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Spin-dependent Seebeck effect in 3D interconnected nanowire network

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Abstract

Track-etched polymer membranes with crossed nanochannels have been successful templates for the growth of three-dimensional interconnected magnetic nanowire networks through metals electrodeposition inside the pores. This reliable technique has enabled to produce unique nanowire structures while keeping an accurate control over the morphology, the material composition as well as the density of nanowires. This innovative interconnected architecture combines mechanical stability and electrical conductivity within the self-supported sample together with flexibility and thermal stability provided by the polycarbonate template. The electrons flow along the nanowires axis while the global transport of heat and charges takes place in the centimeter scale film plane. From this configuration results the possibility to perform suitable macroscopic electrical and thermal measurements after removing a part of the cathode by ions sputtering to create a two-probe design. The successive ferromagnetic (NiFe) and non-magnetic (Cu) layers with the alloy composition ranging from 40% to 93% of Ni allow to switch from a natural antiparallel arrangement of the magnetic moments to a parallel alignment when applying an external magnetic field. These two arrangements have shown different behaviors for the spin-up and spin-down electrons resulting in an alteration of the transport properties. An appropriate magnetic field is therefore at the origin of the relatively tunable electrical resistance and Seebeck coefficient characterizing the thermoelectric power. Results have demonstrated a giant magnetoresistance of 20% as well as a magneto-thermopower of 26% at room temperature for $\text{Ni}_{80}\text{Fe}_{20}/\text{Cu}$, these values have been drastically outperformed when decreasing the temperature reaching both 60% at respectively 15 K and 70 K. Moreover, properly designed experiments allow to extract large spin-dependent Seebeck coefficients exhibiting a gap of $-13.57 \mu\text{V/K}$ and $-17.18 \mu\text{V/K}$ at temperatures of 300 K and 320 K for $\text{Ni}_{93}\text{Fe}_7/\text{Cu}$. In addition, this switch of magnetic state is very sensitive since it only requires an external magnetic field of around 2 kOe. Theory suggests that this difference could be even larger for a further Ni enrichment giving rise to exciting perspectives. All these benefits make these samples good candidates for light and flexible spintronics, thermoelectric, and spin caloritronics systems with large magnetic control over the network transport properties. This technology is then promised to a brilliant future with advanced applications such as magnetic modulated active cooling devices embedded into flexible films.

Keywords: Nanostructures, 3D nanowire networks, Nickel-iron alloys, Giant magnetoresistance, Spin-dependent Seebeck coefficient.

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Acronyms

Symbols	Name
3D	Three-dimensional
Ω	Ohm (unit)
A	Ampere (unit)
Ag	Silver (element)
AMR	Anisotropic magnetoresistance
AP	Antiparallel
Ar	Argon (element)
Au	Gold (element)
BCC	Body-centered cubic
CGS	centimetre–gram–second (unit system)
CIP	Current-in-plane
CNT	Crossed nanotube
CNWs	Crossed nanowire
CPP	Current-perpendicular-to-plane
Cr	Chromium (element)
Cu	Copper (element)
DOS	Density of states
EDX	Energy-dispersive X-ray spectroscopy
eff	Effective
eV	Electron volt
FCC	Face-centered cubic
Fe	Iron (element)
FeSO ₄	Iron(II) sulphate
FE-SEM	Field-emission scanning electron microscope
FM	Ferromagnetic metal
G	Gauss (unit)
GMR	Giant magnetoresistance
HCP	Hexagonal close packed
HCl	Hydrochloric acid
HCNWs	Homogeneous crossed nanowire network
HDD	Hard disk drive
H ₃ BO ₃	Acid boric
H ₂ O ₃	Water
H ₂ SO ₄	Sulphuric acid
IP	In-plane
K	Kelvin (unit)

Symbols	Name
K_{α}	Characteristic X-ray
K_{β}	Characteristic X-ray
l	Litre (unit)
m	Meter (unit)
M	Molar (unit)
MC	Magnetocrystalline
ME	Magnetoelastic
MLCNWs	Multilayered crossed nanowire network
MPF	Magneto-power factor
MR	Magnetoresistance
MRAM	Magnetic random access memory
MRI	Magnetic resonance imaging
MS	Magnetostatic
MTP	Magneto-thermoelectric power
NaOH	Sodium hydroxide
Ni	Nickel (element)
NiFe	Nickel-iron alloys
NiSO_4	Nickel(II) sulfate
NM	Non-magnetic metal
NT	Nanotube
NW	Nanowire
Oe	Oersted (unit)
OOP	Out-of-plane
P	Parallel
PC	Polycarbonate
PF	Power factor
pH	Potential hydrogen
PID	Proportional–integral–derivative
Pt	Platinum
Py	Permalloy
RRR	Residual resistivity ratio
RT	Room temperature
SEM	Scanning electron microscope
SI	International unit system
T	Tesla (unit)
TEP	Thermoelectric power
TMR	Tunnelling magnetoresistance
UCLouvain	Université catholique de Louvain
UV	Ultraviolet
V	Volt (unit)
W	Watt (unit)
WF	Wiedemann Franz (law)
XR	X-ray
ZAF	Algorithm using the atomic number Z, the absorbance A and the fluorescence F

Symbols

Symbols	Name	SI units
α	Spin asymmetry coefficient	-
β	Bulk spin asymmetry coefficient	-
Γ	Volume	m ³
ΔT	Temperature difference	K
ΔV	Voltage difference	V
δ	Domain wall thickness	m
η	Spin asymmetry coefficient for thermopower	-
η_{th}	Thermoelectric efficiency	-
ϵ_{F}	Fermi energy	eV
ϵ_g	band gap energy	eV
ϵ	Electron energy	eV
λ	Magnetic and non-magnetic layer thicknesses ratio	m
λ_e	Electron mean free path	m
λ_p	Phonon mean free path	m
κ	Thermal conductivity	Wm ⁻¹ K ⁻¹
κ_e	Electronic thermal conductivity	Wm ⁻¹ K ⁻¹
κ_l	Lattice thermal conductivity	Wm ⁻¹ K ⁻¹
θ	Nanowire angle with respect to the network film normal	°
θ_{D}	Debye temperature	K
μ	Electron mobility	m ² V ⁻¹ s ⁻¹
μ_{r}	Relative permeability	-
Ω	Ohm (unit)	Ω
π	Peltier coefficient	V
ρ	Resistivity	Ωm
ρ_{AP}	Resistivity for antiparallel arrangement of the ferromagnetic layers	Ωm
ρ_{avg}	Averaged resistivity of a demagnetized sample	Ωm
ρ_{LT}	Low temperature resistivity	Ωm
ρ_{i}	Ideal resistivity	Ωm
$\rho_{\parallel}$	Resistivity for parallel arrangement between the magnetization and the current	Ωm
$\rho_{\perp}$	Resistivity for perpendicular arrangement between the magnetization and the current	Ωm
ρ_{r}	Residual resistivity	Ωm
ρ_{RT}	Room temperature resistivity	Ωm

Symbols	Name	SI units
$\rho_{\uparrow}$	Resistivity of majority electrons	Ωm
$\rho_{\downarrow}$	Resistivity of minority electrons	Ωm
σ	Electrical conductivity	$\Omega^{-1}\text{m}^{-1}$
$\sigma_{\uparrow}$	Conductivity contribution of majority electrons	$\Omega^{-1}\text{m}^{-1}$
$\sigma_{\downarrow}$	Conductivity contribution of minority electrons	$\Omega^{-1}\text{m}^{-1}$
τ	Relaxation time	s
ϕ	Nanofiber diameter	m
ϕ	Angle between spin couple	$^{\circ}$
χ	Magnetic susceptibility	-
ζ	Form factor	-
a	Lattice parameter	m
a	Thermodynamic activity	-
at. %	Atomic percentage (unit)	%
$\mathbf{B}$	Magnetic induction vector	T
B	Magnetic induction intensity	T
B	Constant	-
C_{ℓ}	Lattice heat capacity	JK^{-1}
$\mathcal{D}$	Density of state	$\text{eV}^{-1}\text{m}^{-3}$
D_{p}	Pores density	porescm^{-2}
$\mathcal{D}^{\uparrow}$	Density of states for spin-up electrons	$\text{eV}^{-1}\text{m}^{-3}$
$\mathcal{D}^{\downarrow}$	Density of states for spin-down electrons	$\text{eV}^{-1}\text{m}^{-3}$
$\mathcal{D}_{\text{d}}$	Density of states for the d electrons	$\text{eV}^{-1}\text{m}^{-3}$
$\mathcal{D}_{\text{s}}$	Density of states for the s electrons	$\text{eV}^{-1}\text{m}^{-3}$
$\mathbf{E}$	Electric field vector	Vm^{-1}
E	Electric field intensity	Vm^{-1}
E	Potential	Vm^{-1}
E_0	Normal electrode potential in standard conditions	V
E_{a}	Anisotropic energy	Jm^{-3}
E_{eq}	Equilibrium potential	V
E_{ex}	Exchange energy	J
E_{ms}	Magnetostriction energy	Jm^{-3}
E_{z}	Zeeman energy	Jm^{-3}
$\mathbf{H}$	Magnetic field vector	Am^{-1}
H	Magnetic field intensity	Am^{-1}
H_{a}	Magnetocrystalline anisotropy field	Am^{-1}
H_{c}	Coercive field	Am^{-1}
$\mathbf{H}_{\text{d}}$	Demagnetizing field vector	Am^{-1}
H_{d}	Demagnetizing field intensity	Am^{-1}
H_{eff}	Effective anisotropy field	Am^{-1}
H_{ms}	Magnetostatic anisotropy field	Am^{-1}
H_{sat}	Saturation field	Am^{-1}
H_{dip}	Dipolar magnetic field	Am^{-1}
$\mathbf{I}$	Electrical current vector	A

Symbols	Name	SI units
I	Electrical current intensity	A
j	Current density	Am^{-2}
J	Exchange integral	J
j_q	Heat flux density	Jm^{-2}
K_u	Uniaxial anisotropy constant	Jm^{-3}
ℓ_{sf}	Spin diffusion length	m
$\mathbf{m}_i$	Magnetic moment	Am^2
$\mathbf{M}$	Magnetization vector	Am^{-1}
M	Magnetization intensity	Am^{-1}
M_0	Saturated magnetization at zero temperature	Am^{-1}
M_r	Remanent magnetization	Am^{-1}
M_s	Saturated magnetization	Am^{-1}
m^*	Electron effective mass	kg
n	Oxidation number	-
n	Density electronic	m^{-3}
n_w	Weiss constant	-
$\mathcal{N}_x, \mathcal{N}_y, \mathcal{N}_z$	Demagnetizing factors along the x -axis, y -axis, and z -axis direction	-
N_{ij}	Demagnetizing tensor	-
$n_{\uparrow}$	Density of spin-up electrons	m^{-3}
$n_{\downarrow}$	Density of spin-down electrons	m^{-3}
P	Network packing factor	%
q	Heat flow	Wm^{-2}
Q	Charge deposited	C
R	Resistance	Ω
R_0	Resistance in absence of magnetic field	Ω
R_{AP}	Resistance for antiparallel arrangement of the ferromagnetic layers	Ω
R_{IP}	Resistance at saturation in the in-plane direction	Ω
R_{OOP}	Resistance at saturation in the out-of-plane direction	Ω
R_{P}	Resistance for parallel arrangement of the ferromagnetic layers	Ω
r	Position vector	m
S	Seebeck coefficient	VK^{-1}
$\mathcal{S}_{\uparrow}$	Majority spin	-
$\mathcal{S}_{\downarrow}$	Minority spin	-
S_{AP}	Seebeck coefficient for antiparallel arrangement of the ferromagnetic layers	VK^{-1}
S_d	Diffusive thermopower	VK^{-1}
S_{md}	Magnon-drag thermopower	VK^{-1}
S_{P}	Seebeck coefficient for parallel arrangement of the ferromagnetic layers	VK^{-1}
S_{pd}	Phonon-drag thermopower	VK^{-1}

Symbols	Name	SI units
$S_{\uparrow}$	Seebeck coefficient contribution of majority electrons	VK^{-1}
$S_{\downarrow}$	Seebeck coefficient contribution of minority electrons	VK^{-1}
T	Temperature	K
T_{C}	Curie temperature	K
T_{c}	Cold temperature	K
t_{FM}	Ferromagnetic layer thickness	m
T_{h}	Hot temperature	K
t_{NM}	Normal metal spacer thickness	m
T_{p}	Pulse duration	s
V	Potential drop	V
v_{p}	Phonon average velocity	ms^{-1}
Z	Number of valence electrons	-
ZT	Figure of merit	-

Symbols	Constant name	Values	SI units
μ_{B}	Bohr magneton	$9.274.10^{-24}$	Am^2
μ_0	Vacuum permeability	$4\pi.10^{-7}$	Hm^{-1}
π	Pi	3.14	-
A	Exchange constant	10^{-11}	Jm^{-1}
e	Electron charge	$1.6.10^{-19}$	C
F	Faraday constant	96485	sAmol^{-1}
k_{B}	Boltzmann constant	$1.38.10^{-23}$	$\text{m}^2\text{kgs}^{-2}\text{K}^{-1}$
L_0	Lorenz number	$2.44.10^{-8}$	$\text{W}\Omega\text{K}^{-2}$
R	Ideal gas constant	8.314	$\text{Jmol}^{-1}\text{K}^{-1}$

Introduction

There's plenty of room at the bottom...

This sentence pronounced by Richard Feynman during a lecture at the annual American Physical Society meeting in 1959 has become the historical symbol of the nano-scale researches [1]. The emergence of nanotechnologies during the end of the last century has confirmed his visionary idea. Nowadays, nanoscale miniaturization is considered as the current technological revolution. The appeal for nanotechnology comes from the fact that this discipline merges the usual threads between science, engineering, and technology. Moreover its development has enabled important improvements and novel applications in various fields as solar cells [2], biosensors [3, 4], energy storage and harvesting [5, 6], quantum computers [7], cutting tools [8], drug delivery [9] and even toothpastes [10].

The key concept of nanotechnologies relies on the fact that physical, mechanical, and optical properties can be controlled when working at the nanoscale. From this unique set of characteristics arises excellent materials used to improve numerous applications. This versatility is related to the tunable arrangement of atoms that directly influence the size of the grains, the defect density, the presence of interfaces, as well as the quantum phenomena.

Among these properties, this master thesis mainly deals with the transport phenomena taken place at the nanoscale. An overview of them is displayed in Figure 1. Thermoelectricity field arises from the association of the charge current and the heat current. As in bulk materials, this effect enables to both transform a temperature gradient into an electrical field or inversely. These phenomena called the Seebeck and the Peltier effects are respectively used in production of electricity from wasted heat and in heating or cooling devices by the application of charge current. Besides for nano-samples, it has been found that the thermoelectric efficiency was improved mainly due to an increase of the heat resistivity as well as, for a certain size limit, a quantum confinement. By looking a bit closer over the charge current in nanoscale multilayers made of successive ferromagnetic (FM) and non-magnetic (NM) materials, A.Fert and P.Grünberg discovered in 1988 the existence of the giant magnetoresistance (GMR) effect under the application of an external magnetic field [11]. This breakthrough highlighted the possible presence of spin-polarized current in such multilayered structures which led to the spintronics revolution. In contrast with the conventional electronics which includes the displacement of charges when submitted to an electric field, the spintronics field couples the charge transport with the electron spin. This additional degree of freedom is for instance responsible for the production of spin-transfer torque created by spin current which enabled advanced progress in magnetic data storage and logic devices. Recently, a new field called spin caloritronics has been studied [12, 13] after the discovery of the Seebeck coefficient spin-dependence in 2008

by Uchida et al.[14]. This emergent field relies on the merger of thermoelectricity and spintronics. Hence, it originates from the interaction of heat current and spin current and exhibits several interests in the improvement of thermoelectric devices. For example, the giant magneto-Seebeck effect has opened the door to a possible magnetic control of the heat flow in wasted heat applications [15]. In the same way, the magnitude of the Peltier effect can be tuned by the utilization of a magnetic field to locally cool electronic devices [16, 17]. Besides, magnetic fields have been used to develop thermally driven spin injection [18] as well as thermal assisted spin-transfer torque [19, 20].

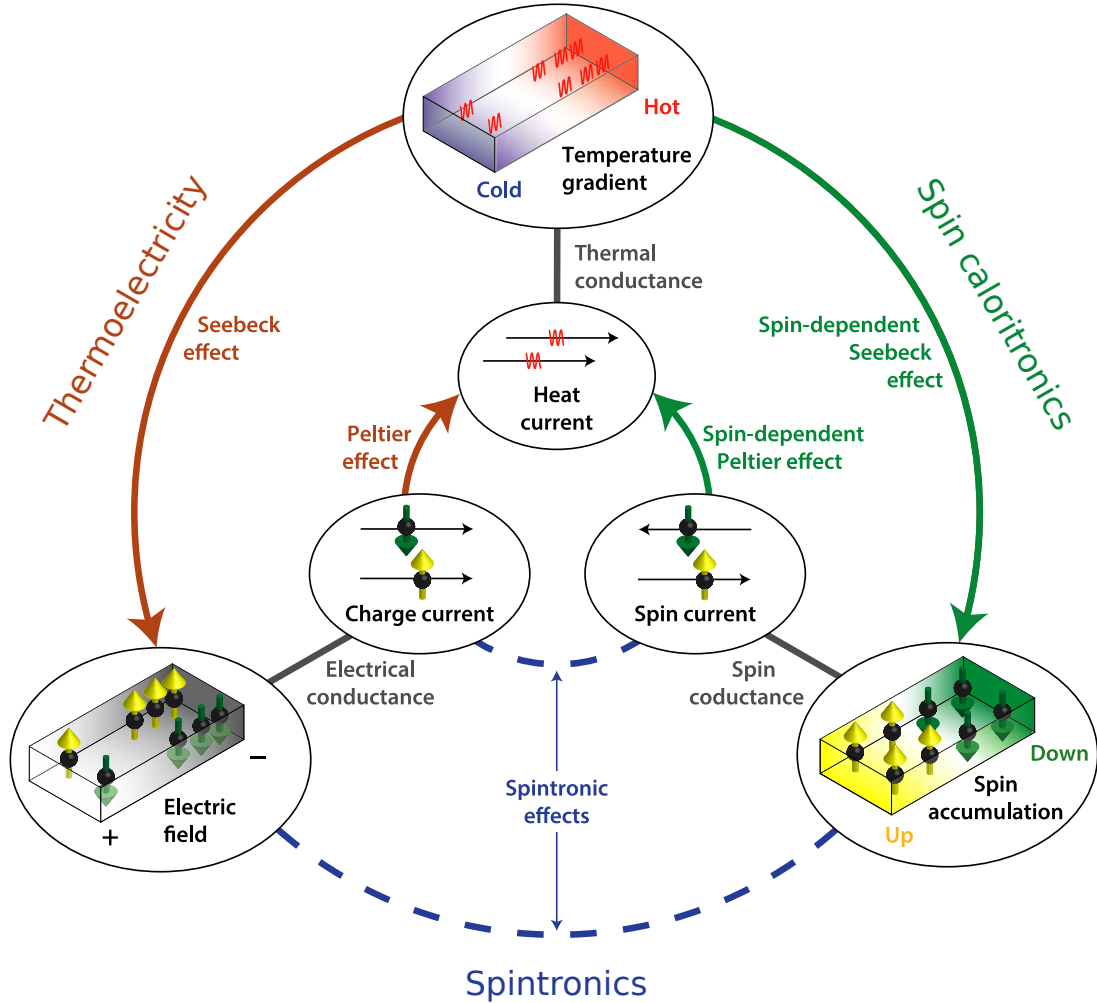


Figure 1: Overview of the different kinds of currents and the effects engendered by their combinations. Hence, thermoelectricity arises from the coupling of heat current and charge current. Spintronics comes from the merge between charge current and spin current, while, spin caloritronics involves the presence of both heat current and spin current [21].

For several years, the group of Pr.Piroux is a pioneer in the study of spintronics and spin caloritronics effects within three-dimensional (3D) nanowire (NW) networks. Up to now, they have mainly focused their work on the determination of the magnetoresistance and the magneto-Seebeck effects either in arrays of parallel multilayered nanowires or more recently in multilayered crossed nanowire networks (MLCNWs) [21–25]. This architecture is of great interest because it allows to perform macroscopic measurements of (magneto)transport properties while keeping the benefits of the nanoscalization. For

instance, in such structures, the transport of charge and heat is unidirectional along the nanowires axis, allowing a better comprehension of the spin-dependent phenomena. Moreover, these networks are embedded in polymer membranes turning them into flexible, shapeable, and lightweight samples while guaranteeing electrical and thermal stability as well as reliable extraction of spin-dependent material properties. Last but not least, the size is not a limitation since the fabrication method is easily expandable into NW network films with much larger dimensions.

The fabrication of such samples is based on a bottom-up approach consisting in track-etched template electrodeposition. This technique is reliable, cheap, and versatile. Hence, nanowires are directly grown from a metallic electrolyte bath, inside the pores of a membrane previously bombarded with energetic atoms. This process is well-mastered and ensures adequate control of the properties such as the composition, the morphology, and the structural properties in order to realize fine and accurate multilayers. This control allows getting samples exhibiting magnetoresistance up to 30% at room temperature (RT)[21].

This thesis aims to investigate 3D multilayered crossed nanowire networks made of successive layers of copper (Cu) and nickel-iron alloys (NiFe). These alloys are of great interest due to their very large Seebeck coefficient together with a significant response under an external magnetic field. Previous researches with promising results have been accomplished on the famous Permalloy (Py) composed of $\text{Ni}_{80}\text{Fe}_{20}$ [26]. The objective of this thesis is to study the influence of the Ni atomic percentage over the thermoelectric power and the degree of spin-dependence. Samples made of $\text{Cu}/\text{Ni}_x\text{Fe}_{100-x}$ with $60 < x < 93$ will therefore be explored.

In this report, Chapter 1 provides an overview of the fundamental magnetism as well as the transport properties inside ferromagnetic transition metals. The transport of charges and heat, especially in multilayered nanostructures is highlighted. Then Chapter 2 is dedicated to the description of the experimentation. It includes explanations over the network fabrication, details about the techniques allowing to characterize the structure and the composition of the samples as well as methods to measure the transport properties. Afterward, Chapter 3 exhibits the results with accurate analysis and discussions. Finally a summary of the main results and an outline of the future perspectives are presented at the end of this thesis.

Chapter 1

State of the art

This chapter is dedicated to the presentation of the theoretical background regarding the magnetism and the transport properties of ferromagnetic transition metals. This knowledge about the fundamental physics is required to understand the spin-dependent effects present at the nanoscale and more precisely in multilayered nanowire networks made of successive ferromagnetic/non-magnetic layers. First, Section 1.1 will provide a detailed overview of the magnetism in ferromagnetic transition metals. Then, Section 1.2 will explain the electrical transport within these specific materials with a special focus on the magnetic field influence. Finally, Section 1.3 describes the thermal transport and its associated thermoelectric effect while highlighting the spin-dependent Seebeck effect caused by the magnetic field.

