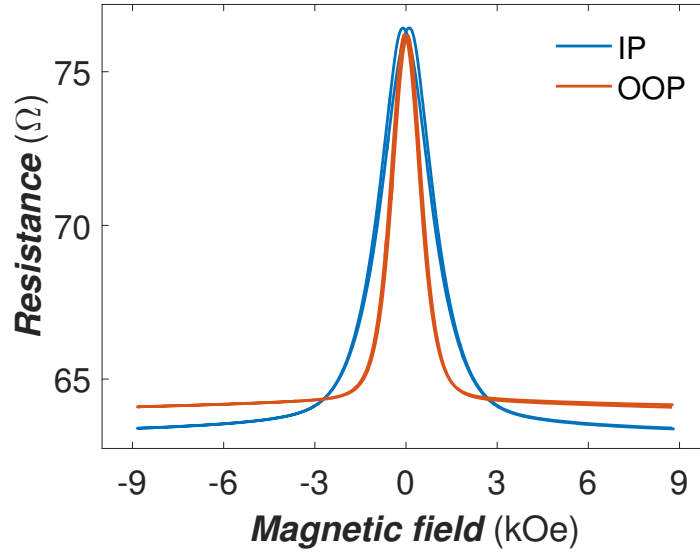


Figure 45: CPP-GMR measurement of the Py/Cu multilayered sample at RT. Measurements in both IP (blue line) and OOP (red line) directions are provided.

external field is applied in the IP direction. This due to the anisotropic magnetoresistance. Indeed, when saturated in the IP direction, the magnetisation of the Py layers exhibit an angle with the current flow higher than in saturation in the OOP direction. Therefore, the difference in resistance at saturation between both directions is related to the AMR ratio. This gap is estimated around 1.2%, a significantly smaller value than the value of the AMR ratio. This arises from the resistivity states at saturating external field in IP and OOP directions both exhibit an certain angle between the magnetisation and the current flow. Therefore, the gap between these resistivity states is smaller than the gap between $\rho_{\parallel}$ and $\rho_{\perp}$.

The evolution of the resistances in AP configuration (R_{AP}) and P configuration (R_P) are provided in Figure 46. The temperature dependence of these resistances is similar to the one presented for the PyCu sample (see Figure 38 in Subsection 3.1.1), with a saturation at sufficiently low temperatures. The maximal uncertainty on R_P and R_{AP} are around 21 mΩ and 25 mΩ respectively. The resistances measured at 75 K do not seem to fit exactly the global behaviour. This is due to a thermal cycling: after the magnetoresistance measurements were performed at 100 K, the temperature was raised up to RT before being put back at 75 K. This thermal cycling increases the residual resistivity ρ_{res} of the sample. This creates a small "mismatch" of the measurements for temperatures below 75 K and above 75 K. The curve has been shifted upwards due to thermal cycling.

The GMR resistance is strongly influenced by the temperature, increasing by almost a factor 3 between the values at 295 K and 15 K. The evolution of the GMR ratio with temperature is provided in Figure 47. The maximal uncertainty on the GMR ratio is around 0.08%. The GMR ratio increases almost linearly when temperature is decreased, reaching a saturation at sufficiently low temperatures. This behaviour is similar to the evolution of the MR of the homogeneous PyCu sample. This similarity was expected regarding the definitions of these ratios (see Equations 47 and 45). The saturation of the GMR ratio is related to the saturation of the resistance at sufficiently low temperatures,

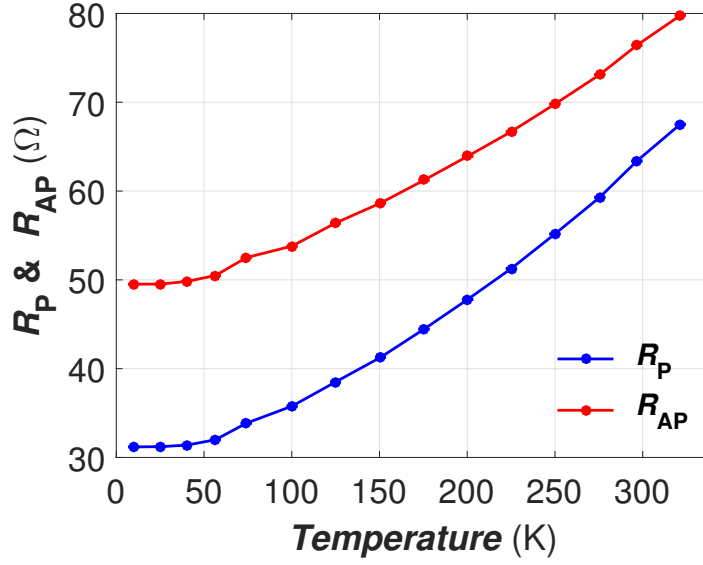


Figure 46: Evolution of R_P and R_{AP} with the temperature for the Py/Cu multilayered sample.

the electrical conductivity being only limited by static defects inside the sample.

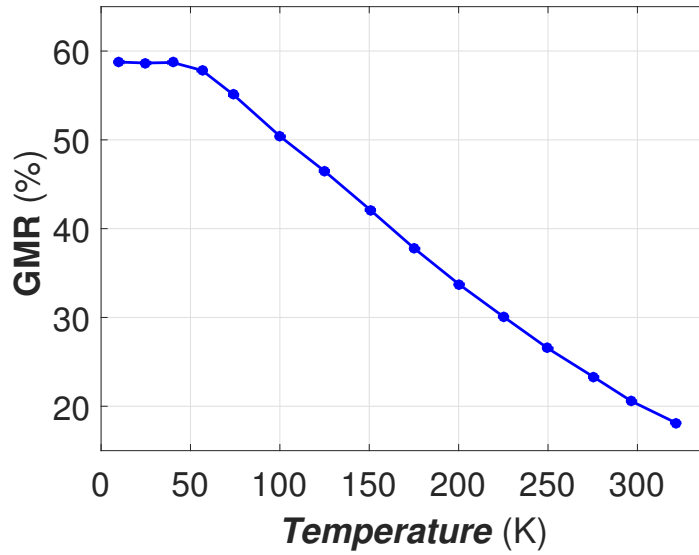


Figure 47: Evolution of the GMR ratio with the temperature for the Py/Cu multilayered sample.