1.1 Magnetic properties of ferromagnetic transition metals

Magnetism has always been part of our world. Its first effects were detected in fragments of magnetized iron ore around 2500 years ago in western Turkey [27]. It has been demonstrated that these pieces of permanent magnets exerted forces on each other. Nowadays, magnetism is present everywhere and useful in various application such as in electromechanics (motors, transformers or generators), in medicine (magnetic resonance imaging), in robotics (sensors, actuators), in day to day life (bank cards) and even in data storage devices [28]. Moreover, in the last decades, interest for magnetic field in nanostructures has been developed to increase the capacity of data storage thanks to giant magnetoresistance (GMR) and tunneling magnetoresistance (TMR) [29]. This section provides the basis of bulk magnetism in metals and particularly in ferromagnetic materials. Besides, the main assets of nanostructures regarding their behavior when submitted to a magnetic field will be developed.

1.1.1 Fundamental magnetism of bulk metals

Every material exhibits a response in presence of an external magnetic field. The importance of this reaction is variable and depends on the number of atoms inside the volume that behaves like tiny magnets. At the atomic scale, electrons gravitate around the nucleus. This motion leads to microscopic current loops, giving rise to an atomic magnetic moment specific to the nature of the atom. An additional intrinsic contribution to the magnetic moment comes from the existence of spinning particles as electrons.

The combination of both the orbital and spin magnetic moment results in the total magnetic moment of the atom $\mathbf{m}_i$. Therefore, the magnetization $\mathbf{M}$ of a material with a density N_i of atoms per unit volume is given by:

$$\mathbf{M} = \sum_i N_i \mathbf{m}_i. \quad (1.1)$$

The magnetization is also defined by the mesoscopic average of the magnetic moments inside a small element of volume Γ :

$$\mathbf{M} = \frac{\delta \mathbf{m}}{\delta \Gamma}. \quad (1.2)$$

Sometimes, in absence of magnetic field, the atomic magnetic moments of all the atoms are randomly distributed, consequently, the material exhibits no global magnetization. On the contrary, in the case of non-zero magnetic moment resultant, the material is said spontaneously magnetized. The application of an external magnetic field $\mathbf{H}$ created by a solenoid always leads to a slight or significant modification of $\mathbf{M}$ inside the solid. This modification is characterized by the magnetic susceptibility χ defined as:

$$\chi = \frac{M}{H}. \quad (1.3)$$

Inside a solid, the magnetic flux density through an area is called the magnetic induction $\mathbf{B}$ and can be expressed in several ways:

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \quad \mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} \quad \mathbf{B} = \mu_0(1 + \chi)\mathbf{H}. \quad (1.4)$$

The first expression for $\mathbf{B}$ is in the international system (SI) and related to $\mathbf{H}$ and $\mathbf{M}$ by the vacuum permeability μ_0 . The second is expressed in another unit system frequently considered, the CGS (centimetre-gram-second) with conversion values displayed in Table 1.1. Finally, the third expression is interesting since it involves the variable χ . It follows that the sign of χ directly indicates the response of the material submitted to an external magnetic field. A positive χ is associated with an enhancement of the field due to a certain alignment of the magnetic moments. On the opposite, a negative χ testifies to the presence of an unfavorable reaction to the magnetic field.

Table 1.1: Conversion between SI and CGS unit systems for the magnetic field, the magnetization, and the magnetic induction.

Variable	SI system	CGS system	Conversion
$\mathbf{H}$	A/m	Oe	1 Oe = $10^3/4\pi$ A/m
$\mathbf{M}$	A/m	Emu/cm ³	1 Emu/cm ³ = 10^3 A/m
$\mathbf{B}$	T	G	1 G= 10^{-4} T

One of the contributions to χ is ascribed to the diamagnetic effect. It arises in presence of a magnetic field leading to a modification of the electrons motion in every material. According to Lenz's law, the variation of the magnetic flux inside an electrical loop induces a current and then a magnetic field opposed to this variation. Hence, an atom without any magnetic moment acquires one extremely weak when placed in a magnetic field. This phenomenon is present in every atoms and molecule and results in a negative contribution to the magnetic susceptibility evaluated around $\chi \approx -10^{-5}$ [30, 31].

However, when atoms have intrinsic magnetic moments, other effects can shade the diamagnetism. As previously said, in a wide number of materials, the magnetic moments are randomly oriented and do not interact with each other, resulting in no global magnetization. Though, under a magnetic field, the magnetic moments tend to align with it, modifying their average orientation. Consequently, a small additional magnetization parallel to the magnetic field appears characterized by $\chi \approx 10^{-3}$ at RT. This phenomenon is called paramagnetism. Finally, some materials exhibit a global interaction between the atomic magnetic moments leading to a spontaneous arrangement with (non-permanent) or without any magnetic field (permanent). These special materials are known as ferromagnetic, antiferromagnetic, and ferrimagnetic.

1.1.2 Origin of ferromagnetism

The collective arrangement in ferromagnetic materials is responsible for the powerful magnetic field created inside the solid itself with typical values of χ being larger than 10^4 . Its existence comes from the influence exerted by the magnetic moment of an atom which tends to align the neighborhood atoms with him. This effect is exponential with the external magnetic field since the larger is the number of atomic magnetic moments aligned, the bigger is the resulting interaction. It has been experimentally demonstrated that for a certain $\mathbf{H}$, $\mathbf{M}$ reaches a maximum. This temperature-dependent point is called the saturation magnetization M_s . The evolution of M_s with the temperature is shown in Figure 1.1 with its higher value situated at 0K and noted M_0 . Microscopically, the saturation occurs when all the magnetic moments are perfectly aligned. On the other hand, this effect self-decelerates together with temperature enhancement, and brutally disappears at the Curie temperature T_C , adopting thenceforth a paramagnetic behavior. As a matter of fact, the thermal energy takes over the magnetic energy, leading to a magnetic moment randomization. Besides, the randomization is amplified because the closest atoms are also less favorable to an alignment giving then a dramatic drop of M_s as seen in the image.

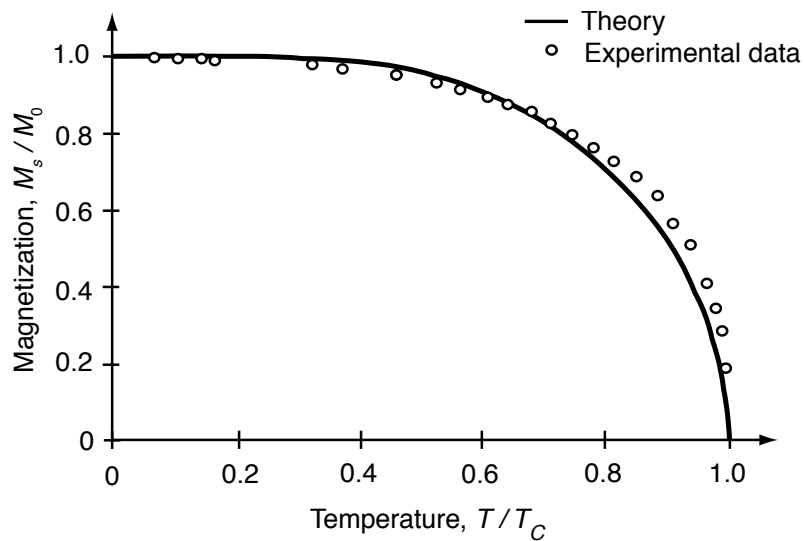


Figure 1.1: Evolution of M_s as a function of the temperature for Ni. The temperature is normalized by T_C , which characterizes the switch from a ferromagnetic behavior to a paramagnetic one. M_s is normalized by M_0 , its maximal value at $T=0K$. The collective arrangement is responsible for the ferromagnetism while the thermal agitation causes the randomization of the magnetic moments [32].

The ferromagnetism key relies then on the collective interaction between the surrounding atoms. This coupling is ascribed to a quantum exchange energy between the atomic magnetic moments. Based on the Heisenberg model, the evaluation of this exchange energy E_{ex} for two atoms i and j is given by: $E_{\text{ex}} = -2JS_i \cdot S_j$ with J the exchange integral and S_i, S_j the respective spins [33]. This expression assumes that the magnetic moments arise uniquely from the spin, which seems to be realistic for transition metals. The sign of J is determinant since in case of $J > 0$, the alignment of the spins, and then the ferromagnetism is favored. This expression can be extended to a solid when considering a specific coupling between all the nearest neighbors. For a solid with n atoms per unit cell, a lattice parameter a , and an angle ϕ between every spin couple, the continuous exchange energy in the direction x is given by:

$$E_{\text{ex}} = -2\frac{n}{a}JS^2 \cos \frac{d\phi}{dx}. \quad (1.5)$$

It emerges that the system minimizes its energy when $\frac{d\phi}{dx} = 0$, thereby a configuration with all the atomic magnetic moments aligned is favored.

This model relies on the fact that atoms have a non-zero intrinsic magnetic moment that can be independently oriented from the others. Nevertheless, a magnetic field does not have any influence on the orientation of a large majority of electrons. Basically, the Pauli exclusion principle together with the Fermi-Dirac statistics impose that electrons filled both the spin-up ($\uparrow$) and spin-down ($\downarrow$) bands by starting with the lower energy states. Therefore, the bands are symmetrically filled up to a certain energy level, defined as the Fermi energy ϵ_F . However, when submitted to magnetic induction, electrons having an intrinsic magnetic moment equal to the Bohr magneton μ_B react by orienting their spin either parallel (P) or antiparallel (AP) to the field for respectively spin $\uparrow$ or spin $\downarrow$. In terms of electronic total energy, it implies a shift of $\pm\mu_B B$ resulting in a new energy $E = \epsilon \pm \mu_B B$ with ϵ the electron kinetic energy. Consequently, the bands shift in opposite directions, leading to an asymmetry of $2\mu_B B$ as illustrated in Figure 1.2(a). To minimize its energy, the system requires to restore a common ϵ_F by flipping some spins situated close to this energy as depicted in Figure 1.2(b).

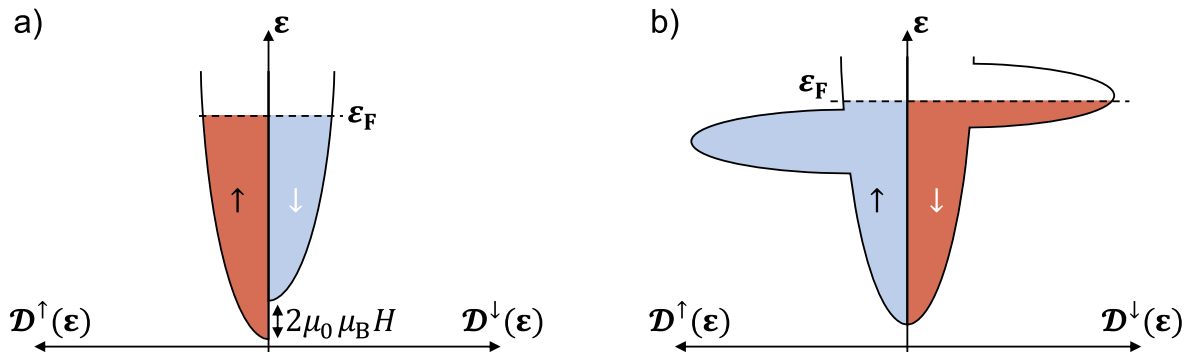


Figure 1.2: Schematic representation of the paramagnetism effect in transition metals with (a) the imbalance of the bands created in response to $\mathbf{H}$ and (b) the restoration of a common energy level ϵ_F which implies several spin flips and a split of the spin-up and spin-down bands. The x-axis and y-axis are respectively the density of states $\mathcal{D}(\epsilon)$ and the electronic energy ϵ . Figure adapted from [21]

From there, the density of spin-up ($n_{\uparrow}$) becomes larger than the density of spin-down ($n_{\downarrow}$) so that a solid acquires a net magnetic moment given by:

$$m = (n_{\uparrow} - n_{\downarrow})\mu_B\Gamma. \quad (1.6)$$

This magnetic band shift explains the paramagnetism observed in some materials including the transition metals. In reality, the transition metals also present a quite bigger spontaneous magnetization under T_C even in absence of a magnetic field. The explanation is again ascribed to a band imbalance caused by exchange phenomena. Hence, in transition metals, a spontaneous split of the 3d bands is favored if the exchange energy gain caused by the magnetic moment alignment is larger than the energy required to split the band. This condition is expressed by the Stoner criterion where n_w is the Weiss constant:

$$\mu_0\mu_B^2 n_w \mathcal{D}(\epsilon_F) > 1. \quad (1.7)$$

Some transition metals meet this condition giving rise to a 3d band split as shown in Figure 1.2(b), among them: Ni, Fe and, Co. In these metals, ϵ_F is situated in an overlap between the 4s band and the 3d band. The merge of the very narrow 4s band and the large 3d band composed of electrons localized close to the nucleus leads to a high density of states close to the Fermi level $\mathcal{D}(\epsilon_F)$. As seen in Equation 1.7, this factor favors the spontaneous band split responsible for the important magnetism of ferromagnetic materials even in absence of external magnetic field. Besides, the binary alloys containing Ni, Fe, or Co also exhibit the band ferromagnetism as confirmed in the Figure 1.3, which illustrates the curve of the atomic magnetic moment depending on the average number of conduction electrons Z .

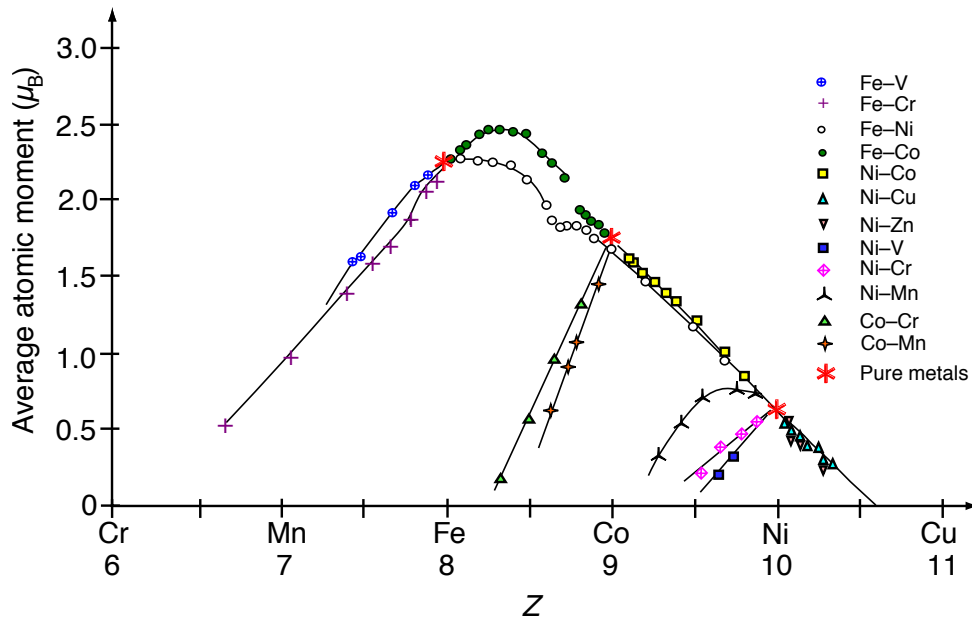


Figure 1.3: The Slater-Pauling curve indicating the average atomic moment μ_B depending on the number of conduction electrons Z for transition metals and alloys [21]

Considering ferromagnetic materials under T_C , all the atomic magnetic moments should have been oriented in parallel to each others to minimize E_{ex} . However, it has been proved that the magnetization is not uniform inside such materials suggesting that other energetic parameters are taken into account, gathered as magnetic anisotropy.

1.1.3 Magnetic anisotropy

The magnetic anisotropy means that the magnetization of a material is favored along some orientations. The directions minimizing the total energy are called the easy-axes while the hard-axes are difficult to magnetize because of their important energy costs. The global magnetic anisotropy contains three main contributions with different origins. Firstly, the magnetocrystalline (MC) anisotropy is related to the microscopic structure of the materials, being thus an intrinsic property. Secondly, the magnetostatic (MS) anisotropy which favors some orientations depending on the material geometry. Finally, the magnetoelastic anisotropy (ME) is the consequence of a material treatment involving stress inside the solid. By considering a FM material exhibiting only one easy-axis and a magnetization making an angle θ with respect to this axis, the anisotropic energy E_a is written:

$$E_a = K_u \sin^2 \theta, \quad (1.8)$$

with K_u the uniaxial anisotropic constant. In terms of anisotropic magnetic field H_a , defined as the field required to saturate a hard-axis [31], it is expressed as:

$$H_a = \frac{2K_u}{\mu_0 M_s}. \quad (1.9)$$

Magnetocrystalline anisotropy

The MC anisotropy appears during the material formation and is related to the crystallographic symmetries. Figure 1.4 shows the magnetization curves of single crystals of Fe, Ni, and Co along different directions highlighting the magnetocrystalline anisotropy. In the case of Fe (BCC structure) and Ni (FCC structure), it can be seen that the saturation magnetization is quickly reached for respectively the $\langle 100 \rangle$ and $\langle 111 \rangle$ direction. Nevertheless, this anisotropy stays weak compared to Co (HCP structure) which exhibits a stronger effect with an easy-direction along the c-axis. Physically, the origin of the weak anisotropy in transition metals exhibiting a cubic structure does not come from exchange interactions but is the consequence of some spin-orbit coupling. The 3d electrons responsible for the magnetism are strongly coupled with the crystal lattice reducing the orbital moment. On the other hand, the origin of the anisotropy for Co reflects the dipole-dipole interaction. It has been demonstrated that the configuration head-to-tail of two dipoles is energetically favorable. The sum over the entire lattice leads to a important anisotropy for HCP structure as Co while this contribution vanishes for cubic lattice.

Magnetostatic anisotropy

The MS anisotropy is related to the geometry of the sample. It is ascribed to both the sample shape and the dipolar coupling. The key of the shape anisotropy relies on the existence of a demagnetizing field H_d tending to counteract the original magnetization as depicted in Figure 1.5. It has been observed that the magnetization of a material initiates the creation of monopoles¹ at its edges. Hence, the interaction between the pole + and - at the extremities of the sample is at the origin of H_d .

¹In fact magnetic monopole does not exist, it is only a representation helping the comprehension since the poles are not stable and engendered by motions of electrical charges

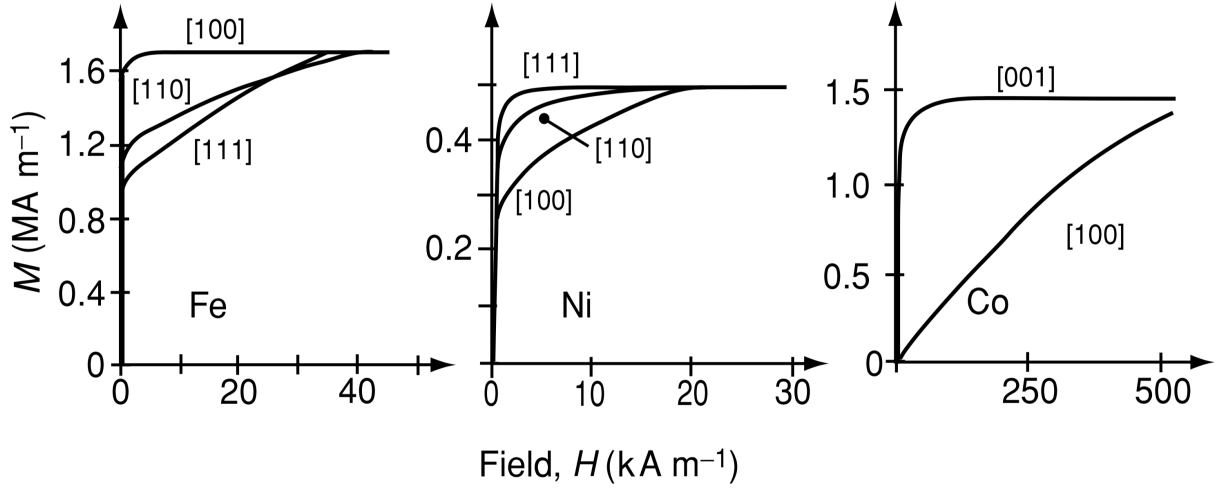


Figure 1.4: Magnetization curves of single crystals of BCC-Fe, FCC-Ni, and HCP-Co highlighting the presence of easy-axes and hard-axes arising from crystalline structure symmetries. It can be seen that HCP structures exhibit higher MC anisotropy than cubic structures [32].

The final internal magnetic field H_i , can be expressed as $\mathbf{H}_i = \mathbf{H} + \mathbf{H}_d$ with:

$$\mathbf{H}_{d,j} = -\mathcal{N}_{ij}M_j \quad i, j = x, y, z, \quad (1.10)$$

$\mathcal{N}_{ij}$ is a tensor which can be diagonal in a system parallel to the main axes with $\mathcal{N}_x + \mathcal{N}_y + \mathcal{N}_z = 1$. Besides, the geometry of solids exhibiting symmetries leads to equal coefficients making their determination easier. Coefficient values for typical geometries are exposed in Table 1.2. It can be seen that the magnetization is preferentially oriented along the larger dimension of the sample.

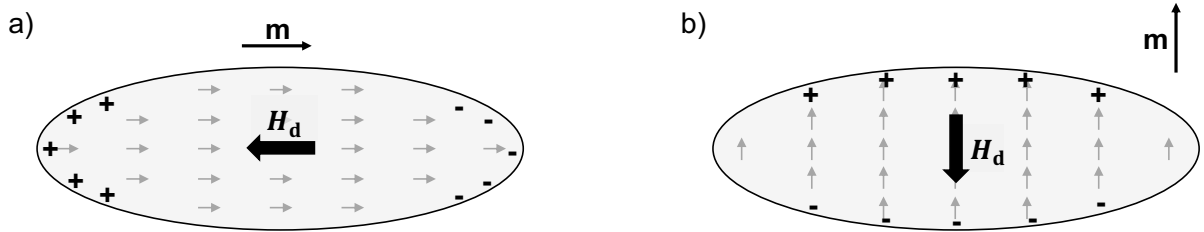


Figure 1.5: Illustration of the demagnetization field H_d arising from the existence of monopoles at the edges of the sample. This field H_d is lower along (a) the long elliptic radius than (b) the smaller elliptic radius and opposite to the initial magnetization. Figure from [21]

The second source of MS anisotropy comes from dipolar coupling produced by dipole-dipole interaction between monopoles of different objects. This phenomenon is largely dependent on the distance so that it becomes negligible when separation length increases.

Table 1.2: Demagnetizing factors for typical geometries. Data from [32].

Shape	Magnetization direction	$\mathcal{N}$
Sphere	All directions	1/3
Long wire	Parallel to the wire	0
	Perpendicular to the wire	1/2
Thin film	Parallel to the film	0
	Perpendicular to the film	1

Magnetoelastic anisotropy

The ME anisotropy is the consequence of material treatments inducing stresses. Physically, the magnetization and the stress are related by the magnetostriction coefficients. Considering positive magnetostriction, the application of a tension pushes the magnetic moments to self-orient parallel to the tension. On the other hand, compression favors the magnetization in the perpendicular direction. In the case of negative magnetostriction the effects are reversed. This contribution results in an additional energetic term noted E_{ms}

1.1.4 Domains formation and polarization of ferromagnetic materials

Under T_C , the atomic magnetic moments of ferromagnetic materials should all be parallel due to the exchange coupling. However, this configuration creates monopoles costing a lot of anisotropic energy for the system as previously detailed. Therefore, the system tends to minimize its energy by finding a compromise between reducing the exchange energy with parallel magnetic moments and reducing the MS energy by avoiding strong monopoles. The solution arises from the domains theory as illustrated in Figure 1.6. The particular situation of a unique domain exhibiting a homogeneous magnetization within the material is highlighted in Figure 1.6(a). It reveals that an intense magnetic field going out of the material is required to close the field lines caused by the monopoles. Although it is quite unfavorable, some specific materials known as strong permanent magnets adopt this monodomain configuration. Generally, the formation of several domains is more advantageous since it allows to keep the majority of magnetic lines within the material as shown in Figure 1.6(b-c). From then, every domain has its own homogeneous magnetization and can be seen as a dipole interacting with the others by dipolar interaction to spare energy. In this configuration, the resultant magnetic moment is the sum of the individual magnetic moments of each domain. This value is determined by the domain volume Γ_i and the average magnetization inside the domain $\mathbf{M}_i$ leading to $\mathbf{m} = \sum_i \mathbf{M}_i \Gamma_i$ [34].

Domains exhibiting a different magnetization are delimited by interfaces called domain walls. Within these walls, the change of magnetization is not discontinuous but takes place over several atomic distances characterizing the thickness of the wall δ . Considering the exchange energy expression as defined in Equation 1.5, it emerges that infinitesimally small angles ϕ are required to minimize the exchange energy leading to an infinite wall thickness. However, it implies that magnetic moments included in the walls move away from the easy-axis direction along which they are preferably oriented.

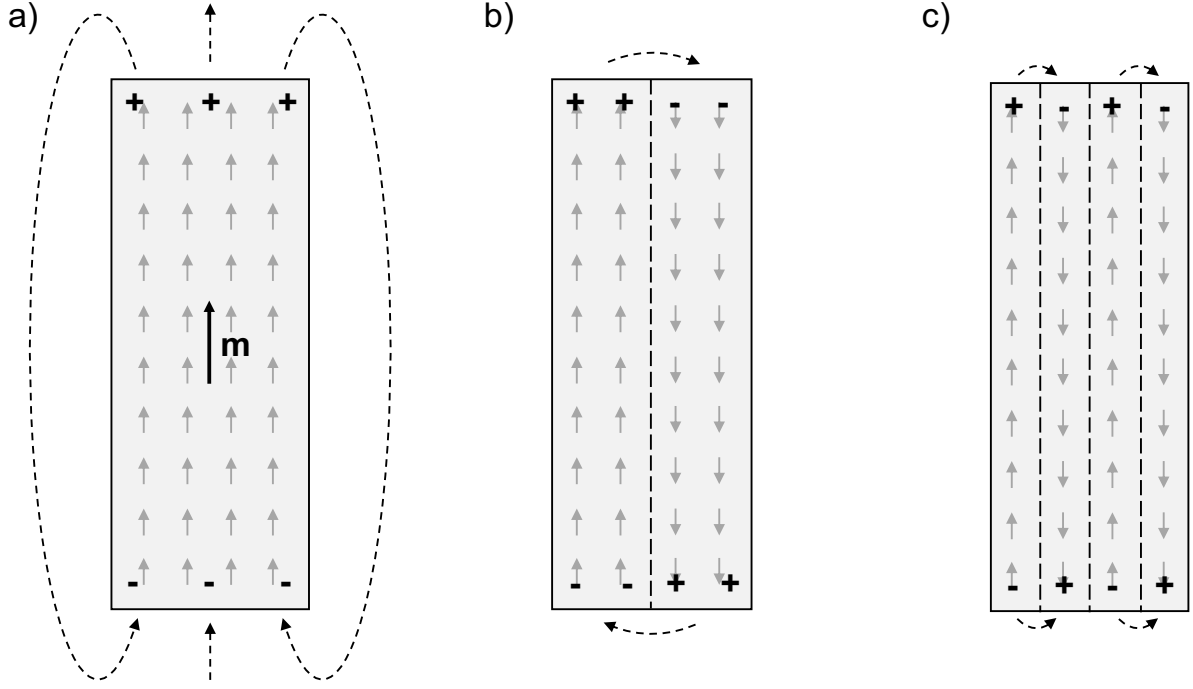


Figure 1.6: Schematic representation of the domain theory for (a) a strong permanent magnet, and (b-c) materials without any global magnetization due to the presence of respectively two and four magnetic domains. The presence of magnetic lines outside the monodomain yields to significant energetic factors whereas the dipolar coupling energy is reduced for multi-domains. Figure from [21]

Therefore, an additional anisotropic energy proportional to δ must be taken into account yielding to a wall thickness:

$$\delta \approx \pi \sqrt{\frac{A}{K}}, \quad (1.11)$$

with K the anisotropic constant and $A \approx 10^{-11}$ J/m the exchange constant [31]. Depending on the geometry, different wall configurations are possible. Among the simple and common ones, the Bloch wall illustrated in Figure 1.7(a) presents a helical structure with the magnetization rotating in the domain wall whereas the Néel wall displayed in Figure 1.7(b) exhibits the magnetization rotation within the domain wall plane. This Néel arrangement is often found in thin-film structures. In nature, several other domain walls exhibiting complex structures are possible.

It is important to clarify that walls are mobile, particularly in presence of magnetic fields. As a matter of fact, the application of an external magnetic field gives rise to an additional energy factor called the Zeeman energy E_Z expressed for one domain as:

$$E_Z = -\mu_0 \mathbf{m}_i \cdot \mathbf{H} = -\mu_0 m_i H \cos(\theta), \quad (1.12)$$

with $\mathbf{m}_i$ the atomic dipole undergoing a torque to be aligned parallel to $\mathbf{H}$ and θ the angle between $\mathbf{H}$ and $\mathbf{m}_i$. Moreover, in a multi-domain structure, E_Z is evaluated by taking the integral of this energy over all the directions:

$$E_Z = -\mu_0 \int \mathbf{M}(\mathbf{r}) \cdot \mathbf{H} \, d^3\mathbf{r} = -\mu_0 \int M(\mathbf{r}) H \cos(\theta(\mathbf{r})) \, d^3\mathbf{r}. \quad (1.13)$$

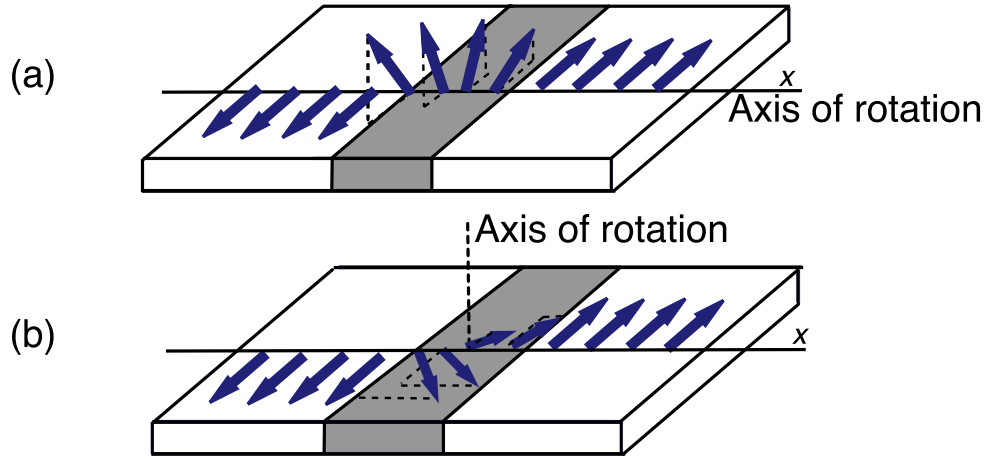


Figure 1.7: Schematic representation of (a) a Bloch wall having a helical structure with the magnetization rotating in the domain wall and (b) a Néel wall exhibiting the magnetization rotation within the domain wall plane. These configurations are simple but nature frequently contains more complex structures. Figure adapted from [30]

This supplementary energy is proportional to $\mathbf{H}$ and leads to a redistribution of the domain walls. Hence, starting from an initial demagnetized multi-domains material and increasing $\mathbf{H}$ up to reach the saturation state, the magnetization is constantly evolving forming a hysteresis loop as depicted in Figure 1.8. In the beginning, for a slight $\mathbf{H}$, the walls move to extend the domains oriented favorably with respect to the magnetic field whereas the domains with orientation far-off it are shortened. Thereafter, for a stronger $\mathbf{H}$, the domain magnetic moments start to rotate in order to be aligned with it. The end of the process is characterized by the presence of a unique domain parallel to $\mathbf{H}$ reaching the magnetization M_s . Afterward, if the field is decreased, the material keeps a certain magnetization due to the fact that only a part of the domains returns to their original orientation. From then, even after the application of the magnetic field, the material still exhibits a remanent magnetization M_r . Finally the opposite magnetic field required to vanish the global magnetization by reversing a given number of domains is called the coercive magnetic field H_c .

A closer look at the hysteresis curve allows to classify the materials into two categories. The first group contains the soft ferromagnets characterized by moderate H_c values. This category presents then thin hysteresis loops with small areas, meaning that the energy loss in the form of heat is low. Besides, they are associated with low M_r and M_s values making them particularly interesting for several applications. For instance, they are used in transformers to limit the heat loss, in electromagnets requiring high induction from small external magnetic fields or until recently in the fabrication of hard disk drive [29]. The second category is composed of the hard ferromagnetic materials exhibiting squared hysteresis loop with high M_r and H_c values. They are more commonly called permanent magnets since a lot of energy is required to inverse their magnetization because of strong anisotropies. These anisotropies are induced either by the intrinsic atomic structure, by the material shape, or during a post-treatment involving external stresses. As they have a permanent magnetic moment even in absence of magnetic field, they can be useful to fabricate magnets for the fridge, speakers, or to deviate the electron beam in a scanning electron microscope (SEM) as used in Chapter 2.

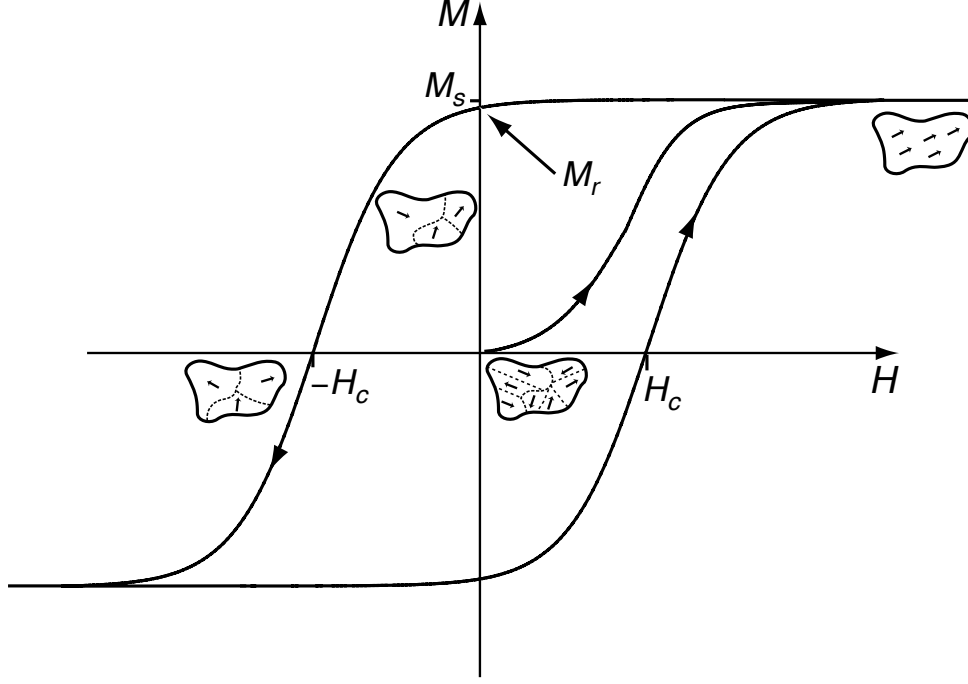


Figure 1.8: Representation of the hysteresis loop of a multi-domains material initially demagnetized. M_s is the saturation magnetization, M_r the remanent magnetization, and H_c the coercive field. Figure from [21]

1.1.5 Magnetic behavior of NiFe/Cu interconnected nanowire networks

All the previous explanations are valid for bulk ferromagnetic materials. However, this thesis is focused on interconnected 3D nanowire networks made of a stack of NiFe/Cu layers. Some complementary information regarding these specific samples together with the change of scale needs to be provided. The T_C values of the metals and alloys dealt in the frame of this work are gathered in Table 1.3. It can be seen that they are all sufficiently high to always guarantee a ferromagnetic behavior.

Table 1.3: Curie temperature of some transition metals together with Ni-Fe alloys used in the frame of this work. Data from [31, 35]

Materials	Fe	Ni	Ni ₉₃ Fe ₇	Ni ₈₀ Fe ₂₀	Ni ₇₀ Fe ₃₀	Ni ₆₀ Fe ₄₀
T_C (K)	1044	628	723	853	888	863

Anisotropic constant values are highlighted in Table 1.4. It reveals that the Ni and Fe samples are dominated by the shape anisotropy due to a difference of two orders of magnitude. On the opposite, the Co sample exhibits both significant magnetocrystalline and shape anisotropy. The explanation is found in the structure since Fe and Ni are respectively BCC and FCC while Co has an HCP structure. Given the absence of treatment after the manufacturing of the samples, the ME anisotropy is neglected.

Table 1.4: Comparison of the importance of magnetocrystalline anisotropy and shape anisotropy from their constant anisotropic values K_u (J/m³) for films made of Fe, Ni, and Co [31].

K_u (J/m ³)	BCC-Fe	FCC-Ni	HCP-Co
MC anisotropy	$5 \cdot 10^4$	$5 \cdot 10^3$	$5 \cdot 10^5$
Shape anisotropy	10^6	10^5	10^6

Ni, Fe, and their alloys in bulk state are usually considered as soft FM materials with small anisotropy. However, it has been investigated that the nanoscale implies a change in their magnetic behavior. Indeed, the MS energy evolves with the volume of the materials d^3 while the energy resulting of the domain walls creation is dependent on the area d^2 . Therefore, it exists for a particle, a certain critical diameter d_c below which the single-domain state is favored [32]. Although mathematical and experimental determination of d_c are complicated to perform due to the uncertain anisotropy constant and the difficulty to isolate and measure such small particles, estimations around 40 nm have been carried out for Fe [29]. Even though the critical radius is smaller than the 80 nm diameter of the nanowires inside the samples, they are considered as single monodomains. This arises from the very high shape anisotropy ascribed to the long and thin wire geometry as displayed in Table 1.2

A single nanowire is then a monodomain because of the strong shape anisotropy. Consequently, the magnetization is spontaneously oriented along the nanowire axis. In the case of an external magnetic field, the nanowire depicts a particular hysteresis loop as described by Figure 1.9(b). The main energetic terms to consider are the shape anisotropic energy and the Zeeman energy since the magnetization is uniform. The application of $\mathbf{H}$ along the nanowire does not influence the magnetization as all the magnetic moments are already oriented along the axis. However, when $\mathbf{H}$ is oriented in the opposite direction, the Zeeman energy gradually increases with the magnitude of the field up to exceed the anisotropic energy. Once this point is reached, the magnetization is suddenly reversed justifying the squared hysteresis loop. The reversal process starts with the nucleation of a new domain wall at the nanowire edges thanks to a local curling effect. After that, this new domain wall is quickly extended along the entire nanowire, leading to a global volte-face of the magnetization [21, 36, 37]. If one considers a perpendicular field, a higher magnitude is required to align the magnetic moments against their natural orientation. Furthermore, the relaxation of the field causes a direct return to the initial magnetization state along the axis, so that there is no hysteresis [38].

An array of parallel nanowires consists of several single nanowires gathered in a common surface area. The comprehension of the magnetic behavior of this array is a necessary path toward the understanding of the interconnected multilayered nanowire networks. In contrast with the single nanowire, an additional energy term is involved due to some dipolar coupling giving rise to a different hysteresis loop. This interaction between the NWs results in a transverse component H_d with respect to the nanowire axis which is highly dependent on the NWs aspect ratio as illustrated in Figure 1.10. The magnitude of this effect is related to the separation distance between the nanowires and therefore to the NW packing factor P , which directly arises from the porosity of the template.

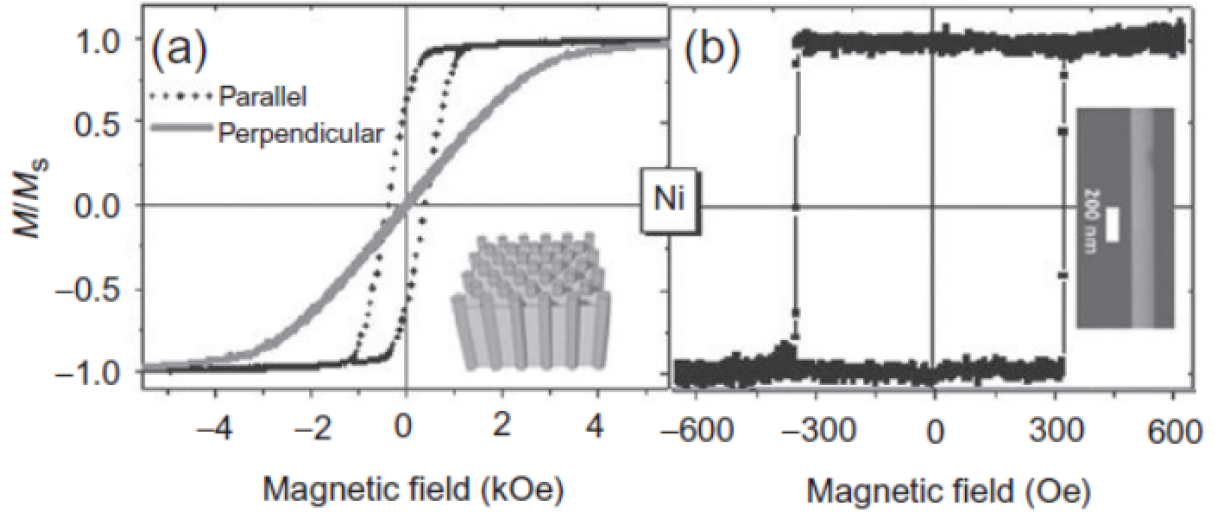


Figure 1.9: Hysteresis loop of (a) an array of parallel Ni nanowires and (b) a single Ni nanowire. The single nanowire exhibits a squared loop resulting from the sudden magnetization reversal while the array of nanowires have a thinner hysteresis loop because of the dipolar contribution. Figure from [39]

In the case of large P , the resulting dipolar coupling is strong because of the significant interactions. However, this thesis deals with samples having small $P \approx 3\%$ which dramatically reduces this contribution. A way to quantify the magnetostatic magnetic field H_{ms} resulting from both the shape anisotropy and the dipolar coupling is expressed depending on P by: [23, 40]:

$$H_{ms} = 2\pi M_s(1 - 3P). \quad (1.14)$$

From this equation, it appears that the case of $P=0$ simply corresponds to an infinite single nanowire while the case of $P=1$ can be associated to a thin film, networks of NW being an intermediate situation in between. In comparison to the single nanowire, the contribution of the dipolar coupling within the interconnected/parallel arrays can be observed in the difference of hysteresis curve which presents a less squared shape as shown in Figure 1.9(a). Physically, the magnetization flip within the NWs does not occur for the same magnetic field leading to a smoother magnetization reversal. Furthermore, another consequence of this dipolar interaction arises from the M_r which is not equal to M_s anymore but is a bit lower. Indeed, when relaxing the magnetic field, some NWs spontaneously flip their magnetization to adopt an antiparallel arrangement which is energetically more stable.

In the framework of this thesis, interconnected networks were analyzed, only slightly changing the magnetic behavior compared to an array of parallel NWs. The samples are composed of nanowires oriented with an angle of $\pm 25^\circ$ with respect to the normal of the film plane. Hence, every single nanowire presents a natural magnetization along its axis leading, as for the parallel arrays, to a global easy direction oriented out-of-plane (OOP). By convention, the directions perpendicular to the axis are called the in-plane (IP) directions². Nevertheless, the interconnections add some complexity to the structure analysis. Indeed, the density and the volume of interconnections are difficult to estimate turning the magnetic simulations at these special points uneasy to perform.

²The IP/OOP directions refer to the planes of the successive layers.

However, since the fraction of interconnections is much smaller than the fraction of uniform magnetization within the nanowires, their influence can be neglected.

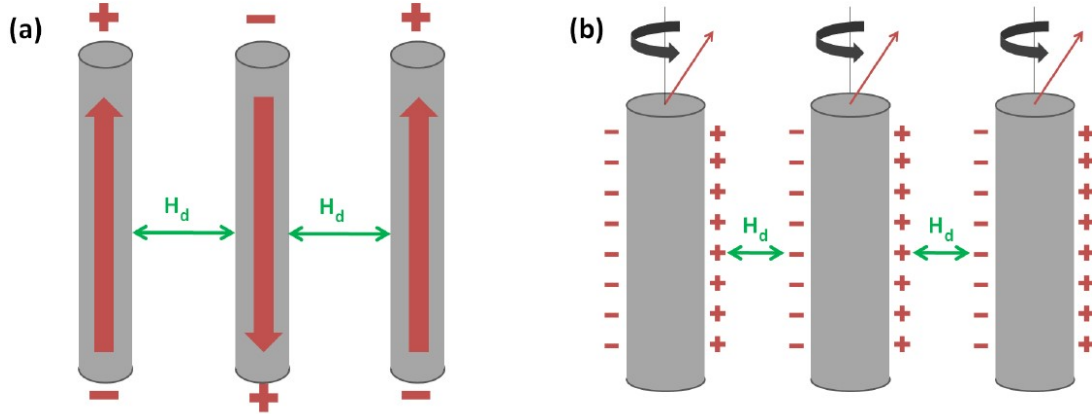


Figure 1.10: Schematic representation of the dipolar coupling within a (a) an array of thin nanowires and (b) an array of thick nanowires. The aspect ratio is essential, the thin nanowires exhibit a natural antiparallel arrangement whereas the thick nanowires are parallelly magnetized with a precession around the easy axis. H_d is the field resulting from the dipolar interactions. Figure from [22].

Up to now, the influence of the Cu layers was not taken into account, though the presence of these NM layers drastically modifies the magnetic behavior of the crossed nanowires (CNWs). Indeed, depending on the layer thicknesses of both the ferromagnetic material t_{FM} and the non-magnetic material t_{NM} compared to the nanowire diameter ϕ , the layers can be considered as cylinders if $t_{\text{FM/NM}} > \phi$ or as thin films if $t_{\text{FM/NM}} < \phi$. To keep the spontaneous magnetization along the axis instead of perpendicular to it, it is essential to preserve the shape anisotropy and therefore $t_{\text{FM}} > \phi$.