The determination of the spin-dependent Seebeck coefficients also relies on the magnetoresistance through the MR ratio value (see Equation 38). The analogous expression of MR for multilayered CNWs compared to homogeneous samples is given by:

$$\text{MR} = 100 \frac{R_{AP} - R_P}{R_{AP}} \quad [\%]. \quad (48)$$

This expression is similar to the one used to define the GMR ratio (see Equation 28 in

Subsection 1.2.2). Therefore, the evolution of MR with temperature is analogous to the one of the GMR ratio. The MR ratio increases as temperature drops until remaining constant at low temperatures. This plateau is related to the constant resistance at sufficiently low temperatures. The value of the MR is significantly smaller than the value of the GMR ratio. This arises from the normalisation by the higher resistance state R_{AP} for the MR. Similarly to the case of the PyCu sample, the magnetoresistance measurements allow to evaluate the sample quality by computing the RRR. The evaluation was based using the resistance in AP configuration R_{AP} at 300 K and 10 K. The ratio gives a value of 1.54, slightly lower than the RRR ratio of the homogeneous PyCu sample. This smaller value is coherent with the static defects arising from interfaces between the Py layers and the Cu layers, which adds to the Cu impurities present in both Py layers of the Py/Cu multilayered and PyCu homogeneous sample.

Furthermore, the resistivity in P configuration (ρ_P) and in AP configuration (ρ_{AP}) at RT can be approximated (See Supplementary material in [4]). The model is based on a simple circuit in series for the multilayered stack. The resistivity in P configuration at RT is decomposed in two contributions following Mathiessen's rule:

$$\rho_P^{RT} = \rho_P^0 + \frac{\rho_{Py}^{RT} t_{Py} + \rho_{Cu}^{RT} t_{Cu}}{t_{Py} + t_{Cu}} \quad [\Omega m], \quad (49)$$

ρ_P^{RT} being the resistivity in P configuration at RT, ρ_P^0 the residual resistivity in P configuration, ρ_{Py}^{RT} and ρ_{Cu}^{RT} the ideal resistivity at RT of Py and Cu respectively, and t_{Py} and t_{Cu} the thickness of the Py and Cu layers respectively. Neglecting the temperature dependence of the interfaces scattering and considering the ratio of the layers thicknesses $\lambda = t_{Py}/t_{Cu}$, ρ_P and ρ_{AP} at RT can be approximated by:

$$\begin{aligned} \rho_P &\approx \frac{\rho_{Py}^{RT} + \rho_{Cu}^{RT}}{(1 + \lambda)(1 - RRR^{-1})} \\ \rho_{AP} &= \frac{\rho_P}{1 - MR} \end{aligned} \quad [\Omega m]. \quad (50)$$

Using ideal resistivities of Py and Cu found in the literature [73] and considering $\eta = 1$, ρ_P and ρ_{AP} are evaluated around $22.1 \mu\Omega cm$ and $26.53 \mu\Omega cm$ respectively. These resistivities are comparable with the resistivity at RT of the PyCu homogeneous sample.

3.2.3 Magneto-Seebeck characterisation

The magneto-Seebeck measurement is provided in Figure 48. As for the homogeneous PyCu sample, the magneto-Seebeck curve is very similar to the CPP-GMR measurement. Moreover, this measurement exhibits a high quality, mainly due to the high signal provided by the sample. Indeed, a high GMR effect induces a large MTP. The maximal uncertainty on the Seebeck coefficient is around 76 nV/K.

Again, the shape of the multilayered NWs and the dipolar coupling between the FM

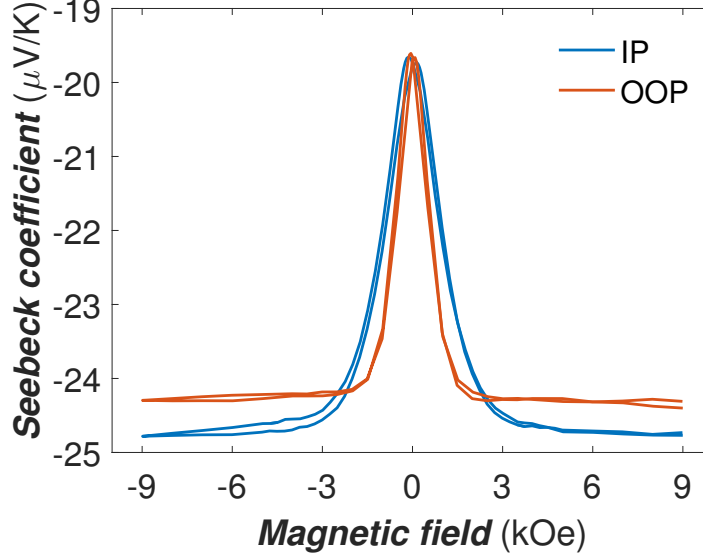


Figure 48: Magneto-Seebeck measurement of the Py/Cu multilayered sample at RT. The IP direction is represented by the blue line, while the OOP direction is depicted by the orange line.

layers are emphasised in this curve. Indeed, the saturation of Seebeck coefficient is easily reached in the OOP direction. Similarly to the case of the GMR measurements on the Py/Cu sample (see Figure 45), a gap is observed between the Seebeck coefficients at saturating external field in IP and OOP directions. This gap corresponds to a value of 1.5%, comparable to the one observed in the GMR measurement. As the Seebeck coefficient is related to the resistivity by Mott's formula (see Equation 30), the gap observed for S is indirectly related to the AMR effect.

On the other hand, S is higher in absolute value at saturation in the IP direction. Considering the multilayered stack, the Seebeck coefficient measured is significantly influenced by the geometry of the measurement: CIP (in the plane of the layers) or CPP (perpendicular to the layers). Using a simple Kirchoff's laws, it is possible to express the Seebeck coefficient in both types of measurements [5]:

$$S_{\text{CPP}} = \frac{S_{\text{Cu}}\kappa_{\text{Py}} + \lambda S_{\text{Py}}\kappa_{\text{Cu}}}{\lambda\kappa_{\text{Cu}} + \kappa_{\text{Py}}} \quad [\text{V/K}], \quad (51)$$

S_{CPP} being the Seebeck coefficient in the CPP measurement configuration, S_{Cu} and S_{Py} the Seebeck coefficient of copper and permalloy, κ_{Cu} and κ_{Py} the thermal conductivity of Cu and Py. Assuming that the Wiedemann-Franz law can be applied for the metallic alloy, the expression of S_{CPP} reduces to:

$$S_{\text{CPP}} = \frac{S_{\text{Cu}}\rho_{\text{Cu}} + \lambda S_{\text{Py}}\rho_{\text{Py}}}{\lambda\rho_{\text{Py}} + \rho_{\text{Cu}}} \quad [\text{V/K}], \quad (52)$$

ρ_{Cu} and ρ_{Py} being the electrical resistivity of Cu and Py respectively. In contrast, the Seebeck coefficient in the CIP measurement configuration is given by:

$$S_{\text{CIP}} = \frac{S_{\text{Cu}}\rho_{\text{Py}} + \lambda S_{\text{Py}}\rho_{\text{Cu}}}{\lambda\rho_{\text{Cu}} + \rho_{\text{Py}}} \quad [\text{V/K}]. \quad (53)$$

Using the ideal resistivity values for ρ_{Py} and ρ_{Cu} at RT, the evolution of S_{CIP} and S_{CPP} with respect to λ is provided in Figure 49. Note that the use of Wiedemann-Franz law to link the thermal conductivity to the electrical resistivity is not straightforward for metallic alloys. Therefore, Figure 49 does not give quantitative results: the measured S of the multilayered sample is significantly lower than the one of the homogeneous sample. The aim is to emphasise the interest of using CPP configuration instead of CIP for thermoelectric devices with large Seebeck coefficients. Indeed, the case of $\lambda \rightarrow \infty$ leads to the homogeneous crossed NWs of Py. However, using CPP configuration, the Seebeck coefficient reaches faster the one of the FM material. This difference between CIP and CPP measurement is enhanced as $S_{\text{Py}} \gg S_{\text{Cu}}$ and $\rho_{\text{Py}} \gg \rho_{\text{Cu}}$.

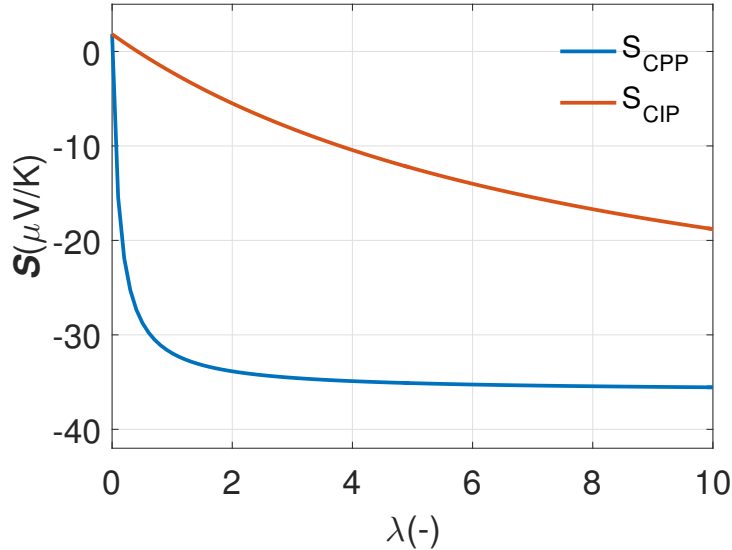


Figure 49: Evolution of the Seebeck coefficient measured in CIP and CPP configuration with the ratio of layers thickness $\lambda = t_{\text{FM}}/t_{\text{NM}}$.

The evolution of the mean temperature and the applied temperature difference are provided by Figure 50. As for the PyCu sample, their variation is quite small, typically ranging in few tens of mK. The external field does not seem to alter both the mean T and ΔT : no clear relationship with the external field can be extracted from Figures 41 and 50.

The different Seebeck coefficients with respect to temperature are represented in Figure 51. The Seebeck coefficients in P and AP configuration were measured applying the external field in the IP direction. The spin-dependent Seebeck coefficients were computed following Equation 38. The maximal uncertainty on S_{P} , S_{AP} , $S_{\uparrow}$ and $S_{\downarrow}$ are around 107 nV/K, 104 nV/K, 175 nV/K and 170 nV/K respectively.

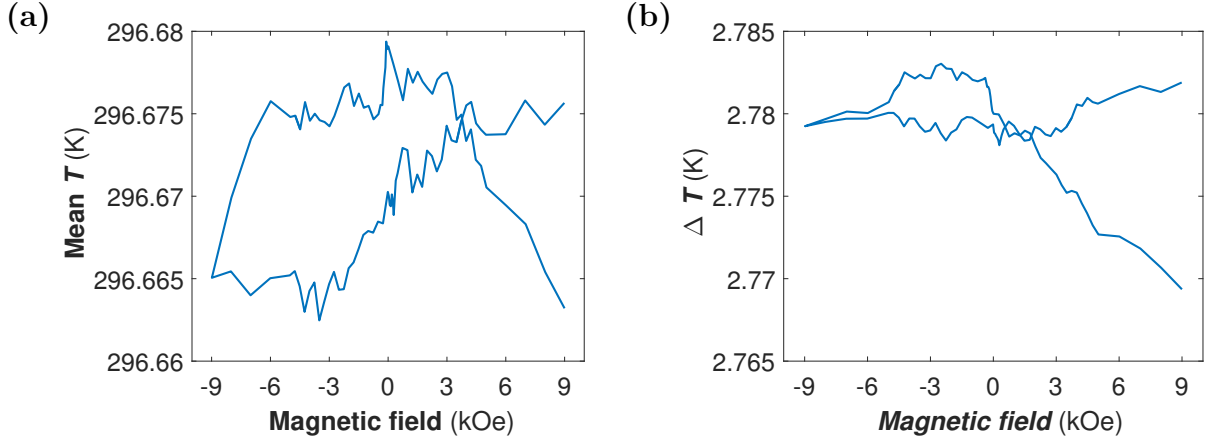


Figure 50: Evolution of (a) the mean temperature and, (b) the temperature difference with the external field for the Py/Cu multilayered sample.