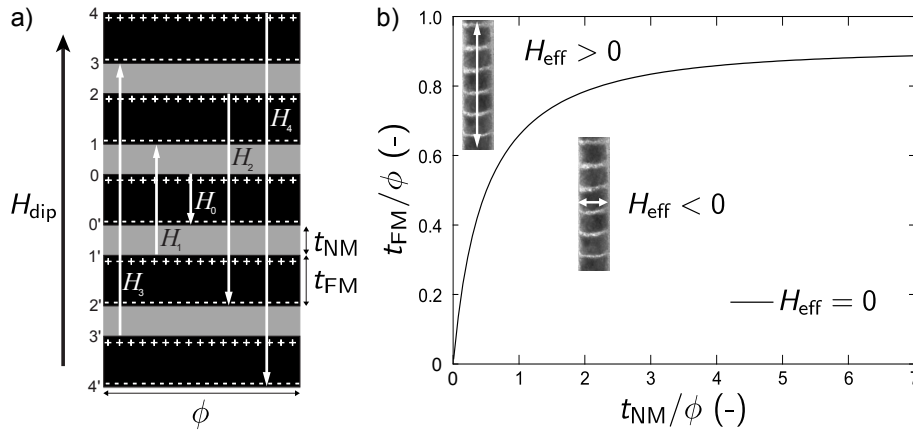


Figure 1.11: (a) Schematic representation of a multilayered nanowire with H_0 the magnetic field ascribed to the shape anisotropy and H_{dip} the magnetic field coming from the dipolar interactions between the closest ferromagnetic layers. (b) Anisotropy diagram illustrating the direction of H_{eff} being the sum of H_0 and H_{dip} , as function of the ferromagnetic layer thickness t_{FM} and the non-magnetic layer thickness t_{NM} normalized by the diameter ϕ . The continuous line shows the situations where $H_{\text{eff}} = 0$

Another factor to take into consideration is the dipolar interaction between the successive layers. This effect is schematically depicted in Figure 1.11(a). Hence, a demagnetizing

field originates from the layer itself H_0 and from the dipolar interactions with the first four neighbored layers so that it produces H_{dip} being the sum of H_1, H_2, H_3, H_4 . The effective MS anisotropy field H_{eff} results from both the shape anisotropy contribution (H_0) and the dipolar coupling H_{dip} . Figure 1.11(b) sums up the possible directions of H_{eff} depending on the t_{FM}/ϕ and t_{NM}/ϕ ratios. The line represents the couple thicknesses where the shape anisotropy and the dipolar interaction compensate each other so that $H_{\text{eff}} = 0$. It appears that when $t_{\text{FM}}/\phi \rightarrow 1$ the H_{eff} points up or down the axis since both contributions are oriented in this direction. However, for lower values, the resultant direction of H_{eff} can be either parallel or perpendicular to the axis depending on the layer thickness ratio expressed as $\lambda = t_{\text{FM}}/t_{\text{NM}}$. Large values of λ are required to keep H_{eff} oriented along the axis whereas smaller values give rise to a transverse H_{eff} [21, 41, 42].

1.2 Electrical transport in ferromagnetic transition metals

This part aims to describe the fundamental transport of charges within ferromagnetic metals. From the bulk state to the nanostructures, the electron scattering processes responsible for the resistance are exposed. Moreover, the temperature influence is explained. Finally, the origin of spin currents leading to the development of spintronics is highlighted.

1.2.1 Fundamental electrical transport of bulk materials

The electrical transport is related to the capacity of charges to move inside a material when submitted to an electrical field $\mathbf{E}$. This phenomenon is characterized by the conductivity σ , which is an intrinsic parameter related to the electronic structure of materials. At room temperature, σ is spread over 24 orders of magnitude depending on the material class as illustrated in Figure 1.12.

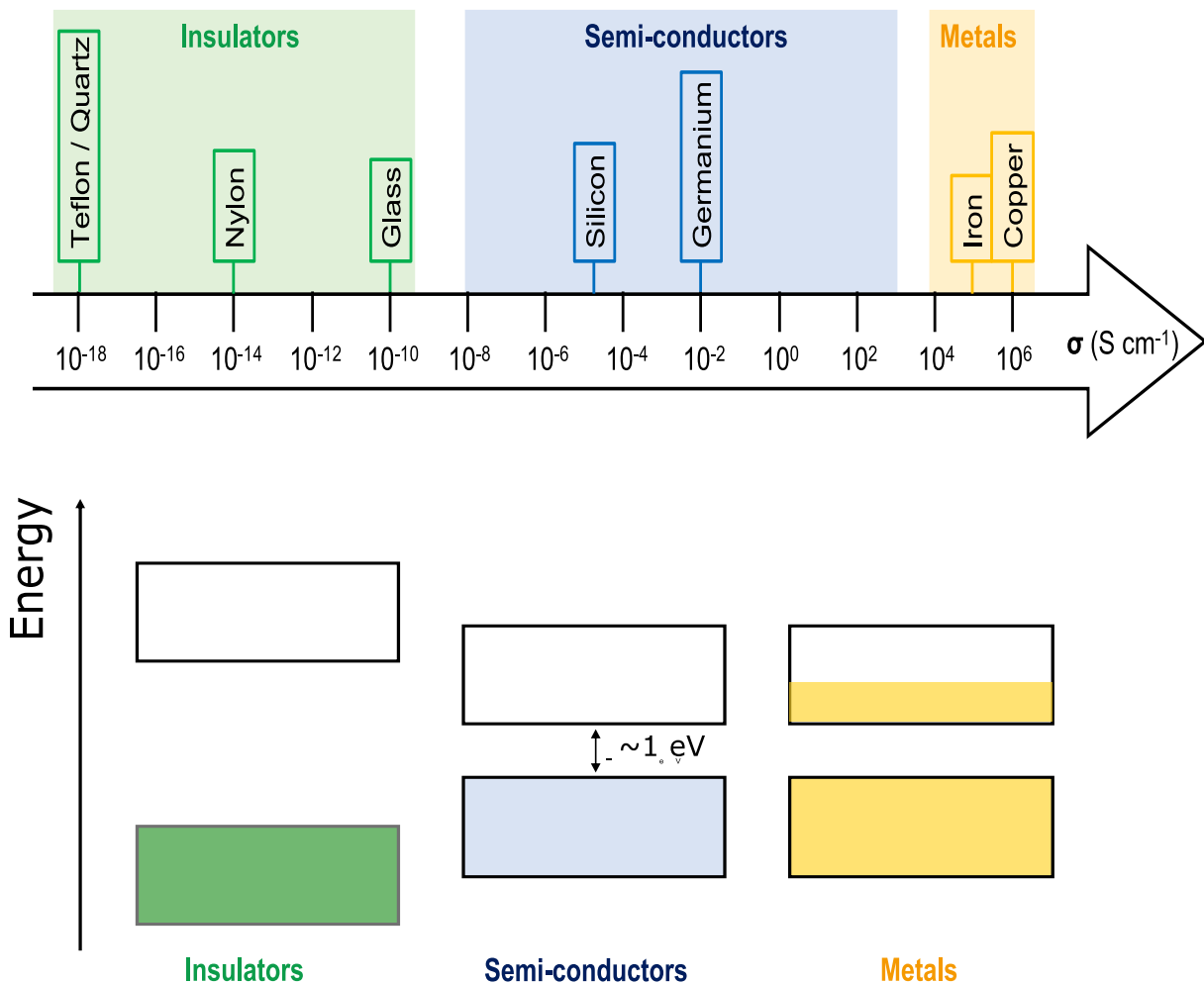


Figure 1.12: Electrical conductivity for several materials ranging from $10^{-18} \text{ S/cm}^{-1}$ to 10^6 S/cm^{-1} . Adapted from [21]

It can be seen that materials are classified into three categories finding their origins in the band structure. Firstly, insulators are materials preventing the displacement of charges. Physically, it is due to the large band gap ϵ_g of a few eV between the filled valence band and the empty conduction band preventing the crossing of electrons. The second category, called the semi-conductors presents an intermediary behavior meaning that they can be seen as insulators or conductors. This particularity comes from the fact that at very low temperature the thermal energy is not sufficient compared to the gap $\epsilon_g \approx 1$ eV so that the conductivity is limited. However, a temperature enhancement turns these materials into conductors since the higher thermal energy allows the electrons to cross the energy barrier and flow in the conduction band. Moreover, a process called doping consists in injecting impurities in semi-conductors to ensure a net improvement of σ . The last category gathered the metals which exhibit large conductivity values because of their partially filled conduction band.

The conductivity of metals arises then from the conduction electrons which are free to move in the lattice composing the physical structure of the solid. Therefore, the conductivity is related to the electronic density n , the electronic charge e , and is expressed as:

$$\sigma = ne\mu, \quad (1.15)$$

with μ the mobility characterizing the ability of the electrons to move into the solid. This parameter is defined thanks to the relaxation time τ and the effective electron mass m^* as:

$$\mu = \frac{e\tau(\epsilon_F)}{m^*}. \quad (1.16)$$

By using the relation of μ , it is possible to rewrite the conductivity equation as:

$$\sigma = \frac{ne^2\tau(\epsilon_F)}{m^*}. \quad (1.17)$$

It can be noticed that the current flow only involves the electrons situated near ϵ_F . This is due to the fact that $\mathbf{E}$ shifts only a small part of the Fermi surface while the majority of electrons stay in energy states already occupied. This minority of electrons is then free to move. Nevertheless, they can be slowed down by scattering inducing a transfer to an empty energy state. The number of scattering is then at the origin of the resistance and is material-dependent. On the other end, n does almost not vary with the temperature. The key parameter is therefore the relaxation time which represents the time between two scatterings or the inverse of the electronic mean free path λ_e .

Considering a macroscopic solid, the electrons undergo collisions from two different mechanisms giving rise to the total resistivity ρ . The first one involves the electron-phonon scatterings and results in the ideal resistivity ρ_i . Since the phonon density is proportional to the temperature, ρ_i is temperature-dependent. On the contrary, the other mechanism involves uniquely the static defects as the impurities, the dislocations, the vacancies, or the grain boundaries. Therefore, this contribution only relies on the material purity and is characterized by the residual resistivity ρ_r . The sum results in the total resistivity ρ expressed by the Matthiesen's rule given by:

$$\rho(T) = \rho_r + \rho_i(T). \quad (1.18)$$

The temperature dependence is outlined in Figure 1.13. It reveals that at very low temperature, the constant residual resistivity dominates since there is no lattice vibration (phonon). However, an increase in temperature leads to a growth of phonon density as well as an improvement of the scattering efficiency. Hence a T^5 regime followed by a linear regime can be observed.

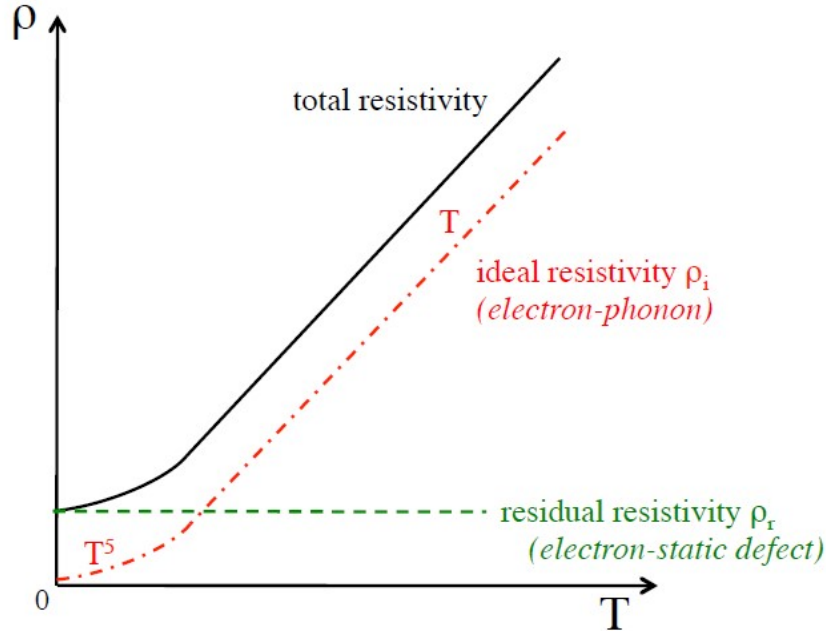


Figure 1.13: Matthiessen's law for the electrical resistivity (black) being the sum of the ideal resistivity ρ_i (red) and the constant residual resistivity ρ_r (green). Figure from [43].

Looking a bit closer at ρ_r allows to characterize the purity of the sample. Indeed, the presence of undesired impurities or the addition of other materials to create alloys leads to a dramatic increase in the static defect density. Consequently for alloys, ρ_r evolves almost linearly with the impurity concentration. Besides, when dealing with nanostructures having dimensions smaller than λ_e , additional contribution arises from the collisions with the edges of the sample so that ρ_r is shifted. As a matter of fact, the smaller is the sample, the bigger is this effect

Supposing that at low temperature $\rho = \rho_r = \rho^{LT}$ and at room temperature $\rho^{RT} = \rho_r + \rho_i^{RT}$, the "residual resistivity ratio" RRR can be expressed as:

$$\text{RRR} = \frac{\rho^{RT}}{\rho^{LT}} \quad \rho_r = \frac{\rho_i^{RT}}{\text{RRR} - 1}. \quad (1.19)$$

RRR is an indicator of the crystalline quality and allows to directly estimate the ρ_r thanks to the values of ρ_i^{RT} found in the literature and displayed in Table 1.5.

When talking about current I , the Ohm's relation $I = V/R$ is frequently used. It relates the potential drop $V = EL$ between two edges of a solid separated by a distance L , and

Materials	Cu	Fe	Ni	Ni ₉₅ Fe ₅	Ni ₉₀ Fe ₁₀	Ni ₈₀ Fe ₂₀	Ni ₇₀ Fe ₃₀	Ni ₆₀ Fe ₄₀
$\rho_i^{\text{RT}} (\mu\Omega\text{cm})$	1.7	9.8	7	9.17	9.95	11.32	13.24	16.76

Table 1.5: Ideal resistivity measured at room temperature for different bulk metals and alloys. Data from [44, 45]

the resistance R . It can be noticed that in the frame of this thesis, both R and ρ are used. The difference comes from the fact that ρ is an intrinsic characteristic of the materials whereas R is dependent on the sample geometry. However, they are linked by the relation $R = \rho L/S$ where S and L are respectively the section and the length of the sample.

1.2.2 From magnetoresistance to spin-dependent electrical transport

Now that the physics core of the electronic transport is known, the influence of a magnetic field on the electrons flow called the magnetoresistance effect will be explored. The first example of this effect arises from the Lorentz Force $\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$ that deviates charges q , having a velocity v , when submitted to a magnetic field. Nonetheless, other magnetoresistance effects exist in presence of ferromagnetic materials leading to interesting applications.

Anisotropic magnetoresistance

The anisotropic magnetoresistance effect (AMR) relies on the fact that the resistance of some metals slightly varies depending on the angle formed by the current and the magnetization within the material. This effect is ascribed to the electron spin-orbit coupling. Physically, it is due to a larger probability of s-d scattering when electrons are moving parallel to the magnetization than for a transverse motion. Therefore, as it appears in Figure 1.14 the resistivity reaches a maximum when the current is applied parallel to the magnetization whereas it gets to a minimum in case of a perpendicular current. For any other angle θ between the magnetization and the current, the situation is intermediate and the resistivity is given by:

$$\rho(\theta) = \rho_{\perp} + \Delta\rho \cos^2(\theta) \quad \Delta\rho = \rho_{\parallel} - \rho_{\perp}, \quad (1.20)$$

with $\rho_{\parallel}$ and $\rho_{\perp}$ being respectively the resistivity when the current is applied parallel and perpendicular to the magnetization. The magnitude of the AMR effect is computed with Equation 1.21 and can only attain a few percents for pure ferromagnetic metals. However, this ratio is inversely proportional to the temperature so that values of 20% have already been reached for binary alloys at low temperature³[47]. In the AMR expression, ρ_{avg} is considered as the resistivity in absence of magnetic field, meaning that all the domains are randomly oriented. Therefore, it corresponds to an average between the parallel direction and the two different perpendicular directions.

$$\text{AMR} = \frac{\Delta\rho}{\rho_0} \quad \rho_{\text{avg}} = \frac{1}{3}\rho_{\parallel} + \frac{2}{3}\rho_{\perp}. \quad (1.21)$$

³It should be specified that some diluted alloys may also exhibit a small negative AMR ratio [46]

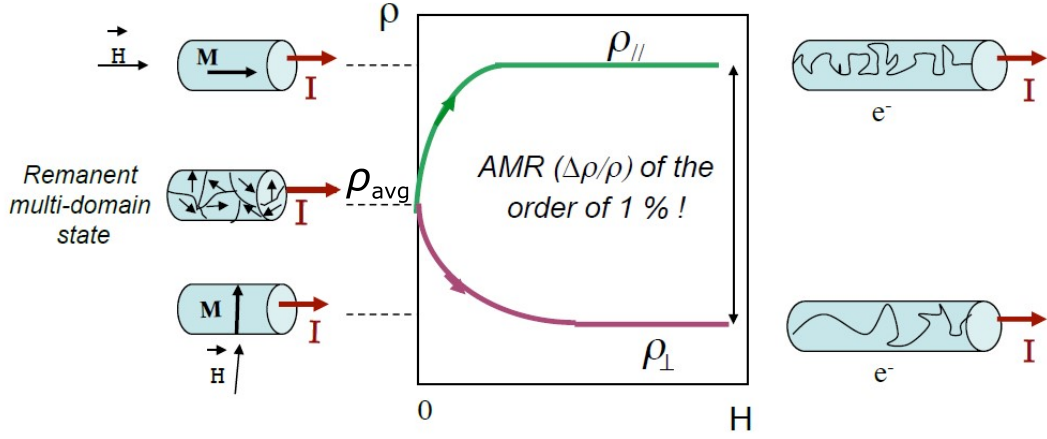


Figure 1.14: Schematic representation of the AMR effect in polycrystalline ferromagnetic materials. The resistivity reaches a maximum when the current is applied parallel to the magnetization whereas it gets to a minimum in case of a perpendicular current. Figure adapted from [43]

Nowadays, applications relying on this effect are mainly magnetic sensors that can for instance detect the motion of objects without any contacts thanks to the AMR [48]. In the past, this effect was also widely used in the development of reading head for hard disk drives (HDD) [49]. From then, the spintronics emergence completely transformed the data storage density thanks to the magnetic random access memory (MRAM) based successively on the giant magnetoresistance (GMR) and tunneling magnetoresistance (TMR) effects discovered in nanostructures.

Spintronics emergence

For decades, our world has been composed of a growing number of electronics devices, and circuits packed into space always smaller. Unfortunately, physical limits were reached preventing further rescaling. The solution arose from a new branch of electronics resulting from the merger between electronics and magnetism which has been developed in the eighties. In addition to classical electronics that use the negative charge of the electron to manipulate its motion or store information, spintronics relies on the electron spin as a new degree of freedom. Since the spin is directly coupled with the magnetic momentum of the electron, it can be easily handled by the means of an external magnetic field [50]. It should be specified that although AMR is already considered as spintronics, its veritable rise is associated with the GMR discovery in nanostructures [11].

Two-current model

Even though other materials can be used [51, 52], the GMR effect is frequently associated with ferromagnetic materials because of their unique band structure allowing a simple manipulation of the spin. As seen in Subsection 1.1.1, the superposition of the 3d and 4s band is responsible for the imbalance in the spin-up ($\mathcal{S}_\uparrow$) and spin-down ($\mathcal{S}_\downarrow$) density of states leading to spontaneous magnetization. Moreover, this imbalance is also at the origin of the spin-dependent electrical transport. Electrons having a magnetic moment parallel/antiparallel to the magnetization are respectively called the majority/minority electrons. By convention, $\mathcal{S}_\uparrow$ are considered as majority electrons while $\mathcal{S}_\downarrow$ are the minority electrons.

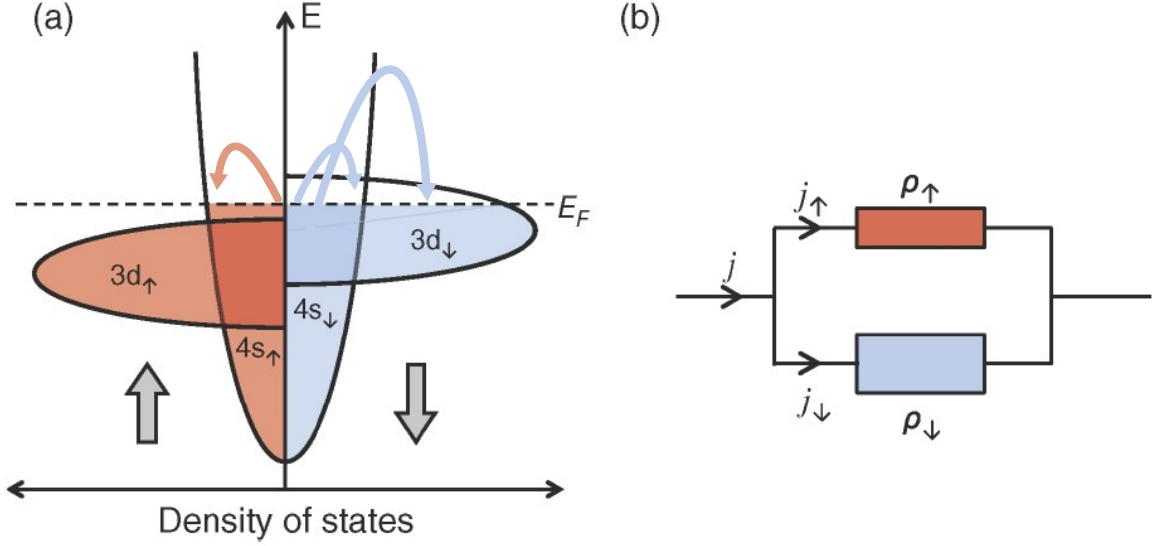


Figure 1.15: (a) Schematic representation of the band structure for transition metals exhibiting strong ferromagnetic behavior. (b) Representation of the two-current model equivalent circuit. Figure adapted from [53]

Considering the band structure displayed in Figure 1.15(a), it appears that at ϵ_F the density of states (DOS) available in $\mathcal{S}_{\downarrow}$ subband is quite larger than for the $\mathcal{S}_{\uparrow}$ subband. This comes from the fact that both the large $3d_{\downarrow}$ and the narrow $4s_{\downarrow}$ bands are partially filled while only the $4s_{\uparrow}$ band provides empty energy states in the $\mathcal{S}_{\uparrow}$ subband. Therefore, since electron scattering events are possible on condition of having the same spin and energy level, electrons have different resistivity whether their magnetic moment is parallel to the magnetization ($\mathcal{S}_{\uparrow}$) or antiparallel ($\mathcal{S}_{\downarrow}$). Indeed, for $\mathcal{S}_{\downarrow}$ electrons both s-s and s-d scattering are allowed whereas only s-s scattering events are possible for $\mathcal{S}_{\uparrow}$ due to the full $3d_{\uparrow}$. The minority conduction electrons of the 4s band have therefore a higher probability to be scattered so that they have a higher resistivity $\rho_{\downarrow} > \rho_{\uparrow}$. Under the assumption that electron's spin is conserved during several scattering events, the $\mathcal{S}_{\uparrow}$ and $\mathcal{S}_{\downarrow}$ electrons can be represented in two independent parallel conduction channels having different resistivity as shown in Figure 1.15(b). The condition to avoid the mixing of the two channels and conserve the spin current behavior is to have a small probability of spin-flip compared to the number of scattering. This is schematically illustrated in Figure 1.16 showing that the electron mean free path λ_e is quite smaller than the spin-flip diffusion length l_{sf} , what is true up to room temperature⁴. However, when the temperature is enhanced, the probability of spin-flip scattering by magnons⁵ becomes more important limiting l_{sf} so that the two conduction channels are mixed [55].