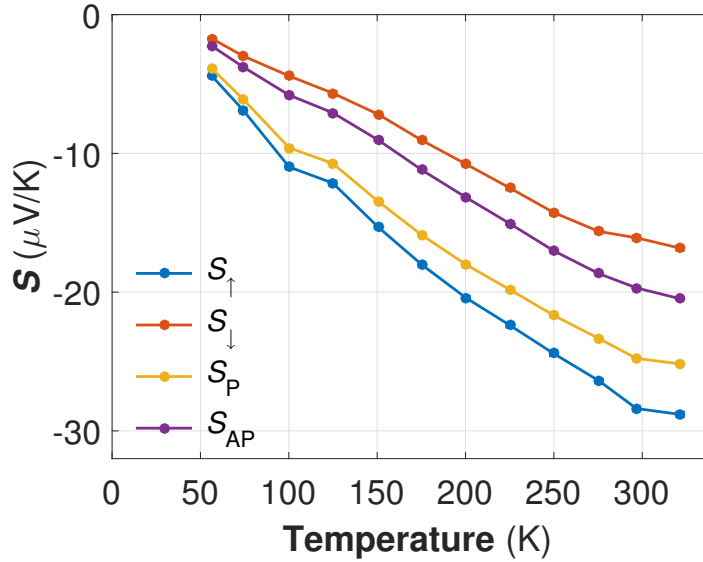


Figure 51: Measured Seebeck coefficients in the AP configuration S_{AP} (purple line) and at saturating external field S_P (yellow line), along with the computed $S_{\uparrow}$ (blue line) and $S_{\downarrow}$ (red line).

The evolution of S_P , S_{AP} , $S_{\uparrow}$ and $S_{\downarrow}$ is similar to the one of the PyCu sample depicted in Figure 42. The behaviour is close to a linear relationship, highlighting the diffusion regime that dominates. The data for temperatures lower than 100 K seem to exhibit a slope different than data for temperatures higher than 100 K. This is due to a thermal cycling experienced by the sample: the temperature was raised up to RT before going down again to 100 K. Therefore, the Seebeck coefficient slightly decreases in absolute value due to this thermal cycling of the sample.

The presence of the Cu layers decreases the Seebeck coefficient compared to the PyCu homogeneous sample, S dropping from $-36 \mu\text{V/K}$ in the homogeneous sample to $-20 \mu\text{V/K}$ in the AP configuration of the multilayered sample. This is namely due to the interconnections, where the multilayered stack is not sure regarding quality, and the influence of interfaces.

On the other hand, the evolution of $S_{\uparrow}$ is close to the one of S_P . This is also the case for $S_{\downarrow}$ and S_{AP} . This arises from Equation 38 and the value of β . Indeed, if this spin asymmetry coefficient tends to 1, then $S_{\uparrow} \rightarrow S_P$ and $S_{\downarrow} \rightarrow S_{AP}$. Therefore, the closer β is to 1, the more similar are the behaviours of $S_{\uparrow}$ and S_P (and in parallel $S_{\downarrow}$ and S_{AP}). The value of β at RT is around 0.413 with an uncertainty of $5 \cdot 10^{-4}$. From this value, the spin-dependent Seebeck coefficients can be evaluated, according to Equation 38 (see Subsection 1.3.2). Data at RT are provided in Table 13

S_P [$\mu\text{V/K}$]	S_{AP} [$\mu\text{V/K}$]	β [-]	$S_{\uparrow}$ [$\mu\text{V/K}$]	$S_{\downarrow}$ [$\mu\text{V/K}$]
-24.8	-19.7	0.413	-28.4	-16.08

Table 13: Data on S_P , S_{AP} , β , $S_{\uparrow}$ and $S_{\downarrow}$ at RT obtained for the multilayered Py/Cu sample.

The difference between the spin-dependent Seebeck coefficients $S_{\uparrow} - S_{\downarrow}$ increases as temperature is raised, both tending to zero when $T \rightarrow 0$ K. This difference is $-12.3 \mu\text{V/K}$ at 300 K. This value is significantly higher than the one found in Py nanopillar spin valves, which gave $S_{\uparrow} - S_{\downarrow} = -4.5 \mu\text{V/K}$ [74].

Figure 52 provides the comparison between the linear relation $\Delta S = B\Delta(1/R)$ described in Equation 34 in Subsection 1.3.2 and the experimental measurements. The data points represent the experimental data, while the full line represents the theoretical linear relation. Data are provided at four different temperatures: 56 K, 100 K, 200 K and 297 K.

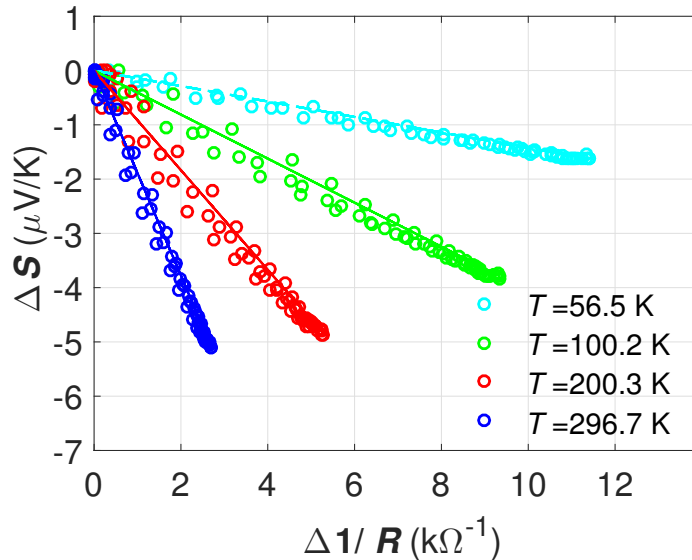


Figure 52: Linear relation of $\Delta S(H)$ vs $\Delta 1/R(H)$ of the multilayered Py/Cu sample at different temperatures. The experimental data emphasises the domination of the diffusive regime regarding the Seebeck effect.

The global behaviour of the experimental data fits relatively well the theoretical linear relationship described by Equation 34, specially at low temperature and RT. The experimental data are a bit more dispersed at intermediate temperature (100 K and 200 K).

This dispersion may be due to other contributions as magnon-drag explained in Subsection 1.3.2. However, the global behaviour is coherent with a domination of the diffusive regime regarding the Seebeck effect, already emphasised by the linear relation of the Seebeck coefficients with temperature (see Figure 51).

The MR ratio and MTP at different temperatures are depicted at Figure 53. The MTP is here higher than the MR unlike the PyCu sample (see Figure 43). Again, the evolution of MTP can not be explained by Mott's formula, but the high values are related to the large GMR effect that is observed in the Py/Cu sample. The value of MTP at RT is around $-25.8 \pm 0.5 \mu\text{V/K}$ comparable to the one found for NiCo/Cu sample on the same system [4]. On the other hand, MTP increases significantly when temperature drops, reaching a value of $72 \pm 3 \mu\text{V/K}$ around 50 K. This behaviour was not observed for the NiCo/Cu sample [4]. The maximal uncertainty for the MR ratio and MTP are around 0.05% and 2%, respectively.