The key relies thus on the different resistivities $\rho_{\uparrow}$ and $\rho_{\downarrow}$ which both contribute to the total resistivity of a material expressed as:

$$\rho = \frac{\rho_{\uparrow}\rho_{\downarrow}}{\rho_{\uparrow} + \rho_{\downarrow}}. \quad (1.22)$$

⁴For the Permalloy l_{sf} is estimated around 4.3 nm at 77K [54]

⁵Magnons are spin waves considered as bosonic quasi-particles and will be detailed in Subsection 1.3.2

Besides, the magnitude of this difference can be quantified by the spin asymmetry coefficients α and β expressed as:

$$\alpha = \frac{\rho_{\downarrow}}{\rho_{\uparrow}} \quad \beta = \frac{\rho_{\downarrow} - \rho_{\uparrow}}{\rho_{\downarrow} + \rho_{\uparrow}} = \frac{\alpha - 1}{\alpha + 1}. \quad (1.23)$$

Typical values for 3d ferromagnets are $2 < \alpha < 10$ and $0.3 < |\beta| < 0.8$ [43].

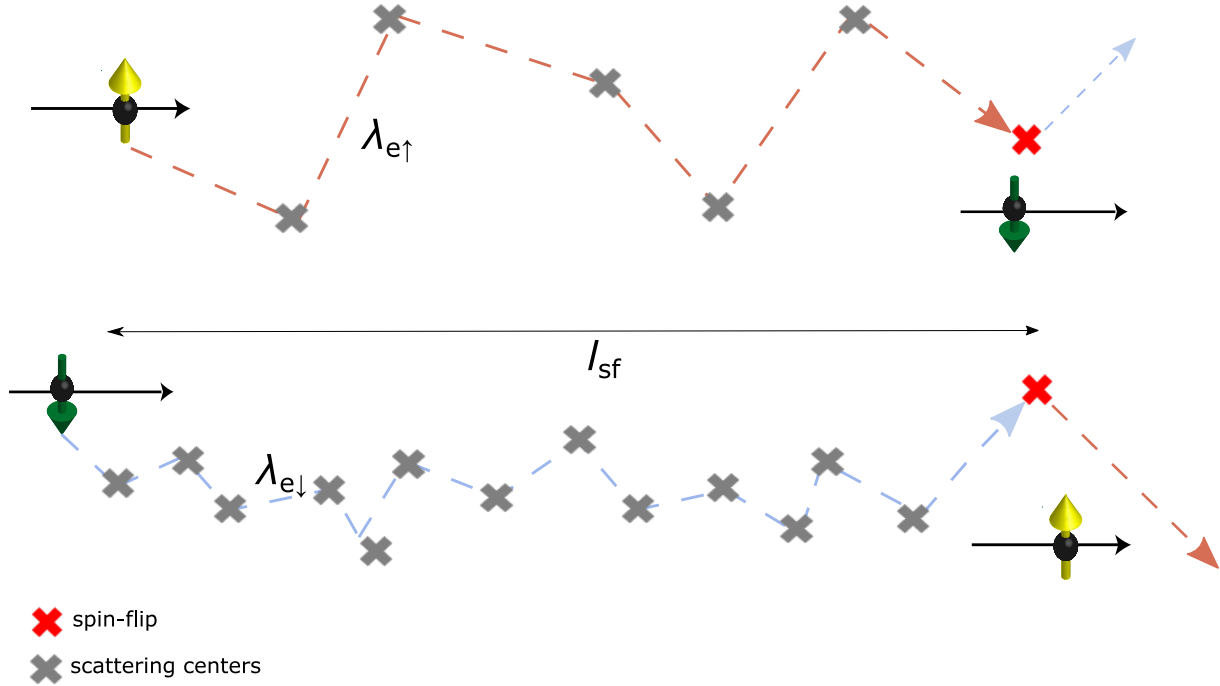


Figure 1.16: Schematic representation of the flow path for the majority and minority electrons. It can be observed that the electron mean free path λ_e is always much smaller than the spin-flip diffusion length l_{sf} . Furthermore, minority electrons undergo more scattering events leading to a higher resistivity.

1.2.3 Giant magnetoresistance

Historically, the two-current model has been developed to understand the spin-dependent resistivity in materials doped with impurities [53]. However, this theory has also been useful to explain the GMR effect observed in nanoscopic multilayered samples. Considering a stack composed of FM layers separated by NM layers, every FM layer can be independently magnetized either parallel (P) or antiparallel (AP) with respect to the previous one. Two extreme cases can be distinguished as shown in Figure 1.17. In absence of external magnetic field, the AP configuration is energetically favored meaning that the majority of successive layers have their magnetic moments in opposite directions. Therefore, both the $\mathcal{S}_{\uparrow}$ and $\mathcal{S}_{\downarrow}$ are equally scattered so that they exhibit a similar resistivity. On the contrary, the application of an external magnetic field results in an alignment of the magnetization within the FM layers, associated with a parallel configuration. As a result, the flowing current is spin-polarized since the majority electrons manifest a resistivity drastically smaller. Finally, the resistivity for the AP and P configuration can be expressed as:

$$\rho_{AP} = \frac{\rho_{\uparrow} + \rho_{\downarrow}}{4} \quad \rho_P = \frac{\rho_{\uparrow}\rho_{\downarrow}}{\rho_{\uparrow} + \rho_{\downarrow}}. \quad (1.24)$$

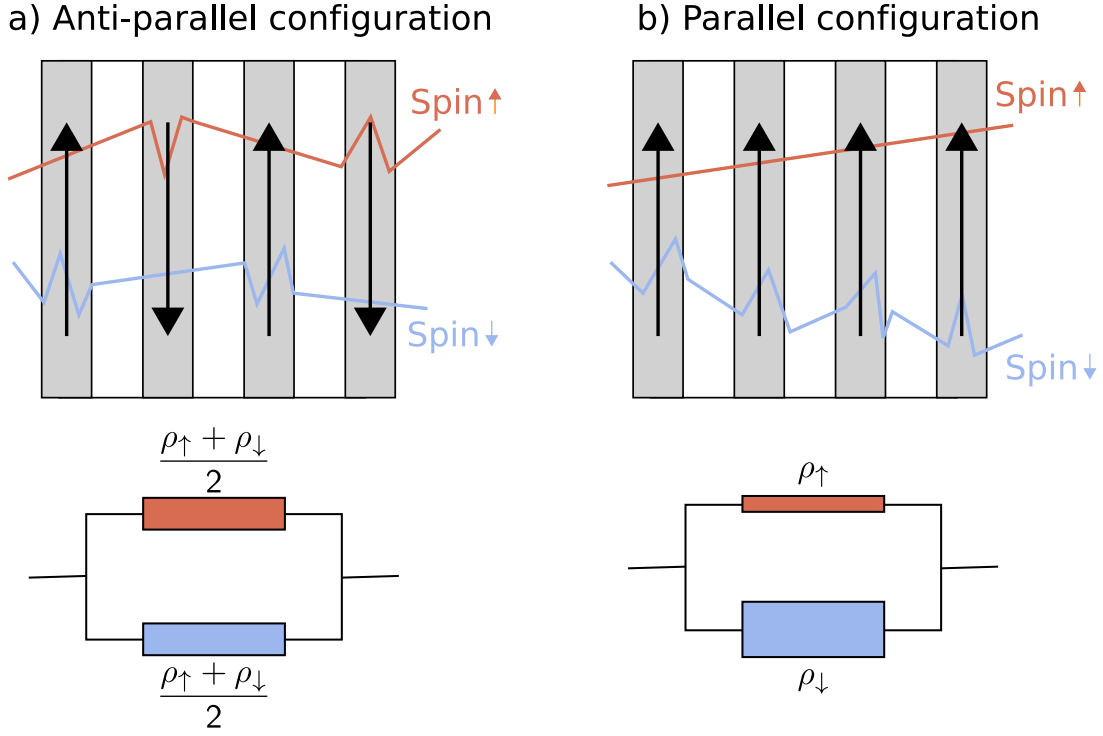


Figure 1.17: Schematic representation of the two extreme possible cases in a multilayered stack made of successive FM and NM materials. The AP configuration is usually adopted in absence of external magnetic field and exhibits a higher resistivity ρ_{AP} whereas the application of a magnetic field leads to a P configuration with a smaller resistivity ρ_P . Adapted from [21]

Supposing a ferromagnetic materials with $\alpha \neq 1$, the GMR and the MR ratio can finally be determined as:

$$\text{GMR} = \frac{\rho_{AP} - \rho_P}{\rho_P} \quad \text{MR} = \frac{\rho_{AP} - \rho_P}{\rho_{AP}}. \quad (1.25)$$

Figure 1.18(a) represents the original results obtained by Albert Fert's team in 1988 [11]. They did not only establish that the GMR ratio for Fe/Cr sample was extremely high (around 80%) but also that the thickness of the NM spacers influenced the magnitude of this effect. This is ascribed to the exchange coupling between the successive FM layers which is function of the NM layer thickness as exhibited in Figure 1.18(b). Hence, an oscillating behavior leading either to ferromagnetic or antiferromagnetic coupling is observed. This tendency slowly disappears as the NM spacer thickness becomes larger. To get an optimal effect, no coupling or an antiferromagnetic coupling is required. Indeed, a ferromagnetic coupling generates a P configuration either in absence or in presence of magnetic field, without any resistivity change. Therefore, it is essential to either have very accurate control of the NM layers or to impose sufficiently thick NM spacers ($t_{NM} >$ a few nm) to suppress the exchange coupling. Basically, the random configuration is more or less similar to the AP configuration. It exists other solutions to guarantee the AP configuration for zero or small magnetic field. An efficient one is the spin valve consisting of one NM spacer placed in between a FM layer with fixed magnetization and a FM layer

with controllable magnetization. The key relies then on the fixed magnetization which can be blocked thanks to an additional antiferromagnetic layer. This configuration called spin valve allows to produce the conventional GMR reading heads. It is worth to note that other nanostructures can give rise to GMR as multilayered granular systems composed of conducting NM matrix with embedded FM nano-clusters [56].

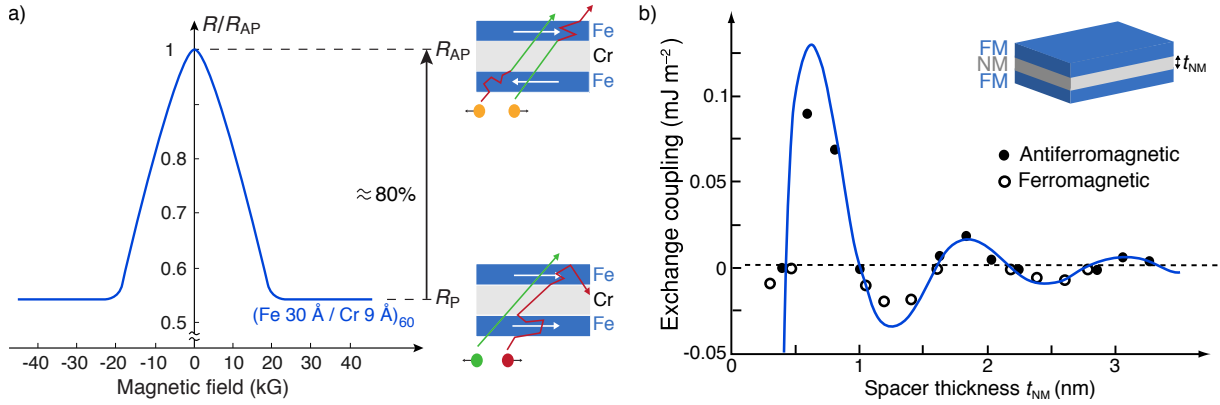


Figure 1.18: (a) Original giant magnetoresistance curve obtained by the A.Fert's team in 1988 for a Fe/Cr multilayered at 4.2 K. (b) Exchange coupling between the successive FM layers as a function of the NM spacer thickness t_{NM} . It is possible to get either ferromagnetic or anti-ferromagnetic coupling for small t_{NM} but this phenomenon tends to disappear for larger t_{NM} . Figure from [21].

Considering classical multilayered samples, measurements can be performed either with a current-in-plane (CIP) or with a current-perpendicular-to-the-plane (CPP) arrangement. These two configurations are illustrated in Figure 1.19. This thesis only contains CPP measurements which are significantly easier to model and understand. The CPP configuration requires l_{sf} larger than λ_e to avoid the spin-mixing, which is a condition easily satisfied [57]. On the contrary, the CIP configuration is related to heavy limitations. Indeed on average, electrons flow perpendicularly to the layers with a length equal to λ_e [58, 59]. Therefore, to observe the GMR effects, the layer thicknesses must be much smaller than λ_e to ensure that electrons travel through several layers. However, at this scale ($\approx$ several nm) the coupling exchange is strong, requiring careful control over the layer thickness to ensure a FM coupling.

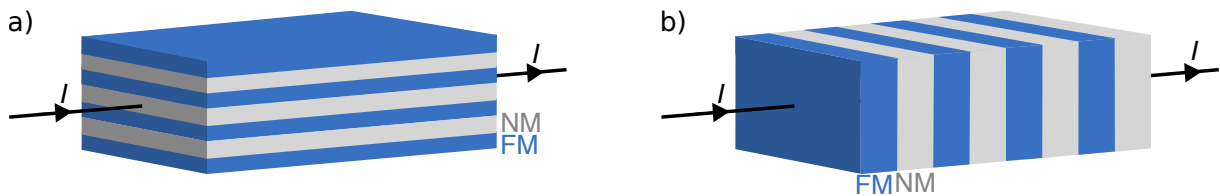


Figure 1.19: Schematic representation of (a) the CIP configuration with the current flowing in the plane of the layers and (b) CPP configuration with the current injected perpendicular to the layer planes. Figure from [21]

1.3 Thermoelectric properties of ferromagnetic transition metals

Thermoelectricity has been discovered in 1821 by T.J. Seebeck [60]. Although it is not recent, this effect allowing to convert heat into electrical energy and vice versa is very powerful. On one hand, it does not require moving part and does not release by-products. Furthermore, thermoelectric systems have proved a long lifetime and are environmentally friendly [61]. This technology is sometimes used for power generation from wasted heat and has also applications in heating or cooling down systems from current injections. Nevertheless, the use of thermoelectric materials for these purposes is quite limited because of the low power thermoelectric conversion efficiency η_{th} always remaining much smaller than the Carnot efficiency reached for conventional systems. Hence:

$$\eta_{\text{th}} < \frac{T_{\text{h}} - T_{\text{c}}}{T_{\text{h}}}, \quad (1.26)$$

where T_{h} and T_{c} are respectively the hot and the cold temperature of the system. As a matter of fact, for some reasons explained in the following lines, η_{th} only approaches values around 8% for $\Delta T = 250\text{K}$ [43]. Thenceforth, during years and years after the discovery of a voltage generated from a temperature gradient, researchers have looked for efficiency improvements by the means of new materials and conditions. However, it always stays challenging since the factors included in η_{th} , especially the electrical conductivity σ and the thermal conductivity κ , are related to each other by an inversely proportional relation. One way to decouple their behavior is to work with nanostructures having sizes larger than λ_e but smaller than the phonon mean free path λ_p . Besides, it has been discovered that multilayered nano-objects could exhibit spin-dependent thermoelectric properties, allowing to tune the thermoelectric characteristics with an external magnetic field. These two discoveries have particularly played in favor of the renewed appeal for thermoelectricity. This section aims to first explain the thermal transport and the thermoelectricity foundations through the Subsections 1.3.1 and 1.3.2. Afterward, spin-dependent thermoelectric effects arising from the merge between the thermoelectricity and the spin-current theory will be highlighted in Subsection 1.3.3.

1.3.1 Fundamental thermal transport in bulk materials

The thermal transport is related to the heat transfer inside a material. The mechanisms are classified into 3 categories. The conduction consists of a transfer of energy through interactions between particles. The convection arises from bulk motions of fluids. Finally, radiations transfer heat by the intermediary of electromagnetic waves. The following is written under the assumption that heat within the solids is uniquely exchanged with conduction involving both electrons and phonons (lattice vibrations) [62]. Considering a temperature gradient ∇T , the heat flux j_q is given by:

$$j_q = -\kappa \nabla T \quad \kappa = \kappa_e + \kappa_\ell \quad (1.27)$$

The heat displacement is therefore quantified by the thermal conductivity κ composed of both the lattice conductivity κ_ℓ and the electronic conductivity κ_e . In contrast with the widely spread electrical conductivity, the values of the heat conductivity range over 5 orders of magnitude from $10^{-2} \text{ Wm}^{-1}\text{K}^{-1}$ for foams to $10^3 \text{ Wm}^{-1}\text{K}^{-1}$ for diamonds and graphene as shown in Figure 1.20.

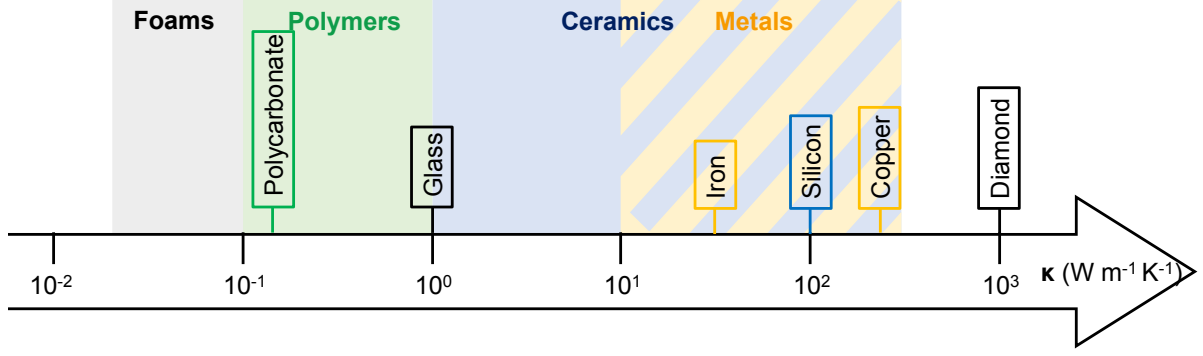


Figure 1.20: Thermal conductivity for different classes of materials. Figure from [63].

Metals and their alloys are good thermal conductors as shown by their κ comprised between 10 and 500 $\text{Wm}^{-1}\text{K}^{-1}$ [63]. Unlike other materials, the electronic contribution dominates in metals due to the presence of a free-electron gas. However, in alloys both the electronic and the lattice contributions have to be taken into account, they are respectively given by:

$$\kappa_e = \sigma L_0 T \quad \kappa_\ell = \frac{1}{3} C_\ell \lambda_p v_p. \quad (1.28)$$

For the lattice expression, C_ℓ refers to the lattice heat capacity, λ_p is the phonon mean free path while v_p is the average phonon velocity. Physically, the lattice is able to store energy in the form of lattice vibrations and displace it throughout the material [30]. Regarding the expression of the electronic thermal conductivity, it is related to the electrical conductivity by the Wiedemann-Franz (WF) relation where $L_0 = 2.45 \cdot 10^{-8} \text{ W}\Omega\text{K}^{-2}$ is the Lorenz number. Therefore, good electrical conductor metals are also good thermal conductors. To be valid, the WF law implies that electrons undergo elastic collisions either with impurities or with phonons. Figure 1.21 exhibiting the validity of this relationship shows that it is the case at high temperature and very low temperature whereas there is a deviation in between. It is ascribed to the fact that for $T \geq \theta_D$ (θ_D being the Debye temperature at which all the vibration modes are activated) collisions between electrons and phonons are efficient without any energy loss. However, for a certain range of temperature above 0 K, the electron-phonon scattering events are more effective in causing thermal resistance than to produce electrical resistance leading to WF law invalidity. Finally, for temperatures close to 0 K, electrons are uniquely elastically scattered by static defects so that the WF law is again valid in this regime.

It can be noticed that this deviation is important for pure metals while alloys exhibit smaller invalidity because of their higher impurity concentration. However, alloys have an additional contribution arising from the lattice, together with a drastic reduction of the electronic conductivity, so that it requires some caution when using this relationship. Even though the thermal conductivity is difficult to evaluate due to the influence of other heat transport phenomena, some values of κ_e and κ_ℓ found in the literature are displayed in Table 1.6. It can be seen that the presence of impurities causes a collapse of the electronic thermal conductivity. Besides, the nickel-iron alloys only exhibit small lattice contributions compared to Chromel and Constantan which are usual materials in thermoelectricity.

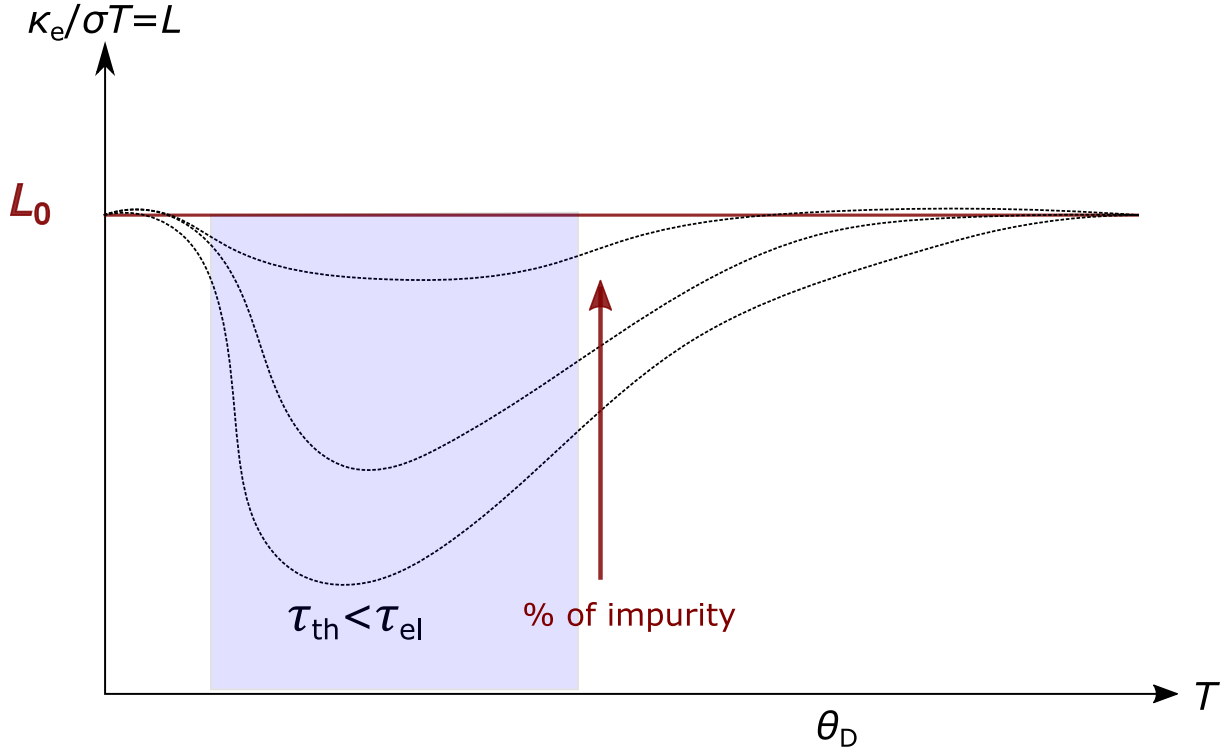


Figure 1.21: Validity of the Wiedemann-Franz law as a function of the temperature. The deviation is important for pure metals in a certain temperature range when $T < \theta_D$. Although this invalidity tends to be reduced with the impurity levels, a supplementary contribution coming from the lattice has to be added for alloys.