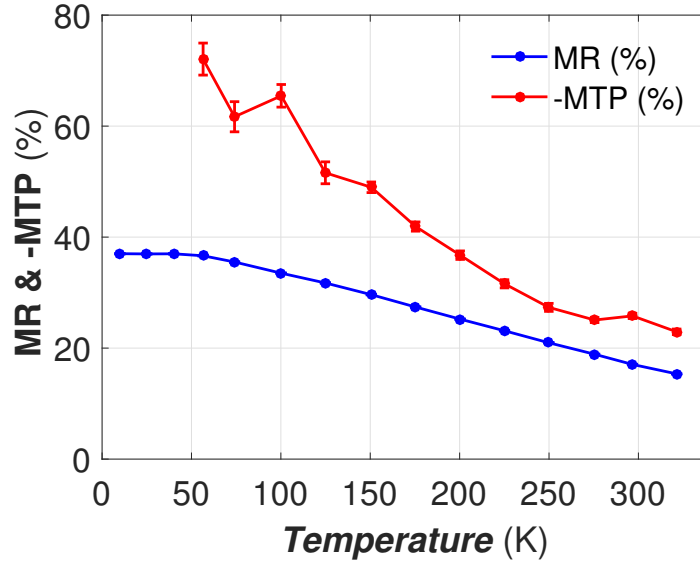


Figure 53: Magnetoresistance MR ratio and magnetothermopower MTP of the Py/Cu sample at different temperatures.

Figure 54 provides the evolution of the magneto-power factor MPF with temperature. To evaluate it, the following formula was used [4]:

$$\text{MPF} = \frac{(1 - \text{MTP})^2}{1 - \text{MR}} - 1 \quad [\%]. \quad (54)$$

Therefore, the evolution of MPF is unsurprisingly related to the evolution of MTP, MR varying linearly with temperature before saturation at low T . The MPF is evaluated at $91\% \pm 0.7$ at RT, a slightly lower value than the one determined for NiCo/Cu sample [4]. However, as for MTP, MPF increases significantly when temperature drops, reaching a value of $370\% \pm 12$ around 50 K. This shows the possible magnetic control for the output thermoelectric power. The maximal uncertainty on the MPF is around 6%.

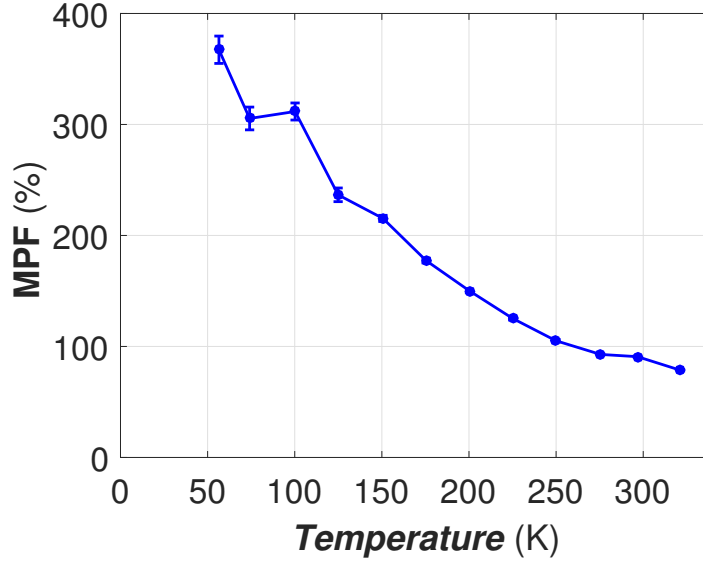


Figure 54: Evolution of the magneto-power factor MPF of the multilayered sample with temperature.

The power factors in P configuration PF_P and AP configuration PF_{AP} of the multilayered stack at RT are determined using the same model used for NiCo/Cu sample [4]. The resistivity in both P and AP configuration have been determined and the Seebeck coefficients in both directions have been measured. These data, along with the computed PF are provided in Table 14.

S_P [$\mu V/K$]	S_{AP} [$\mu V/K$]	ρ_P	ρ_{AP} [$\mu\Omega cm$]	PF_P [mW/K^2m]	PF_{AP} [mW/K^2m]
-24.8	-19.7	22.1	26.53	2.8	1.5

Table 14: Data on the power factors in P and AP configuration of the Py/Cu multilayered sample at RT.

These values are significantly lower than the PF value of the homogeneous PyCu sample, being smaller by a factor higher than 2. On the other hand, these are comparable with the one of the widely used thermoelectric material bismuth telluride, ranging between 1 mW/K^2m and 5 mW/K^2m [51]. These values can only be qualitatively compared to the values for typical thermoelectric materials, as they are only approximations of the true values. Indeed, the magnetic characterisation of the Py/Cu sample exhibits a value of λ higher than unity (see Subsection 3.2.1), meaning that the Py layers thickness is larger than the Cu layers thickness. Computing the PF by considering a higher value of λ reduces slightly its value, but the order of magnitude remains the same.

Similarly to the case of the homogeneous sample, the thermoelectric figure of merit ZT in both P and AP configurations of the Py/Cu sample can be evaluated assuming that Wiedemann-Franz relation holds. This leads to values around 0.025 for the P configuration and 0.016 for the AP configuration at RT. These values are slightly lower than the ones found for NiCo/Cu samples [4], being comparable to those of constantan or chromel (see Table 7 in Subsection 1.3.1).

3.3 Control of the nickel-iron composition and influence of nickel content in alloy properties

In this section the influence of the Ni content on the properties of homogeneous Ni-Fe CNWs will be discussed. The different compositions are presented with the deposition potential used during the electrodeposition step. Afterwards, the static magnetic properties of all homogeneous samples are presented, emphasizing their similar behaviour as expected from the literature. Then, the AMR ratio of the different alloys is presented in comparison with literature. Finally, the Seebeck coefficient of the samples are presented, highlighting the interest of these alloy compositions regarding the thermoelectric properties.

The work done during this thesis focuses on Ni-Fe alloys with a Ni content around 85%, leading to the so-called permalloy system. On the other hand, the electrodeposition process allows to control the composition of the Ni-Fe alloy by modifying the deposition potential E . Indeed, the deposition rate of each material is influenced by E differently for each chemical species, allowing for instance to deposit nickel and iron at the same rate. Figure 55 provides the evolution of the Ni content in the alloy with respect to the deposition potential. The samples were grown on the same template as the one used for the PyCu sample. The alloy composition were determined using EDX spectrum, removing the Cu content to evaluate the ratio between the Ni content and the Fe content.

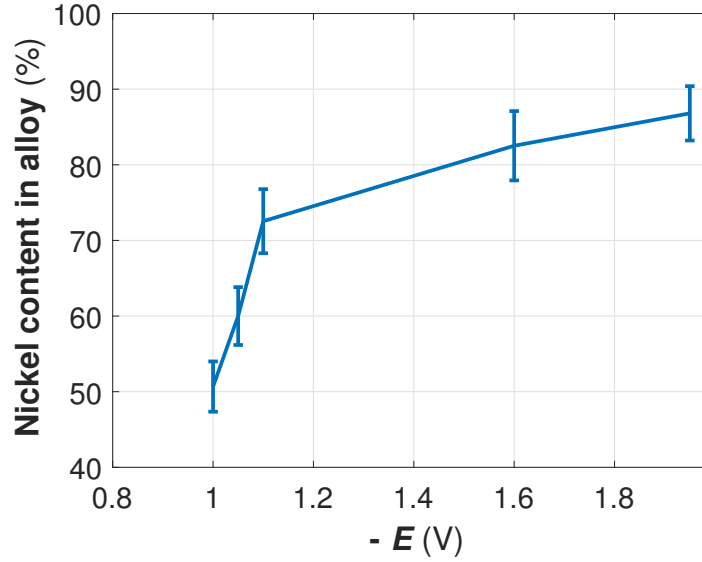


Figure 55: Control of the Ni content in the alloy by the deposition potential E . This content was evaluated considering only nickel and alloy atomic composition meaning that copper was neglecting to determine the alloy composition. The errors provided arise from the typical EDX error for atomic composition determination.

The drop of Ni content in the alloy occurs in a small window, from $E = -1.1$ V and $E = -1$ V, leading to Ni content of around 70% and 50% respectively. Table 9 in Section 2.2 provides the Ni content as well as the Cu content in the homogeneous samples. The uncertainty on the Cu content is typically around 5%.

As both Ni and Fe exhibit a cubic crystalline structure, modifying the composition of the nickel-iron alloy would not lead to the appearance of magnetocrystalline anisotropy. However, as depicted in Figure 4 (see Subsection 1.1.1), the easy and hard axis of magnetisation for bcc-Fe and fcc-Ni are different. Moreover, the magnetic permeability of the Ni-Fe alloy is also influenced by the alloy composition. Therefore, the remanence of the samples could be different for each alloy composition. The AGM measurements of the different samples are provided in Figure 56.

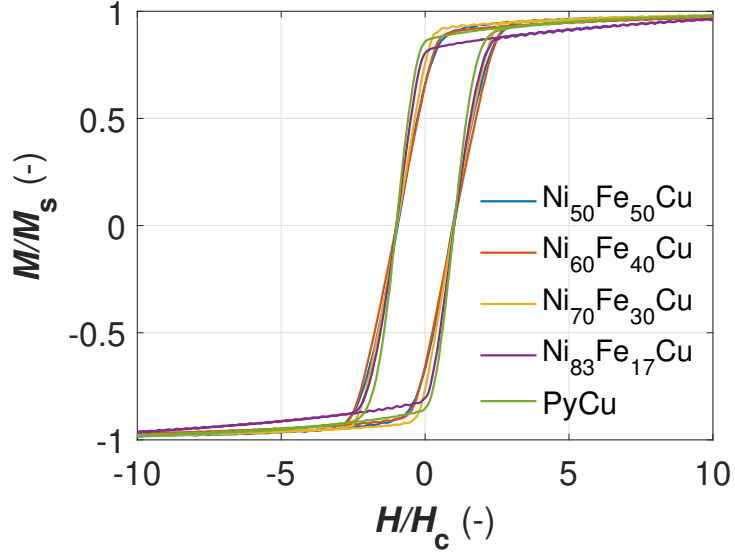


Figure 56: AGM measurements of the normalised magnetisation M/M_s with respect to the normalised external magnetic field H/H_c . The curves of the different homogeneous samples presented in Table 9 are provided. The external magnetic field was applied in the OOP direction, which is the most interesting one regarding the sample geometry.

As mentioned, the global behaviour of the different homogeneous samples are quite similar. The hysteresis loop is mainly dominated by the shape anisotropy arising from the NWs. On the other hand, the remanence normalised by the saturation magnetisation increases as the Ni content rises, except for the balanced composition of the alloy. The coercive field H_c also increases as the Ni content in the alloy raises. This is depicted in Table 15.

Sample label	M_r/M_s [-]	H_c [Oe]
PyCu	0.85	396
Ni ₈₃ Fe ₁₇ Cu	0.8	365
Ni ₇₀ Fe ₃₀ Cu	0.75	337
Ni ₆₀ Fe ₄₀ Cu	0.65	305
Ni ₅₀ Fe ₅₀ Cu	0.65	247

Table 15: Data on the normalised remanence M_r/M_s for the different homogeneous samples.

The impact of the Ni content inside the alloy on the magnetoresistance properties is

depicted in Figure 57, with a comparison of what was found in literature [25].

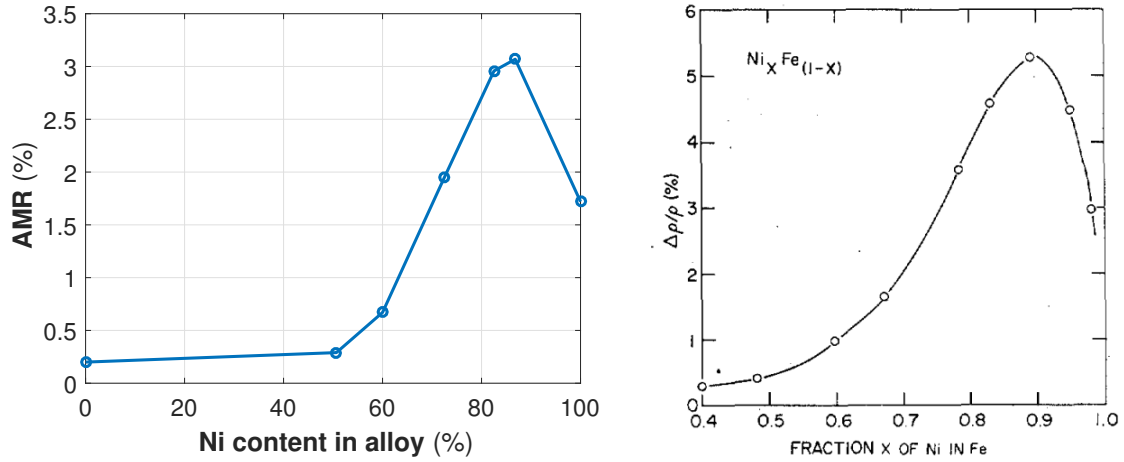


Figure 57: Evolution of the AMR ratio of Ni-Fe alloys with the Ni content. The experimental data obtained in this thesis (left figure) and the results found in literature (right figure) are presented. Right figure from [25].