Table 1.6: Thermal conductivity with distinguished lattice and electronic contributions measured at room temperature for some metals and metallic alloys widely used in thermoelectricity or in this thesis. In the case of nickel-iron alloys, κ_e has been estimated thanks to the WF law and by considering $L_0=2.38.10^{-8} \text{ W}\Omega\text{K}^{-2}$ as found for nickel during an experimental determination [64].

Material	κ (W/Km)	κ_e (W/Km)	κ_ℓ (W/Km)	κ_e/κ (%)	Refs.
Cu ₅₅ Ni ₄₅	22.7	14.7	8.0	64.8	[65]
Ni ₉₀ Cr ₁₀	17.3	10.6	6.7	61.3	[65]
Ni ₆₀ Fe ₄₀	32.7	31.7	1.0	96.9	[45, 64, 66]
Ni ₇₀ Fe ₃₀	41.9	40.3	1.6	96.2	[45, 64, 66]
Ni ₈₀ Fe ₂₀	47.3	46.4	0.9	98.1	[45, 64, 66]
Ni ₉₃ Fe ₇	60.2	60.0	0.2	99.7	[45, 64, 66]
Ni	90.7	-	-	-	[67]
Fe	80.2	74.7	-	93.14	[67]

1.3.2 Fundamentals of thermoelectricity

As previously seen, Seebeck found that a temperature difference maintained at two junctions of a closed-circuit composed of two dissimilar metals induces a current. The magnitude of this effect is characterized by the Seebeck coefficient S defined as:

$$S = \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T}. \quad (1.29)$$

It appears that S is an intrinsic property of materials evolving with the temperature. By convention, negative Seebeck coefficients exhibit a negative potential at the cold end, they are called n-type. On the other hand, positive Seebeck coefficients are p-type thermoelectric materials. Some typical values are exposed in Table 1.7.

Table 1.7: Seebeck coefficient values for some materials and alloys at room temperature.

Material	$S(\mu V/K)$	Refs.
Cu ₅₅ Ni ₄₅	-38	[68]
Ni ₉₀ Cr ₁₀	21.7	[69]
Ni ₆₀ Fe ₄₀	-47.5	[70]
Ni ₇₀ Fe ₃₀	-41.2	[70]
Ni ₈₀ Fe ₂₀	-34.8	[70]
Ni ₉₃ Fe ₇	-26.3	[70]
Ni	-19.5	[71]
Fe	15	[71]
Cu	1.83	[71]

This breakthrough opened the door to a device able to measure the temperature gap via a potential difference between two wires. This device based on the Seebeck phenomenon is represented in Figure 1.22. Mathematically, by using the definition of S and considering that the two tension probes are maintained at the same temperature T_0 , the potential is given by:

$$\Delta V = \int_a^b dV = \int_{T_0}^{T_1} -S_A dT + \int_{T_1}^{T_2} -S_B dT + \int_{T_2}^{T_0} -S_A dT = \int_{T_1}^{T_2} (S_A - S_B) dT = (S_A - S_B) \Delta T.$$

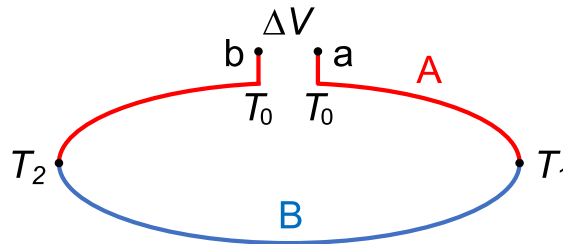


Figure 1.22: Seebeck junction allowing to measure $\Delta T = T_2 - T_1$ from $\Delta V = V_A - V_B$. Figure from [21]

It appears that the temperature determination requires the knowledge of S for both materials A and B. Generally, a couple of n-type and p-type materials is selected like Constantan ($\text{Cu}_{55}\text{Ni}_{45}$) and Chromel ($\text{Ni}_{90}\text{Cr}_{10}$). Indeed, because of their opposite signs, they lead to a significant value of $S_{AB} = S_A - S_B$. As a result, ΔV is larger and then more reliable. An alternative purpose of this junction is to impose ΔT to measure the unknown S of one material, knowing the other. Hence:

$$S_B = S_A - \frac{\Delta V}{\Delta T}. \quad (1.30)$$

Another aspect of such thermoelectric junction is the generation of electricity from heat as shown in Figure 1.24(a). The insertion of a multitude of such junctions inside a device are mainly used to recover energy from wasted heat. Hence, every junction is made of two semiconductor pillars (n-type) and (p-type) arranged electrically in series and thermally in parallel. The temperature gradient between the heat source and the heat sink leads to the displacement of holes and electrons respectively within the p-type and n-type materials in opposite direction. These charge carriers flowing inside the circuit produce a current estimated as the sum of all pillar contributions.

Peltier effect

A few years later, Peltier discovered that the application of a current inside a junction as represented in Figure 1.23 results either in heat liberation at one end and equivalent heat absorption at the other, or inversely, depending on the current direction. This effect is difficult to observe due to the additional heat released by the Joule effect $P = RI^2$ and the natural conduction. However, he detected that the energy absorbed/liberated is proportional to the electrical current magnitude. Moreover, he defined the Peltier coefficient of the junction $\pi_{AB} = \pi_A - \pi_B$ from the intrinsic Peltier coefficient π of both materials which are related to the Seebeck coefficient by the Onsager relation $\pi = ST$. To characterize the relative power of this effect, the heat absorbed or liberated per unit of time Q can be expressed as:

$$Q = (\pi_A - \pi_B)I. \quad (1.31)$$

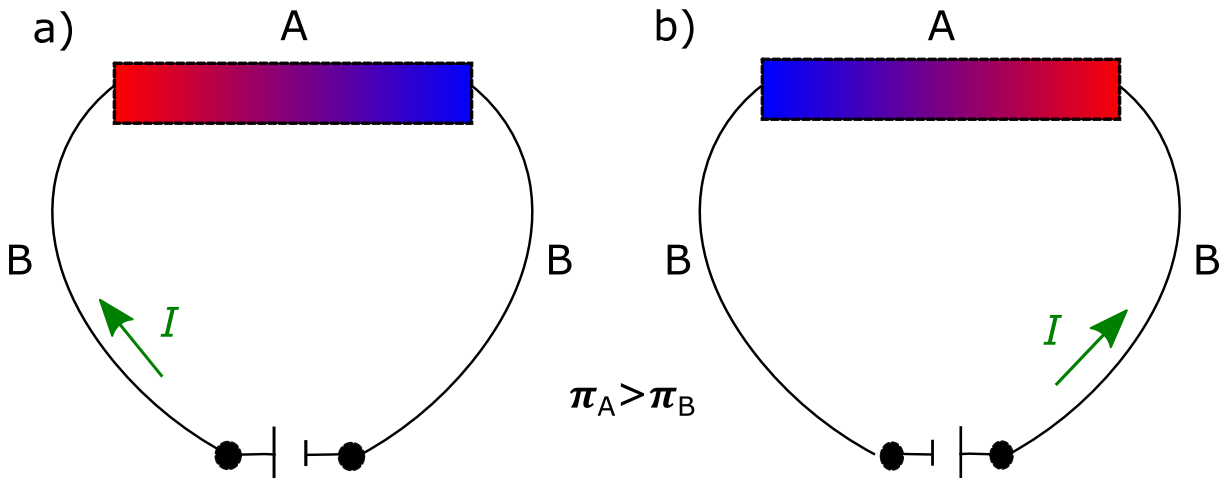


Figure 1.23: Peltier junction, allowing to (a) warm up an extremity of the junction and cool down the other, or (b) inversely, depending on the current direction.

Such junctions can be used, as in the generation power, for the fabrication of cooling devices made of pillars as shown in Figure 1.24(b). The alignment of several of them can lead to a significant active cooling.

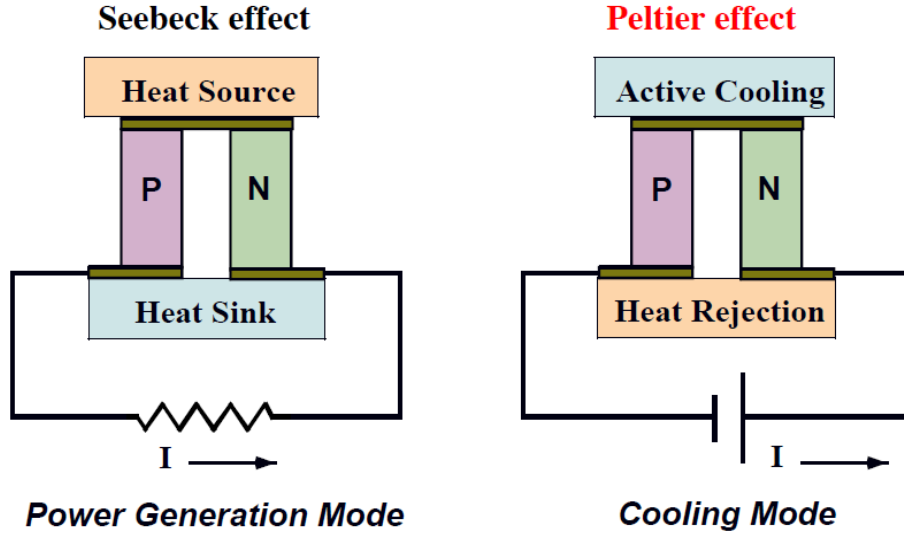


Figure 1.24: (a) Electricity generator using the Seebeck effect to produce a current from a temperature gradient. (b) Active cooling device using the Peltier effect coming from the current flow to cool down an edge. On the contrary, the inversion of the current direction allows to release heat. Both devices are made with two types of semiconductor pillars (n-type and p-type) arranged electrically in series and thermally in parallel. Figure from [43]

The key of the concept results in the intimate link between the transports of heat and charges which form coupled constitutive equations given by:

$$\begin{cases} j = \sigma(E - S\nabla T) \\ j_Q = \kappa\nabla T + \pi j, \end{cases} \quad (1.32)$$

where j is the current density, j_Q is the heat flux density, and E the electric field. It is possible to identify the unknown variables by imposing special conditions. On one hand, a $j \neq 0$ associated with a $\nabla T = 0$ gives rise to the classical Ohm law and the Peltier relation. On the other hand, $j = 0$ and $\nabla T \neq 0$ refers to the Seebeck effect and thermal conduction. It can be mentioned that a third phenomenon called the Thomson effect exists, but it goes beyond the scope of this thesis.

Thermopower origins

The thermoelectric power (TEP) can have contributions from three kinds of particles. The first contribution, called the diffusive thermopower, is related to the electrons. The second is the phonon drag arising as suggested by its name from the phonons. Finally, the magnon drag consists in spin waves that propagate through the solid while dragging electrons.

The intrinsic Seebeck coefficient of a material S is then given by the sum of the three contributions:

$$S = S_d + S_{pd} + S_{md}, \quad (1.33)$$

where S_d is the diffusive thermopower, S_{pd} is the phonon drag thermopower and S_{md} is the magnon drag thermopower.

Considering a bar made of a n-type material with two edges at different temperatures, called the cold and the hot end as represented in Figure 1.25. Basically, the diffusion TEP originates from a different spread of the Fermi-Dirac distribution function caused by the thermal gradient. The right edge exhibits a broadening over an energy $k_B T_c$ whereas the left edge, at a higher temperature, have a larger broadening over $k_B T_h$. Above ϵ_F , the density of states occupied is larger for higher energy. This unbalance can be seen as reservoirs with electrons diffusing from the hot side to the cold side and inversely. Microscopically, for each interval of energy, the electrons tend to diffuse and spread towards places with fewer carriers per state of that energy. Their motion can cause scattering which randomize their energy depending on factors as the local temperature. This loss of energy leads to the emptying of the higher energy states which were previously occupied, allowing new electrons to diffuse in. The combination of diffusion and dissipation favors an overall drift of the electrons towards the lower temperature. Finally in case of open-circuit, the electron accumulation results in the creation of an electric field $\mathbf{E}$ to counterbalance the stream of diffusing charge carriers up to reach a steady state. As regard p-type materials, the phenomenon is similar except that holes have a higher mobility than electrons. Therefore, due to the opposite sign of the charges, it creates an opposite current.

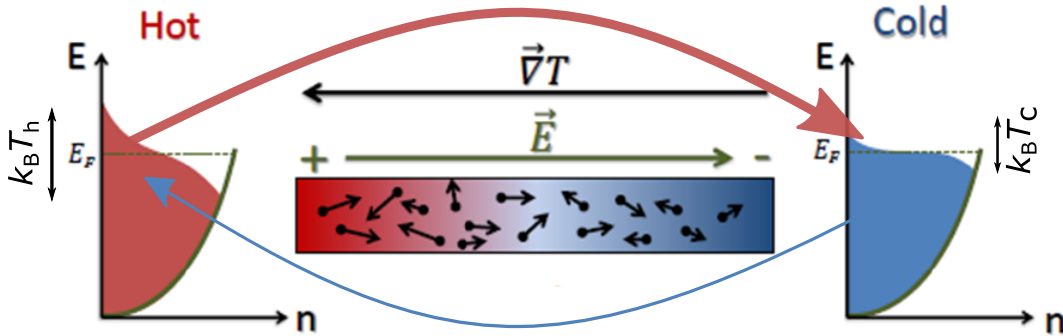


Figure 1.25: Illustration of the diffusive thermopower in n-type metals. The temperature gradient induces a difference in the broadening of the Fermi-Dirac function. Consequently, charge carriers diffuse to balance the density of states occupied leading to accumulation at the cold end. The Seebeck electric field $\mathbf{E}$ acts to counterbalance this diffusion up to reach a steady state. Adapted from [72]

The electron diffusive thermopower is related to the electrical conductivity which varies as a function of the energy $\sigma = \int \sigma(\epsilon) d\epsilon$. Mathematically, S_d can be expressed by the Mott's formula:

$$S_d = -eL_0T \left(\frac{d \ln \sigma(\epsilon)}{d\epsilon} \right) \Big|_{\epsilon=\epsilon_F} \quad (1.34)$$

This equation considers that electrons responsible for the conduction are a minority situated near ϵ_F . This relation exhibits a linear variation with T and can be rewritten as:

$$S_d = \frac{eL_0T}{\rho} \left(\frac{d\rho(\epsilon)}{d\epsilon} \right) \Big|_{\epsilon=\epsilon_F} \quad (1.35)$$

In ferromagnetic materials as explained in Section 1.2.2 $\rho \propto \mathcal{D}_d(\epsilon_F)/\mathcal{D}_s(\epsilon_F)$ which gives [21]:

$$S_d \propto \mathcal{D}_s(\epsilon_F)/\mathcal{D}_d(\epsilon_F) \left(\frac{d(\mathcal{D}_d(\epsilon_F)/\mathcal{D}_s(\epsilon_F))}{d\epsilon} \right) \Big|_{\epsilon=\epsilon_F} \quad (1.36)$$

Besides the fact that the 3d band of ferromagnetic materials is very large, this band also exhibits a pronounced structure arising from the five subbands composing it. Indeed subbands are formed from wave functions having different symmetries so that they are characterized by various shapes. As a result, the density of states can significantly vary for small energy increments, leading to a high derivative of the density of states as required to have elevated S_d [73]. Moreover, it has been proved that the addition of impurity to get alloys may lead to drastic changes of DOS near the Fermi level, inducing a significant variation of the electron diffusion thermoelectric power [74, 75].

In any solid material, a temperature gradient induces transport of heat by the intermediary of phonons. The concentration of phonons being larger for higher temperatures, there is a natural net diffusion from the hot to the cold end. This net diffusion is also the origin of the phonon-drag thermopower, S_{pd} . Indeed, during their displacement, phonons are scattered by charge carriers giving rise to momentum transfers. Charge carriers are then dragged along the sample by the phonon current as in a viscous flow and accumulate at the cold edge [73]. Again, this unbalance produces an internal electrical field $\mathbf{E}$ up to attain a steady-state. Depending on the mobility, the majority charge carriers will be the electrons (n-type) as illustrated in Figure 1.26 or the holes (p-type).

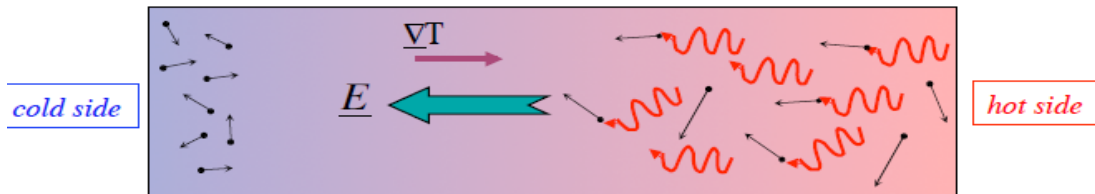


Figure 1.26: Illustration of the phonon-drag thermoelectric power contribution. The temperature gradient leads to a net flux of phonons from the hot side to the cold side. On the way, phonons are scattered by electrons giving rise to momentum transfers and a charge carriers accumulation in the cold edge. This unbalance is compensated by an electric field $\mathbf{E}$. Figure from [43]

The magnitude of this contribution depends then on the density of phonon-charge carriers scattering events as well as the electron mobility. Typically it is expected to vary as $T^{-\frac{9}{2}}$ so that it is rarely observed above room-temperature [76].

In ferromagnetic metals, by analogy to the phonon-drag, the electrons can be dragged along the sample by magnons, quasi-particles as represented in Figure 1.27. Magnons are spin waves, namely collective excitation of the electrons spin structure in the crystal lattice [77].

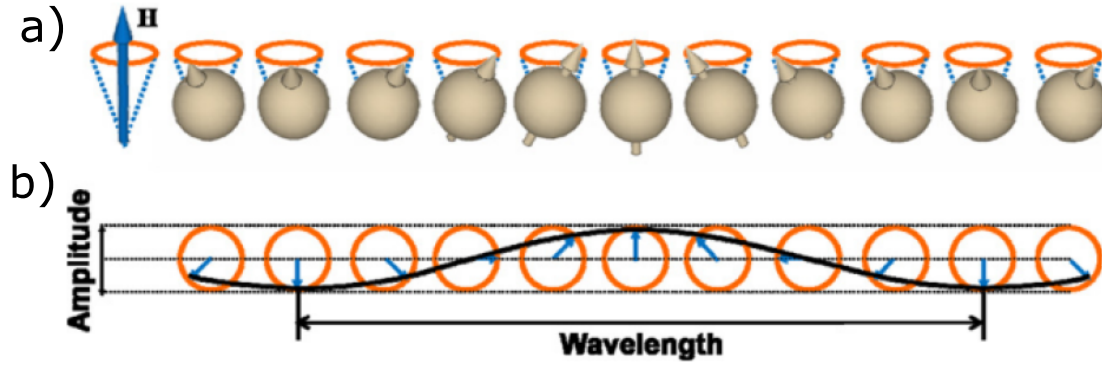


Figure 1.27: Representation of a spin wave contributing to the thermoelectrical power in ferromagnetic transition metals. (a) Side view highlighting the global orientation of the spin wave. (b) Top view indicating the amplitude and wavelength of the spins. Adapted from [78]

Thermoelectric efficiency

As previously explained, the main disadvantage of the thermoelectric effect arises from its small efficiency η_{th} expressed as:

$$\eta_{th} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT_{av}} - 1}{\sqrt{1 + ZT_{av}} + \frac{T_c}{T_h}}, \quad (1.37)$$

This relation gives the amount of heat flowing through the sample that is converted into electricity, typically under 10%. Unfortunately, this small yield prevents the development of cheap industrial thermoelectric generators. In this expression, ZT is a dimensionless factor called the figure of merit allowing to characterize the thermoelectric quality of a material. This factor is defined as:

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l}. \quad (1.38)$$

By looking a bit closer, it can be seen that a high electrical conductivity is required to optimize this ratio. Indeed, it favors the displacement of electrons from the hot side to the cold side (or inversely for the holes) which is an important factor to ensure the generation of a significant counter electric field. By opposition, the thermal conductivity must be sufficiently low to maintain the thermal gradient. Otherwise, the heat diffuses within the material, vanishing the thermal gradient so that the thermoelectric effect disappears. Finally, the presence of T allows to get a dimensionless ratio.

The best thermoelectric materials are the semiconductors as shown in Figure 1.28 which exhibits the figure of merit depending on the number of charge carriers. For instance, BiTeSe (n-type) and BiTeSb (p-type) can reach values around $ZT = 1 - 2$ at RT [79, 80]. Metals tend to have smaller ZT values despite their good conductivity. This is mainly due to the important increase of κ_e ascribed to the free electron gas together with the decline of the Seebeck amplitude coefficient. Assuming that for pure metals, the WF law holds, meaning that $\sigma/\kappa = (L_0 T)^{-1}$ the figure of merit can be simplified by an expression only depending on S :

$$ZT = \frac{S^2}{L_0} \quad (1.39)$$

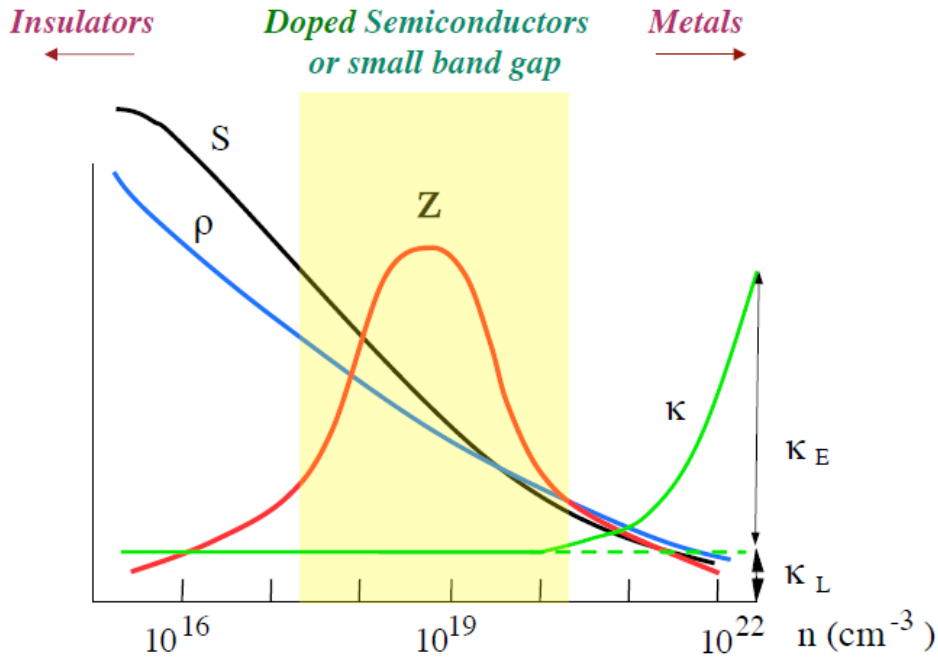


Figure 1.28: Figure of merit ZT for various materials. Semiconductors exhibit the best ZT thanks to intermediate value of S and ρ while keeping a relatively small κ . Despite the enhancement of σ , metals are less efficient due to the reduction of S together with an increase of κ_e . Figure from [43]

Concerning alloys, the lattice contribution is also increased leading to a further decrease of ZT . It is reflected by the heat transport originating from phonons that can be directly associated with a loss of efficiency which must be minimized. Another way to characterize the efficiency of a thermoelectric material is by its output power density expressed by the power factor PF. This indicator allowing to quantify the heat that can be pumped by the system is defined as:

$$PF = \frac{S^2}{\rho}. \quad (1.40)$$

Multiple researches on materials and structures have been performed to improve the thermoelectric efficiency. As a matter of fact, an enhancement of ZT up to 1.5 should be reached to concurrent current technologies for power generation [81]. Moreover, even larger values around 2-4 should be required for competitive cooling applications [82, 83].