The global behaviour of the AMR ratio with the Ni content is similar to the one found by McGuire *et al.* [25]. This was also observed for NiCo CNWs [1], reaching a global behaviour close to the one presented by McGuire *et al.* [25]. However, the values experimentally found are lower than they obtained. This can be explained by the presence of different static impurities inside the homogeneous samples, due to the electrodeposition process which might give rise to a high residual resistivity compared to other process. The presence of this residual resistivity tends to weaken the AMR effect. Moreover, the model used to estimate the AMR ratio is an approximation [3], as it considers only a 2D picture of the NWs exhibiting an angle of 25° with respect to the normal of the template plane. The evolution of the AMR with the Ni content at different temperatures is provided in Figure 58. The global behaviour of the AMR is similar at each temperature. Moreover, the AMR is increased by a factor of almost 3, coherent with what was observed for NiCo CNWs [1].

The last investigations on the impact of Ni content inside the alloy are related to the Seebeck coefficient. Indeed, the recommended values of S for Ni-Fe alloys at RT increases when the Ni content is reduced. The electrodeposited homogeneous samples were analysed by measuring the Seebeck coefficient at RT in absence of external field. The results are provided in Figure 59, along with the values provided in literature [10].

The measured values of S are close to the ones given by Ho *et al.* [10]. This confirms the quality of the measurement of the Seebeck coefficient using the system described in Subsection 2.3.3. The high value of the Seebeck coefficient for $\text{Ni}_{60}\text{Fe}_{40}$ gives some interest regarding thermoelectric generation. However, the electrical resistivity of the nickel-iron alloys increases as the Ni content falls down [73]. Therefore, the increase of S will be followed by an increase of the electrical resistivity. As done for the homogeneous PyCu sample, the PF and thermoelectric figure of merit can be evaluated, using the RRR and

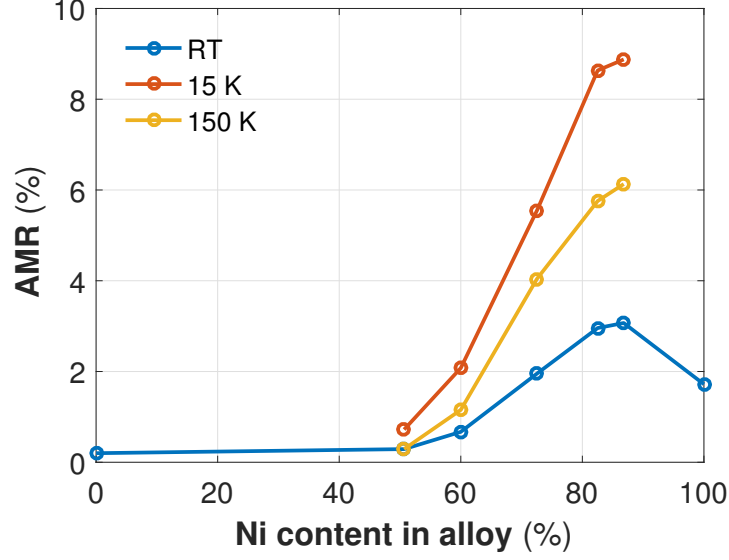


Figure 58: Evolution of the AMR with the Ni content in the alloy at room temperature, 150 K and 15 K.

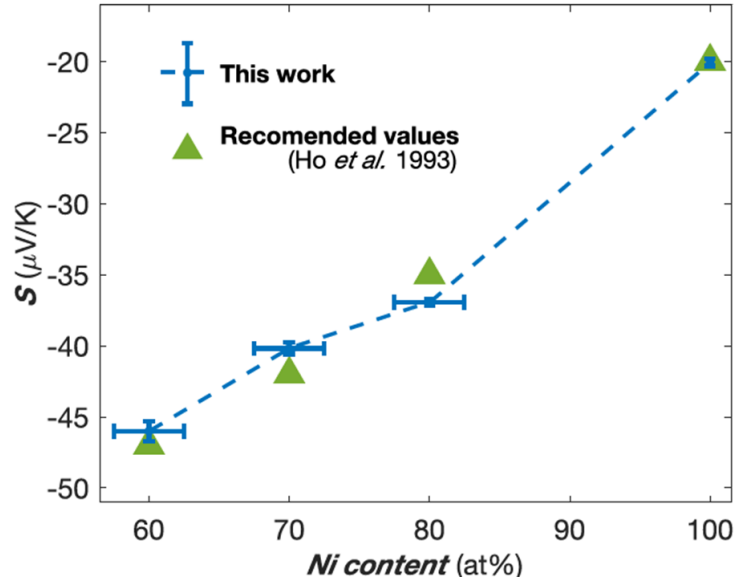


Figure 59: Comparison between the measured Seebeck coefficient in absence of external field S_0 for different Ni content in the alloy with recommended values from [10]. Data for pure Ni sample were obtained by Luc Piraux' group at the Institut of Condensed Matter and Nanosciences (IMCN) at Université Catholique de Louvain. Errors arising from the Ni content determination (horizontal intervals) as well as the errors for S determination (vertical intervals) are provided.

assuming that Wiedemann-Franz relation holds (see Section 3.1 for the details). The data are provided in Table 16.

The PF seems to stay constant when the Ni content in the alloy decreases. This is due to the gain in Seebeck coefficient being compensated by the increase in resistivity [73]. On the other hand, the thermoelectric figure of merit ZT increases when the Ni content

Sample label	S [$\mu\text{V}/\text{K}$]	ρ_i [cm]	RRR [-]	PF [$\text{mW}/\text{K}^2\text{m}$]	ZT [-]
PyCu	-37.4	14 [73]	2.27	5.6	0.057
Ni ₇₀ Fe ₃₀ Cu	-40	17 [73]	2.1	5	0.066
Ni ₆₀ Fe ₄₀ Cu	-46	22 [73]	2.08	5	0.087

Table 16: Data on the Seebeck coefficient S , ideal resistivity ρ_i , RRR, power factor and thermoelectric figure of merit ZT for the different homogeneous Ni-Fe alloy samples at RT. The ideal resistivity at RT was found from [73].

is decreasing, reaching a value higher than for constantan. Note that, the evaluation of ZT is based on Wiedemann-Franz relation. This holds for metallic materials, but this approximation may be rough considering metallic alloys. Moreover, the quality of the electrodeposited may be poor considering the fabrication of balanced Ni-Fe alloys. However, higher PF values than the one found in Table 10 by optimisation of the electrodeposition process to reduce the residual resistivity of the sample.

Conclusion and perspectives

This Master thesis has investigated various magnetotransport properties of interconnected NW networks made of Ni-Fe alloys electrodeposited in porous PC templates. These track-etched templates exhibit crossed nanopores inside which the NWs were grown. The connectivity between them gives a significant mechanical stability of the macroscopic film after the dissolution of the PC template. Moreover, this interconnectivity facilitates the electrical characterisation of the system as shown by the set-up used for magnetoresistance measurements.

The magnetic properties of both homogeneous and multilayered Py/Cu samples have been investigated. These emphasise the dominance of the shape anisotropy for homogeneous CNWs with the easy axis oriented along the NWs. The multilayered sample also exhibits an easy axis oriented in the same direction as for the homogeneous samples, due to both shape anisotropy and dipolar coupling induced by the thin NM layers between the FM layers. This raises a head-to-tail configuration of the successive FM layers magnetisation oriented along the NWs axis.

The AMR of the homogeneous CNWs has been determined using a simple model based on magnetoresistance measurements of the CNWs. The evolution of the AMR with the Ni content in the alloy has been presented, highlighting the peak around a Ni content of around 90%. The values range from 3% for the PyCu sample to 0.3% for the $\text{Ni}_{50}\text{Fe}_{50}\text{Cu}$ sample, in good agreement with the results presented in the literature [25]. Moreover, the temperature dependence of the AMR for the alloys was also presented, highlighting an increase of a factor of almost 3 between values at RT and at 15 K, going from 3% up to 8.9% for the PyCu sample.

The GMR effect of the multilayered Py/Cu has been investigated, exhibiting a high value of 20% at RT, rising up to 58% at 15 K. This significant evolution of the GMR with temperature has already been observed for metallic alloys. These values are similar to those obtained on arrays of parallel NWs, highlighting the small impact of the interconnections for the low porosity samples. The magnetoresistance measurements confirm that the orientation of the easy axis of the FM layers magnetisation is along the NWs axis, emphasizing the contributions of both the shape anisotropy and the dipolar coupling [18].

The thermoelectric and magnetothermoelectric properties of the PyCu sample were investigated through magneto-Seebeck measurements. The global behaviour of these measurements are similar to the one for magnetoresistance characterisation. This highlights the link between ρ and S as depicted in Mott's formula, considering the domination of the diffusion regime in the thermoelectric effect. The measured Seebeck coefficient of $-37 \mu\text{V/K}$ was in good agreement with values found in literature. The temperature

dependence of the Seebeck coefficients at saturation and in absence of external field were also provided. These follow almost a linear relation, which is coherent with a dominating diffusion regime contribution to the Seebeck effect.

A simple model was used to determine the residual resistivity of the electrodeposited PyCu sample based on the RRR. From this value, the resistivity of the sample was evaluated and is around $25 \mu\Omega\text{cm}$. The PF of the PyCu sample could be evaluated from the measured Seebeck coefficient and the computed resistivity, giving rise to a value of $5.6 \text{ mW/K}^2\text{m}$ that is slightly higher than bismuth telluride [51].

Similarly to the case of the homogeneous sample, the thermoelectric and magnetothermoelectric properties of the multilayered Py/Cu sample were explored. Again, the magneto-Seebeck measurements were similar to the ones for magnetoresistance characterisation. Furthermore, a high signal-to-noise ratio was observed, leading to high quality magneto-Seebeck measurements comparable to those of magnetoresistance. The measured Seebeck coefficient at RT was around $-20 \mu\text{V/K}$, a significantly lower value than for the corresponding homogeneous sample. On the other hand, the magnetic control of the Seebeck coefficient, represented by the MTP, reaches around 25% at RT. This ratio even increases when temperature decreases, rising up to 70% at 50 K. These values are comparable with the GMR effect observed in this multilayered sample.

Spin-dependent Seebeck coefficients were determined using both magnetoresistance and magneto-Seebeck measurements. The large GMR effect in the multilayered Py/Cu sample allows to measure a quite large gap between the two spin-dependent Seebeck coefficients $S_{\uparrow} - S_{\downarrow} = -12.3 \mu\text{V/K}$. This gap is almost three times larger than the one in Py nanopillars [74].

Finally, the control of the alloy composition through the fine tuning of the deposition potential during the electrodeposition step was highlighted. Various Ni content were reached in the Ni-Fe alloys. The magnetic characterisation of these homogeneous samples shows a similar behaviour between them, highlighting the absence of magnetocrystalline anisotropy contribution for these alloys. The Seebeck coefficients at RT in absence of external field were measured, exhibiting similar values to the ones found in the literature [10]. The application of the simple model used to determine the PF of those samples leads to values comparable to those of PyCu sample. The increase in absolute value of the Seebeck coefficient is compensated by a higher resistivity when the Ni content in the alloy decreases.

The results presented in this thesis highlights the interest of using interconnected NW networks for both magnetoresistance and magnetothermoelectric characterisations. The quality of the measurements allows to determine accurately (spin-dependent) thermoelectric properties. Ni-Fe alloys are of great interest regarding the large GMR effect along with their high Seebeck coefficient. The Ni-Fe samples allows to reach PF values comparable or even higher than for bismuth telluride, using a simple and cheap electrodeposition fabrication process. This influences the residual resistivity of the sample, the fabrication quality depending on several parameters such as the deposition potential, the deposition time, the electrolyte concentration, etc. Other compositions of the Ni-Fe alloys could reach or exceed the thermoelectric figure of merit of already used materials in thermoelectric devices as constantan or chromel P. This makes them potentially interesting regarding

waste heat recovery for low energy consumption devices. Furthermore, the use of typical high-ZT thermoelectric materials is not interesting regarding electronic cooling applications [75]. The most appropriate materials would be materials exhibiting large PF and thermal conductivity. Therefore, the optimisation of the electrodeposition process for the Ni-Fe alloys could improve the PF and lead to interesting applications for active cooling.

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