Nonetheless, in bulk materials an increase of σ always leads to a parallel rise of κ , preventing high ZT values to be attained. Classical solutions to enhance the efficiency have been considered, including the use of alloys to create artificial point defects scattering the phonons [84]; the use of large atomic mass elements having low phonon velocity [85]; the doping technique with elements having energy level almost resonant with ϵ_F [86] and the elaboration of complex crystal structures limiting the phonon transport [87]. However, it led to insufficient improvement with ceiling value around $ZT \approx 1.5$. An alternative solution to enhance the figure of merit has been envisaged by working with nanostructures. Firstly, at this scale, the size of the samples may become comparable with phonon wavelengths (from a few up to hundreds of nm [88]) causing additional scatterings with the surfaces and interfaces. Hence, nanostructures are expected to reduce the lifetime over a large distribution of phonons so that the thermal transport is limited while keeping the electrical transport unchanged [61]. Furthermore, when dealing with samples having dimensions comparable to electron wavelengths (1-10 nm), a quantum confinement effect is observed. This dimension restriction leads to an enhancement of the DOS near ϵ_F which favors a high thermopower [85].

1.3.3 Spin-dependent thermoelectricity

The interest for the thermoelectric effect in nanostructures has been catalyzed by the possibility to tune the thermoelectric properties of FM with an external magnetic field. By analogy to the spin-dependent resistivity, electrons can carry an amount of heat different depending on the spin direction, meaning that $S_{\uparrow} \neq S_{\downarrow}$. Again, this effect arises from the two currents model and under the assumption of no spin mixing.

Considering structures made of successive layers of FM/NM materials as seen in Section 1.2.3. The Seebeck coefficient $S(H)$ is function of the relative magnetization orientation inside the successive layers. Under the assumption that the main contribution comes from the diffusive thermopower, the Equation 1.35 can be rewritten considering the spin-dependent resistivity $\rho(H)$ and its derivative $\rho'(H) = (d\rho(H, \epsilon)/d\epsilon)|_{\epsilon=\epsilon_F}$:

$$S(H) = eL_0T \frac{\rho'(H)}{\rho(H)} \quad S_{AP} = eL_0T \frac{\rho'_{AP}}{\rho_{AP}} \quad S_P = eL_0T \frac{\rho'_P}{\rho_P}. \quad (1.41)$$

Depending on the amplitude of $\mathbf{H}$, the arrangement of the multilayers can either be antiparallel, leading to S_{AP} or parallel giving S_P . By similarity to the MR ratio, the variation of S coming from the magnetic field can be quantified by the dimensionless magneto-thermopower (MTP) ratio given by:

$$\text{MTP} = \frac{S_{AP} - S_P}{S_{AP}}. \quad (1.42)$$

Previous works have found value up to a few tens of percent [89][25]. Another indicator called the magneto-power factor (MPF) allows to gather both the spin-dependent resistance and the spin-dependent Seebeck in one ratio defined as:

$$\text{MPF} = \frac{\text{PF}_{AP} - \text{PF}_P}{\text{PF}_{AP}}. \quad (1.43)$$

Furthermore, from Equations 1.35 and 1.41, it is possible to relate $S(H)$ and $1/\rho(H)$ by a linear equation involving coefficients A and B [90] as:

$$S(H) = A + B \frac{1}{\rho(H)} \quad A = \frac{S_{AP}\rho_{AP} - S_P\rho_P}{\rho_{AP} - \rho_P} \quad B = \rho_{AP}\rho_P \frac{S_P - S_{AP}}{\rho_{AP} - \rho_P}. \quad (1.44)$$

Although this phenomenon has been observed for magnetic multilayers in CIP configuration [91, 92], it implies strict limitations compared to the CPP arrangement in which the Seebeck spin-dependence has also been observed [93, 94]. Nonetheless, accurate measurements of thermoelectric properties in nanostructures remain challenging, mainly due to the difficulty of estimating or eliminating the contact thermal resistances.

Considering a multilayered stack made of successive FM/NM layers. The two-current model allows to determine the value of both S_{AP} and S_P with the schematic representation of the two channels displayed in Figure 1.29.

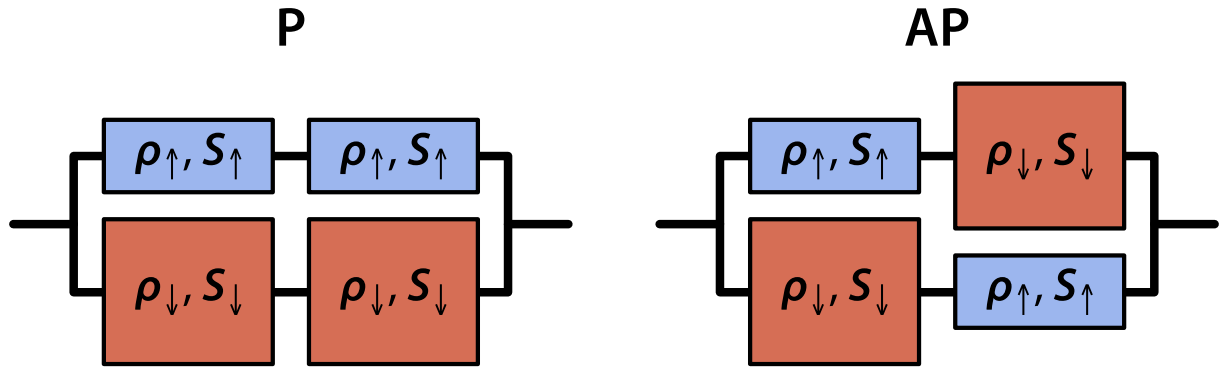


Figure 1.29: Two-current model showing the two channels representation for both the parallel (P) and antiparallel (AP) arrangements. In the P configuration the thermopower, as the electrical conduction, mainly arises from the majority spin $S_{\uparrow}$ electrons since the minority ones $S_{\downarrow}$ are widely scattered. On the contrary in the AP configuration both $S_{\uparrow}$ and $S_{\downarrow}$ are equally scattered giving rise to a higher total resistivity and a smaller Seebeck coefficient amplitude. Adapted from [21]

Hence, under the assumption of no spin-flip events occur, by neglecting the effect of the interfaces and by considering the resistivity of the NM layer insignificant compared to the FM layer, one gets:

$$S_{AP} = \frac{S_{\uparrow}\rho_{\uparrow} + S_{\downarrow}\rho_{\downarrow}}{\rho_{\uparrow} + \rho_{\downarrow}} \quad S_P = \frac{S_{\uparrow}\rho_{\downarrow} + S_{\downarrow}\rho_{\uparrow}}{\rho_{\uparrow} + \rho_{\downarrow}}, \quad (1.45)$$

with $\rho_{\uparrow}$, $\rho_{\downarrow}$, and $S_{\uparrow}$, $S_{\downarrow}$ being respectively the electrical resistivities and the Seebeck coefficients for the majority and minority-spin electrons. Finally, by solving this system, it is possible to directly access the spin-dependent Seebeck coefficients given by:

$$S_{\uparrow} = \frac{1}{2}[S_{AP}(1 - \beta^{-1}) + S_P(1 + \beta^{-1})] \quad S_{\downarrow} = \frac{1}{2}[S_{AP}(1 + \beta^{-1}) + S_P(1 - \beta^{-1})]. \quad (1.46)$$

To sum up, the determination of the spin-dependent coefficients involves the measurements of the Seebeck coefficient for both the P and AP states, as well as the asymmetry coefficient β defined in the Equation 1.23 which can be rewritten as a function of the magnetoresistance only: $\beta = \sqrt{MR}$

1.3.4 Interest for interconnected 3D nanowire networks

Interconnected nanowire networks are of great interest for thermoelectricity. This structure allows to reduce the importance of the thermal contact resistances while ensuring the measurements of macroscopic properties. Therefore, it removes the obligation to work with devices exhibiting signals amplitude in the mK and nV range respectively for the temperature and the voltage so that the measurements are more reliable and easier to perform. Physically, the tiny contacts created by the interconnections enable good electrical conduction. On the other hand, the polymer membrane acting as a thermal insulator prevents the heat conduction so that it is possible to impose a sufficient thermal gradient between both edges of the sample. In addition, the interconnections also serve to increase the robustness of the sample while the contact area is not sufficient to yield to thermal diffusion. Finally, the multilayers give rise to significant spin-dependent transport properties so that a magnetic control can be considered. The choice to work with Ni-Fe alloys is ascribed to their large magnetic control together with their high Seebeck coefficients. The separation layers are made of Cu which associates good electrical conductivity while exhibiting a very small positive Seebeck coefficient so that it does not interfere with the alloy Seebeck coefficient.

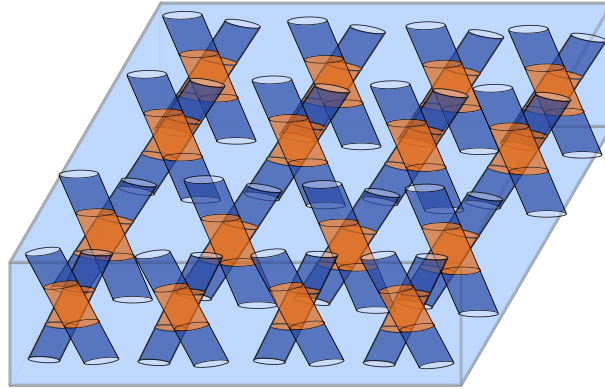


Figure 1.30: Schematic representation of the 3D interconnected nanowire network with the metallic multilayers within the polymer membrane represented in light blue.

Chapter 2

Nanofabrication process and characterization techniques

The goal of this chapter is to describe the production of the 3D interconnected nanowire networks as well as to characterize their physical properties with experimental measurements. Firstly, Section 2.1 will describe the fabrication process. Then, Section 2.2 will provide information regarding the morphology and the composition of the samples. Finally, Section 2.3 will be dedicated to the measurements of the transport properties.

2.1 Overview of the 3D nanowire networks synthesis

The fabrication of 3D nanowire networks relies on a "bottom-up" process mastered at UCLouvain for decades. This process is based on the electrodeposition of metallic elements in porous polymer membranes combining simplicity, cheapness, and efficiency. Besides, this technique is versatile since it enabled to produce nanotubes (NTs), nanocables, or homogeneous crossed nanowire networks (HCNWs) over the past years [21, 36, 38, 95]. A large range of structures could still be considered as several parameters can be tuned during the whole process. For instance, the diameter, the density, and the orientation of the nanopores can be controlled during the membrane bombardment while the composition can be modified when preparing the solution. This thesis focuses on the fabrication of multilayered interconnected 3D nanowire networks from a polycarbonate (PC) template. The layers are deposited with successive electrodeposition pulses of FM metals (Ni-Fe) and NM metals (Cu) in order to reach a $\text{Ni}_x\text{Fe}_{100-x}/\text{Cu}$ morphology with $60 < x < 93$. Figure 2.1 shows the porous membrane before and after the nanopores filling. In the following paragraphs, the process will be described from the track-etched polymer membrane to the electrodeposition of the FM and NM metals, including the solution preparation.

2.1.1 Fabrication of 3D nanoporous polymer templates

The track-etching is a reliable technique to create 3D nanostructures compared to conventional lithography which becomes difficult to perform with complex and accurate shapes. This approach consists of two successive bombardments with heavy ions to create nanoporous templates. So far, it has already been applied to fabricate parallel nanoporous templates from PC and has recently been extended to the fabrication of crossed nanochannels. Although these PC templates present a random distribution of the pores unlike the alumina templates [96], they are suitable for the control of several parameters.

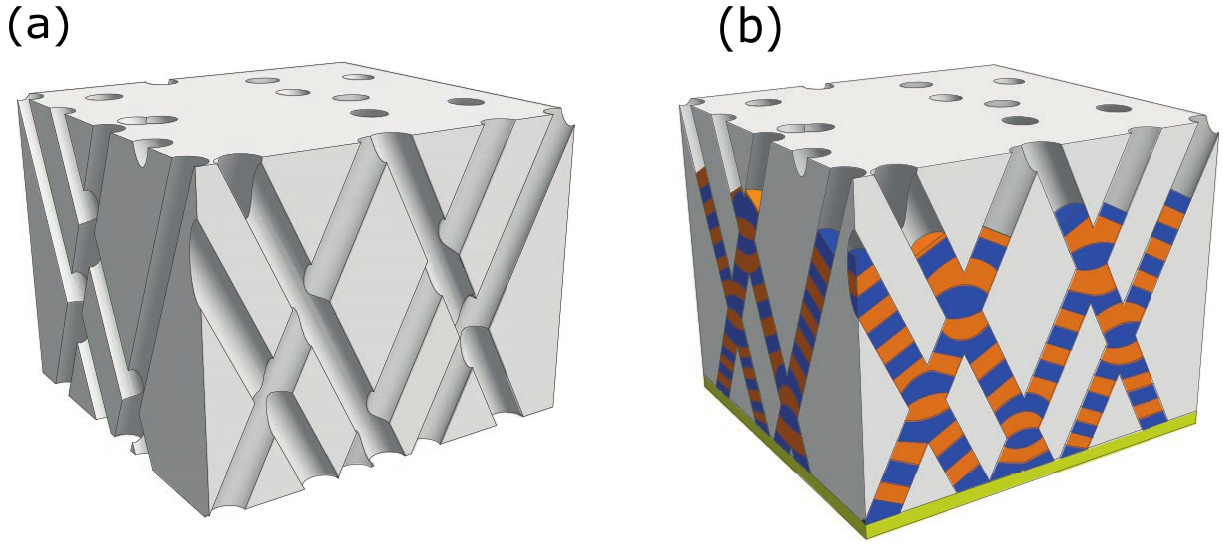


Figure 2.1: Representation of a track-etched 3D nanoporous polymer template (a) before the electrodeposition and (b) after the electrodeposition of successive layers of the ferromagnetic material (NiFe) and the non-magnetic material (Cu) within the pores of the template. Figure adapted from [21]

The process starts with a polymer film which is firstly bombarded with two fixed angles of $\pm 25^\circ$ with respect to the normal of the film. After rotating the sample by 90° in the film plane, a second irradiation is performed with the same angles, both irradiations are illustrated in Figure 2.2. The pores are therefore the consequence of the PC film bombardments with heavy ions of Ar^{9+} , previously accelerated at 200 MeV in a cyclotron. The ions which can be seen as bullets, pass through the membrane while releasing an important amount of heat which induces a modification of the material all around the impact. Ultraviolet (UV) rays are then required to degrade the area, followed by a wet chemical etching with a solution of NaOH 0.5M [97, 98]. This etchant is able to selectively remove the degraded part submitted to the UV giving rise to the final product, a template composed of 3D crossed cylindrical nanochannels network with an angle standard deviation of $\pm 5^\circ$.

Several parameters are important to produce adequate templates. For instance, the etching time can be tuned to get a targeted diameter ϕ ranging from a few nm to a few μm . Regarding the density of the pore D_p , the control of the incident ions flux allows to obtain a panel of values between 10^5 to 10^{10} pores/ cm^2 . The determination of the porosity can then be roughly approximated by $P = D_p \pi \phi^2 / 4$ with a maximum available around 30%. A treatment by hydrolysis is also realized to smoothen the pores in the whole sample. Finally, a 10 nm Cr layer is deposited by sputtering to ensure a good adhesion of a second layer. Generally, it consists of an Au/Cu layer playing both the role of the background in which the growth of nanowires takes place and the cathode for the electrodeposition. This cathode thickness must be thin enough to be properly removed while being sufficient to allow a good deposition. Typically few tens of nm guarantee the full coverage of the pores. The sputtering is performed with an electron beam that collides a piece of metal bringing it to a very high temperature. The resulting metallic cloud can then be deposited on the template. The templates used during this thesis were all provided by the company it4ip based at Louvain-la-Neuve. The properties of these templates are summed up in Table 2.1

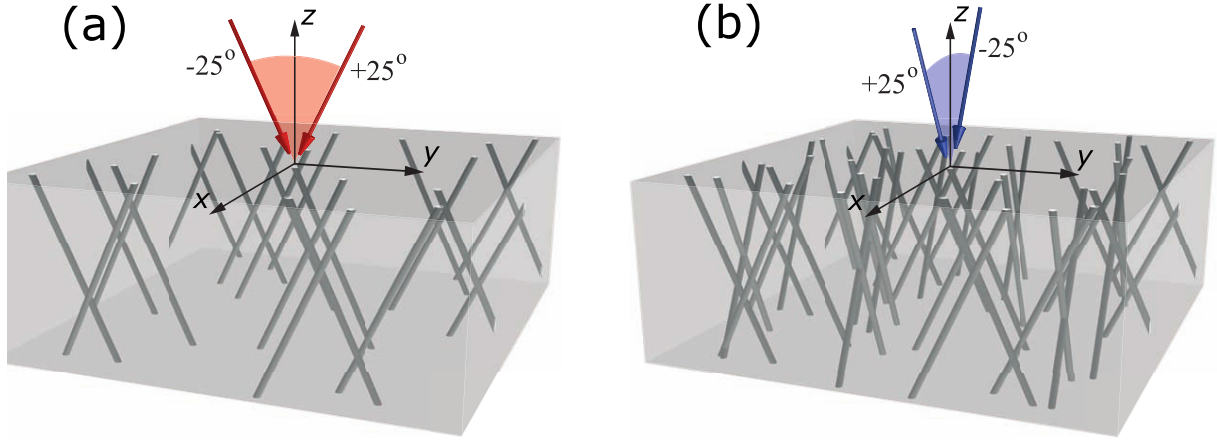


Figure 2.2: The two steps bombardment process to create nanoporous templates from tracked-etched polymer membranes. (a) Shows the first irradiation with fixed angles of $\pm 25^\circ$ with respect to the normal axis of the PC. After the rotation of the sample by 90° , (b) displays the second irradiation with the same fixed angles leading to the final 3D nanoporous template. Adapted from [21]

Table 2.1: Main characteristics of the PC templates including the type, the pore diameter ϕ , the porosity P , and the type of cathode.

Label	Type	ϕ (nm)	P (%)	Cathode
F80-3	Fixed angles $\pm 25^\circ$	80	3	Au

2.1.2 Solutions preparation

The solution used to fill the pores of the template is a homemade recipe requiring accurate quantities of Ni, Fe, Cu, and acid to reach the targeted concentrations inside the nanowire layers. The components were incorporated one after the others in pure water (H_2O) giving rise to an electrolyte solution. In the beginning, H_3BO_3 is added to enhance the acidity and improve the dissolution of the other components. In the end, the pH is adjusted to the target value with some droplets of HCl . Even though the pH does not influence the crystalline structure for this alloy, the acidity is an efficient way to control the rate of deposition. For this reason, the pH is chosen around 2 to ensure a good electrodeposition rate. Furthermore, in a low pH environment, the Fe oxidation is slower leading to a longer solution lifetime of about one week. A summary of the concentrations required to reach $\text{Ni}_x\text{Fe}_{100-x}/\text{Cu}$ with $60 < x < 93$ can be found in Table 2.2. The samples studied in this thesis are made of successive layers of one of these alloys: $\text{Ni}_{60}\text{Fe}_{40}$, $\text{Ni}_{70}\text{Fe}_{30}$, $\text{Ni}_{80}\text{Fe}_{20}$, $\text{Ni}_{93}\text{Fe}_7$, and Cu layers. It can already be seen that the Cu concentration is willingly kept very low to avoid excessive contamination of the $\text{Ni}_x\text{Fe}_{100-x}$ layers. The reason will be explained in Section 2.1.3

2.1.3 Electrodeposition filling the nanoporous 3D templates

The principle of electrodeposition is based on the application of an electrical current inducing the reduction of metallic cations, previously dissolved, at a solid electrode. This method is born from the scientist Brugnatelli in 1805 who utilized the voltaic pile discovered 5 years earlier by Volta [99]. Despite the fact that this technique is old, it remains widely

Table 2.2: Electrolyte concentrations in the solutions allowing to reach the desired MLC-NWs compositions $\text{Ni}_x\text{Fe}_{100-x}\text{-Cu}$ with $60 < x < 93$.

Label	NiSO_4 (mM)	FeSO_4 (mM)	CuSO_4 (mM)	H_3BO_3 (g/l)	pH
$\text{Ni}_{80}\text{Fe}_{20}\text{-Cu}$	60	14	0.5	30	2.00
$\text{Ni}_{70}\text{Fe}_{30}\text{-Cu}$	60	30	0.5	30	2.04
$\text{Ni}_{60}\text{Fe}_{40}\text{-Cu}$	60	40	0.5	30	2.05
$\text{Ni}_{93}\text{Fe}_7\text{-Cu}$	60	5	0.5	30	2.05

used for its robustness in technological fields as protective coating, microelectronics and optoelectronics [100]. Besides, it appeared in the last years as an excellent solution which has proved its efficiency to fill the pores of templates with metallic materials [36, 101, 102]. Therefore, electrodeposition has been revealed to be an excellent technique for the fabrication of complex various 3D architecture as NTs, NWs, HCNWs, and recently MLCNWs [25, 26, 103, 104].

Considering a solution containing metallic ions (M^{n+}) with n the oxidation number, the reduction reaction is given by:



The direction and the rate of this reaction are strictly linked to the equilibrium potential (E_{eq}) determined by the Nernst equation:

$$E_{\text{eq}} = E_0 + \frac{RT}{nF} \ln \frac{a_{\text{M}^{n+}}}{a_{\text{M}}}, \quad (2.2)$$

where E_0 is the normal electrode potential in standard conditions, R is the ideal gas constant, F is the Faraday constant and $a_{\text{M}^{n+}}$ and a_{M} are the activities of the ions M^{n+} and the atoms M respectively. In the case where the potential applied is smaller or equal to E_{eq} , there is respectively a metal oxidation or a macroscopic equilibrium. To ensure the reduction, an additional potential ξ must be applied resulting in the total potential of the cell: $E_{\text{cell}} = E_{\text{eq}} + \xi$. This shifting of the thermodynamic equilibrium induces a cathodic current responsible for the deposition. Physically, the current is created by the ions displacement carrying charges and is proportional to the additional potential. The set-up used to deposit samples can be seen in Figure 2.3.

The electrolyte solution is inserted inside a ceramic tank placed on the template with a circle rubber gasket ensuring a perfect sealing. The solution only fills up the nanopores enclosed inside the circle giving the possibility to selectively grow the nanowires. The potentiostatic mode, meaning that the electrodeposition is monitored by a steady potential, is preferred to its inverse the galvanostatic mode. The constant potential is maintained with the reference electrode made of Ag/AgCl , while the working electrode associated with the substrate gives rise to the cathode deposition. Finally, the counter electrode made of platinum (Pt) closes the circuit and allows the current circulation.

Although this principle is easy and cheap, its ability to produce relatively accurate multilayers through pulses of different times and potentials is a brilliant achievement. It is based on the fact that all the elements are reduced at different potential depending on

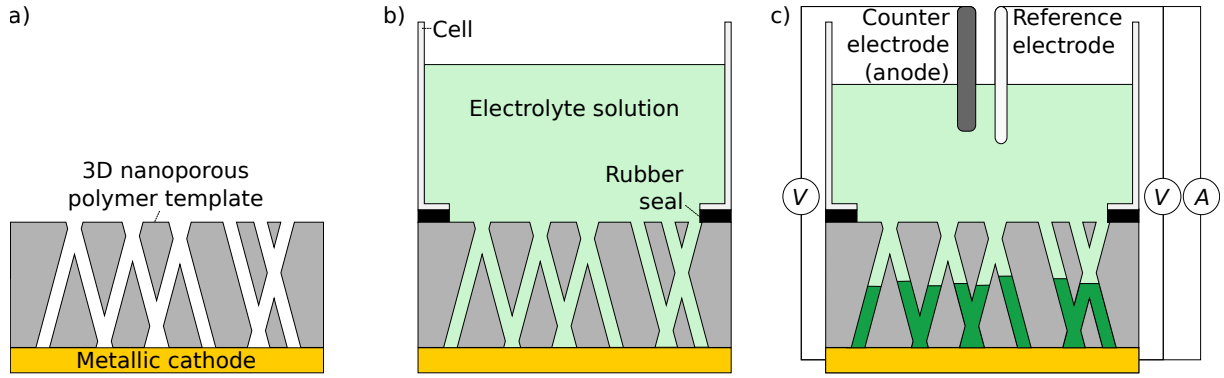


Figure 2.3: Schematic representation of the interconnected nanowire network electrodeposition into a crossed nanoporous template. (a) Track-etched PC template coated with the Au layer serving as cathode. (b) Installation before the electrodeposition with the solution bath containing the electrolytes and the rubber seal. (c) Growth of the nanowires due to the applied potential controlled with the reference electrode. The counter electrode closing the electrical circuit is also represented. Figure from [21].

their nobleness shown in Table 2.3. The key concept is thus the possibility to switch the potentials from one sufficiently low absolute value reducing selectively one or more species, to a bigger value reducing all the metallic ions [105]. Consequently, to avoid the presence of undesired elements during the tension peak, their concentrations must be kept low so that diffusion limitations slow down their deposition. The weak concentrations and low potentials must be combined with a longer pulse time to counterbalance the smaller deposition rate. Thanks to this technique, bilayers with $\text{Ni}_x\text{Fe}_{100-x}/\text{Cu}$ are deposited with the two pulses illustrate in Figure 2.4.

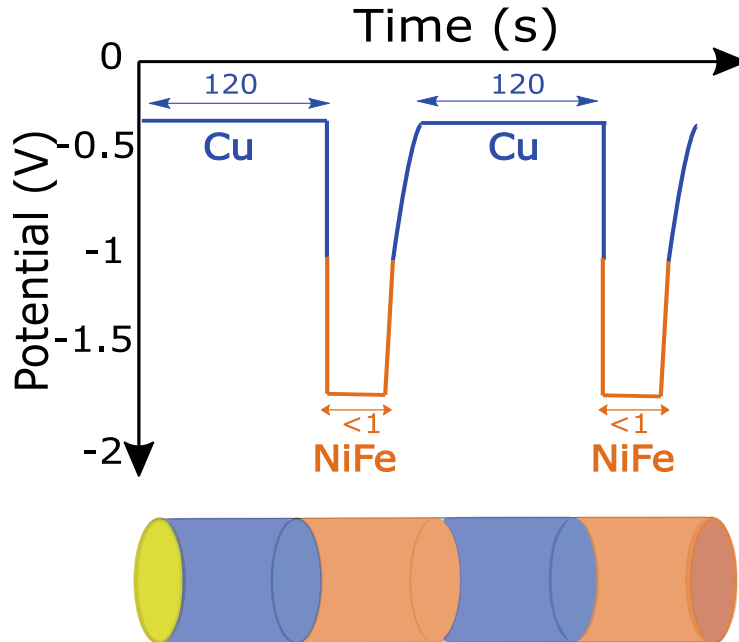


Figure 2.4: Schematic representation of the two pulses serving to form all the bilayers. The first long pulse (120s) is set at low potential to deposit Cu layers while the second sharp pulse (<1s) at higher potential allows to mainly deposit NiFe

The first one molds the Cu layer, as expected the concentration of Cu is kept under 1% in the solution as displayed in Table 2.2. This pulse is maintained during 120s at a potential of 0.3V. Then, a sharp pulse smaller than 1s is applied at a potential around 1.8V resulting in a second layer composed of NiFe and some Cu impurities. These pulses are repeated successively, to give rise to the final nanowire sample composed of 200 bilayers.

Table 2.3: Standard potential E_0 of the redox couples present in the solutions. $\text{H}_2/2\text{H}^+$ is the reference couple and its reduction is a parasitic reaction decreasing the system efficiency. Data from [105]

Couples	$E_0(\text{V})$
Ni/Ni^{2+}	-0.25
Fe/Fe^{2+}	-0.44
Cu/Cu^{2+}	+0.34
$\text{H}_2/2\text{H}^+$	0.00

The current depending on the time $I(t)$ has been recorded for an homogeneous sample and a typical shape is observed providing clues about the growth period of the nanowires as illustrated in Figure 2.5. The first peak coincides with the electrodeposition initiation, meaning that the metal is directly deposited on the cathode inside the pores. Then, a steady-state is reached corresponding to the growth of the nanowires. The time required to fulfill the nanopores may vary slightly but once the overfilling is achieved a sudden step-up of the current can be seen. It is explained by the increments of the accessible area. This phase is followed by a saturation phase once the system is overfilled. Considering MLCNWs, the behavior of the curve is similar with the presence of additional potential pulse.

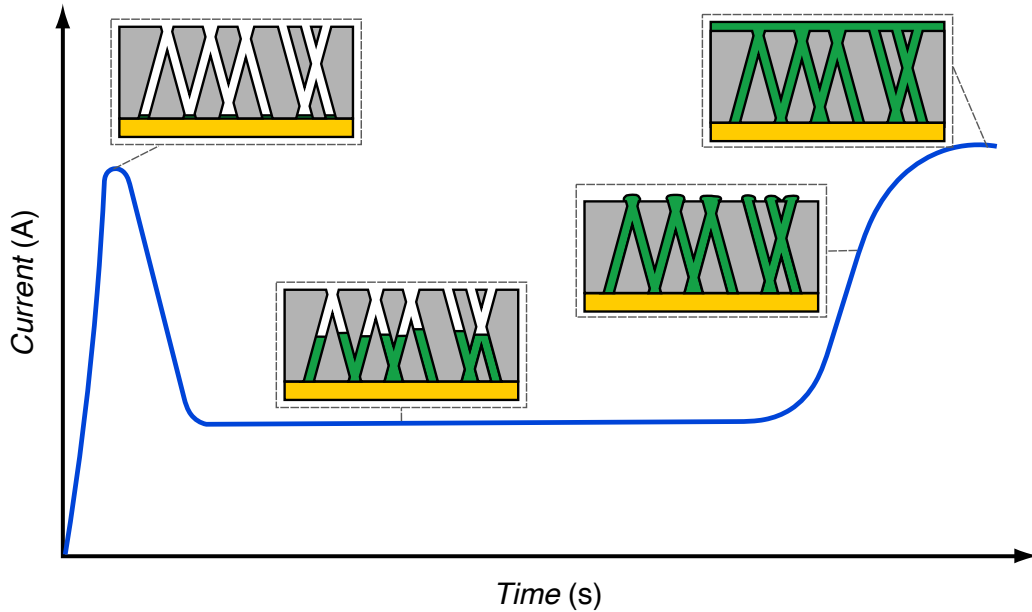


Figure 2.5: Classical curve of the current depending on the time for the constant potential electrodeposition of 3D interconnected nanowire network in a track-etched template. The first peak coincides with the electrodeposition initiation on the cathode. The steady-state corresponds to the typical growth of the nanowires. The sudden step-up is explained by the overfilling of the nanowires leading to an increase of the deposition surface. Figure from [21].

As mentioned in Subsection 1.2.3, the thicknesses of the different layers are essential since they influence the amplitude of the magnetoresistance and the magneto-Seebeck effects. The mass deposited during one pulse can be estimated with the Faraday's law expressed as:

$$m = \frac{M_M Q}{nF}, \quad (2.3)$$

with M_M the molar mass and Q the amount of charge deposited in one pulse during a time T_p which can be evaluated with:

$$Q = \int_0^{T_p} I(t) dt \quad (2.4)$$

Replacing Q in Equation 2.3, and knowing that the layer thickness t_l is related to the mass m and the volumetric mass density ρ :

$$t_l = \frac{m}{\rho A} = \frac{4M_M}{nF\rho_M\pi\phi^2} \int_0^{T_p} I_p(t) dt. \quad (2.5)$$

In practice, this estimation is not that accurate since undesired reactions occur as deposition of hydrogen $2H^+ + 2e^- \rightleftharpoons H_2$. Besides, the rate of deposition is not homogeneous everywhere neither constant during the entire reaction. Nevertheless, the order of magnitude of the layers thickness of both NiFe and Cu has been approximated to 10 nm which seems to give layers of satisfactory quality. It has been estimated by measuring the time to fill the nanopores at constant potential up to the overfilling. From there, the deposition rate has been roughly determined so that the time requires to get the targeted thickness has been computed.

2.2 Morphology and composition characterization

This section is dedicated to the nanoscopic scale characterization to both guarantee the presence of 3D interconnected nanowires and prove the respect of the desired composition. These analyses are based on the interactions of electrons with matter. Indeed, when electrons penetrate a volume, they are submitted to several scattering events generating secondary phenomena as illustrated on the interaction peer in Figure 2.6. From there, information can be extracted from different depths depending on the type of emissions detected. The secondary electrons come from the nm range and give information about the topography whereas backscattered electrons are released a bit deeper (10-100nm) and provide data about the mass variation. Regarding the characteristic X-rays, they arise from the μm range and are used to evaluate the composition. The morphological analysis of the samples will be split into two parts. On one hand, an accurate portrait of the interconnected nanowires network will be drawn from a scanning electron microscope (SEM) analysis. On the other hand, the composition of the nanowires will be characterized by electron-dispersive X-ray spectroscopy (EDX) performed with the same device. Special sample pieces are required for the characterization. Therefore, small pieces of the sample have been cut and plunged into a dichloromethane solution to dissolve the PC while keeping the cathode to ensure stability. The polymer dissolution is essential otherwise, the non-conductive parts could result in charge accumulation interfering with electrons. Finally, the pieces are stuck on adhesive carbon before the introduction in the chamber.

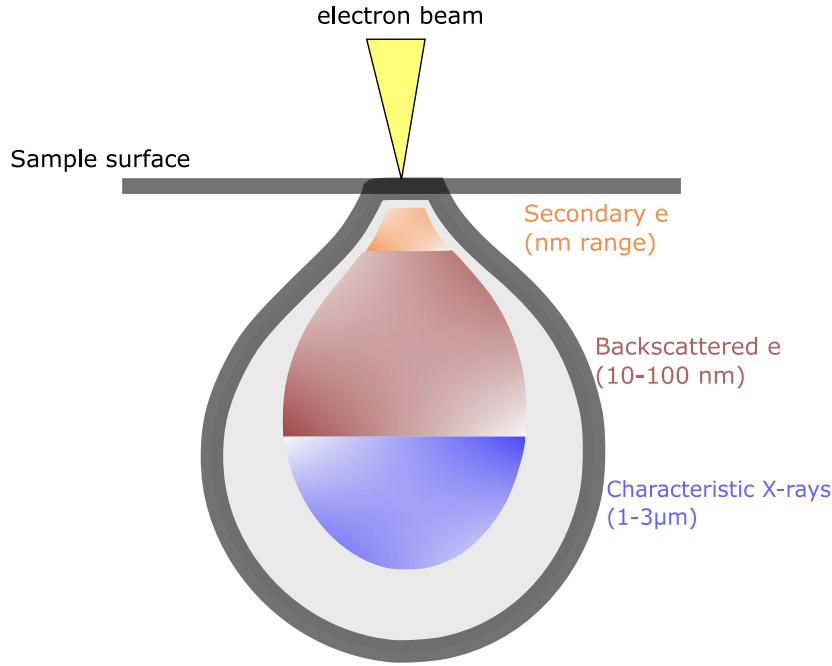


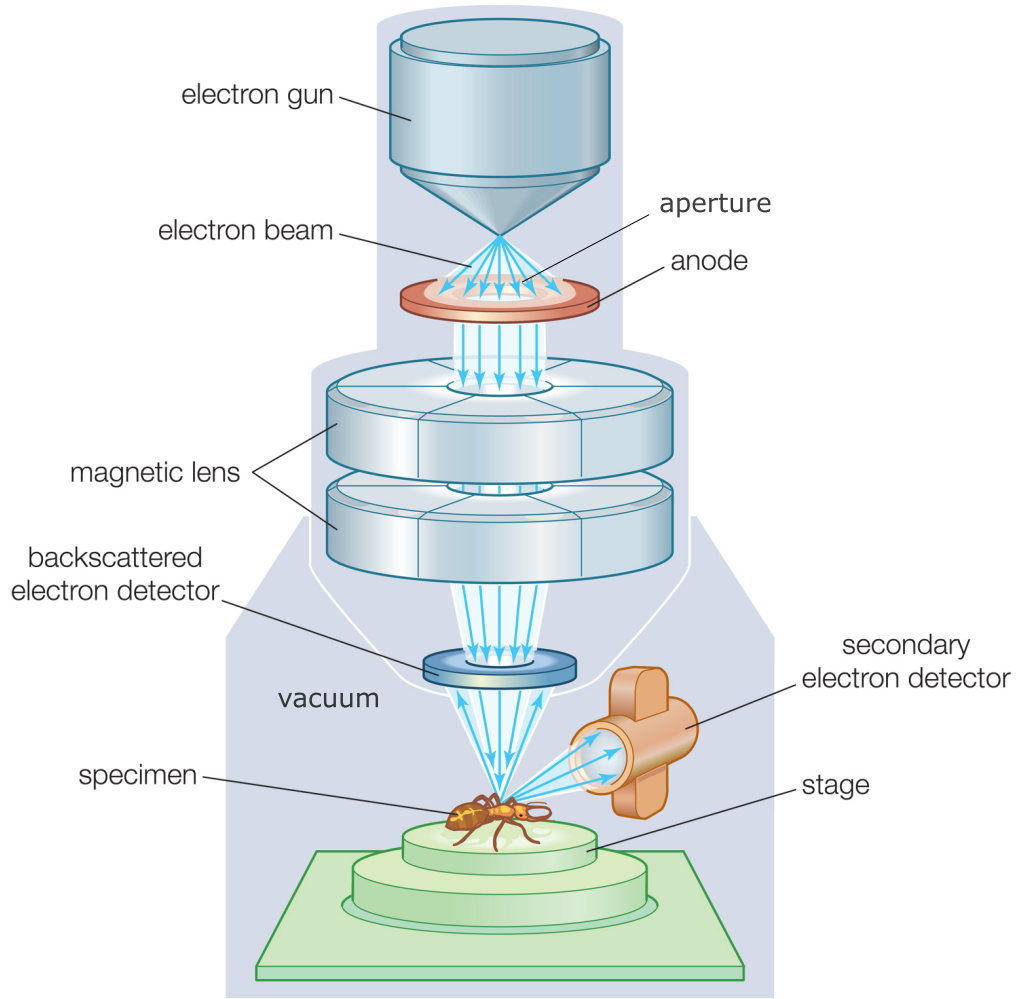
Figure 2.6: Interaction peer characterizing the secondary phenomena caused by the penetration of the incident electron beam in the matter. The secondary electrons come from the nm range and give information about the topography whereas backscattered electrons are released from a bit deeper (10-100nm) and provide data about the mass variation. Regarding the characteristic X-rays, they result from the μm range and are used to evaluate the composition.

2.2.1 Scanning electron microscope

The field-emission scanning electron microscope (FE-SEM) used during the measurements is a JEOL FEG SEM 7600F similar to the one in Figure 2.7. This device is able to record the secondary electrons arising from the inelastic scattering with the atoms of the sample giving information on the topography with a resolution around 10nm. Moreover, backscattered electrons coming from elastic scattering are also detected providing knowledge related to mass variation around 100 nm.

Typically, an energetic electron flux is released from a piece of tungsten heated at a very high temperature. This electron gun is directed into magnetic condenser lenses able to transform the flux into a fine electron beam focused on the sample. The aperture is responsible for the sharpness of the beam while the lenses deflect it into the x and y-axis allowing a scan of the surface. A very high vacuum is required to avoid the collisions between the electrons and other particles. The system achieves the measurements with an acceleration tension of 15 kV and an operating distance of 8 mm. Magnification of the microscope can be modified to either observe the global network or get an accurate image of some crossed nanowires.

Figure 2.8(a) shows an actual view obtained from the SEM displaying the interconnected nanowire network and its ability to be self-supported. In Figure 2.8(b), a bigger magnification highlights a high definition of the nanowires and their intersections. Each nanowire is composed of a large number of trilayers as illustrated in Figure 2.8(c). From this unique ge-



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Figure 2.7: Scanning electron microscope representation. The sample is bombarded by accelerated electrons from the electron gun. The flux is focused on the sample by magnetic condenser lenses which are also responsible for the diminution of astigmatism. Detectors are required to collect the scattering events while a high vacuum is maintained in the chamber to avoid interactions with particles. Figure adapted from [106].

ometry emerges the main asset of the CNWs, the existence of a macroscopic object ensuring electrical and thermoelectric measurements in the film plane while keeping the nanoscopic properties. As a matter of fact, this structure conserves the spin-dependent effect arising from the nanostructure whilst amplifying the signal because of the tremendous number of nanowires composing the core of the network. This bigger signal-to-noise ratio allows more reliable and easier measurements. Microscopically, the current follows the nanowire axis and therefore, cross perpendicularly the multilayers, maximizing the difference of resistivity between the majority and minority spins. Regarding the low packing factor of 3%, it makes the sample fragile and this weakness is amplified by the interfaces between the layers. However, it considerably turns down the proportion of nanowire intersections into the network resulting in a decrease of the crossing effects. Besides, the low packing factor let more space for the insulator PC so that the thermal conductivity is significantly reduced allowing to maintain a stable temperature gradient for thermoelectric applications.

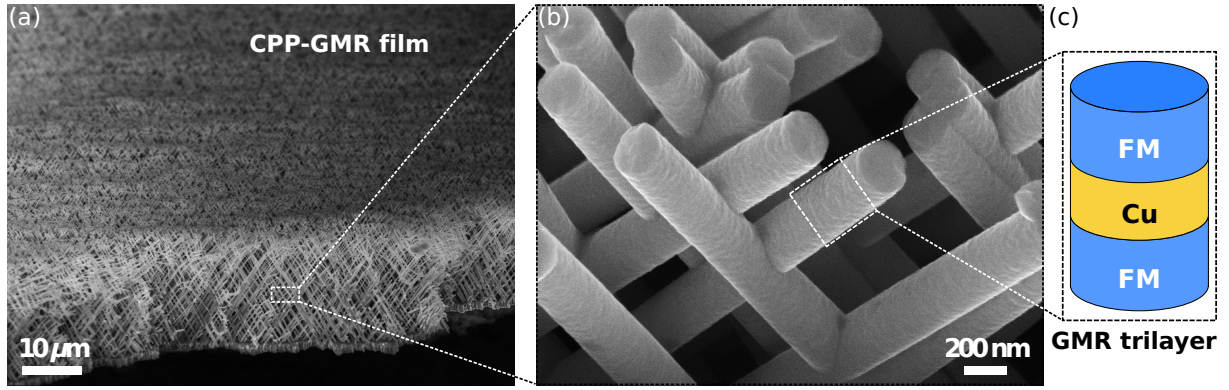


Figure 2.8: SEM image of the self-supported interconnected nanowire networks with (a) 10 μm magnification, (b) 200 nm magnification and (c) a schematic representation of the trilayers composing the nanowires. The significant spin-dependent signals observed in the CPP mode come from the tremendous number of nanowires composing the core of the network. Figure from [21].

2.2.2 Energy dispersive X-ray analysis

The analysis by EDX ensures that the desired compositions were reached for the MLCNWs. The measurements have been performed with a system JEOL JSM2300 integrated in the SEM device. As for the SEM, an acceleration tension of 15kV and an operating distance of 8 mm have been used. The performing current was 1 nA during 100s. Since X-rays come from deeper in the matter than secondary electrons, around μm , the resolution is limited $<129\text{ eV}$ [21]. The principle consists in the detection of the X-rays emitted during the relaxation of atoms, previously excited by an electron beam. As a matter of fact, when an incident electron hits an atom, it may transfer some of its energy to an electron in the atom, bringing it to a higher energy state. This electron excitation is then responsible for the creation of a free energy state in the inner shell, called a hole. After that, there is a natural relaxation of the excited electron into the hole inducing the emission of an X-ray having an energy similar to the difference between the two states. Since atoms have different structures depending on their nature, energy levels and thus the X-rays energies are specific to each chemical element. The detection of all the emitted X-rays as function of their specific energy allows the elaboration of a spectrum. The area of the peaks is proportional to the quantity of each element in the volume. However, some extrinsic parameters can alter the X-rays energy leading to peaks overlap. Besides, the same atom can give rise to different kinds of X-rays represented by K_α , K_β , etc depending on the shell from which the electron is relaxed. Therefore, a quantitative analysis based on the area of the peaks could be complex. Nonetheless, solutions have been developed to improve the resolution between the peaks. The classical "Top Hat Filter" is a method to substrate the continuous Bremsstrahlung caused by the deceleration of charged particles when deflected by other particles [107, 108]. Regarding the atomic peak area quantification, only the K_α peaks will be considered. The ZAF model allows to compute the atomic and weight percentages based on Z the atomic number, A the absorbance and F the fluorescence [108]. Sometimes, it happens that other elements such as O, C or Au are found in the spectrum. They simply come from some contamination or residual particles. As it can be seen in the Py spectrum illustrated in Figure 2.9, the main peaks are NiK_α , FeK_α , and CuK_α . Atomic percentage values for the HCNWs of all the alloys computed thanks to the ZAF algorithm are summarized in Table 2.4.

It must be precised that the compositions are globally the same for the MLCNWs except that Cu is mainly found in the Cu layers leading to almost pure NiFe layers. Furthermore, it finally appears that the atomic percentages are close from the ones desired.

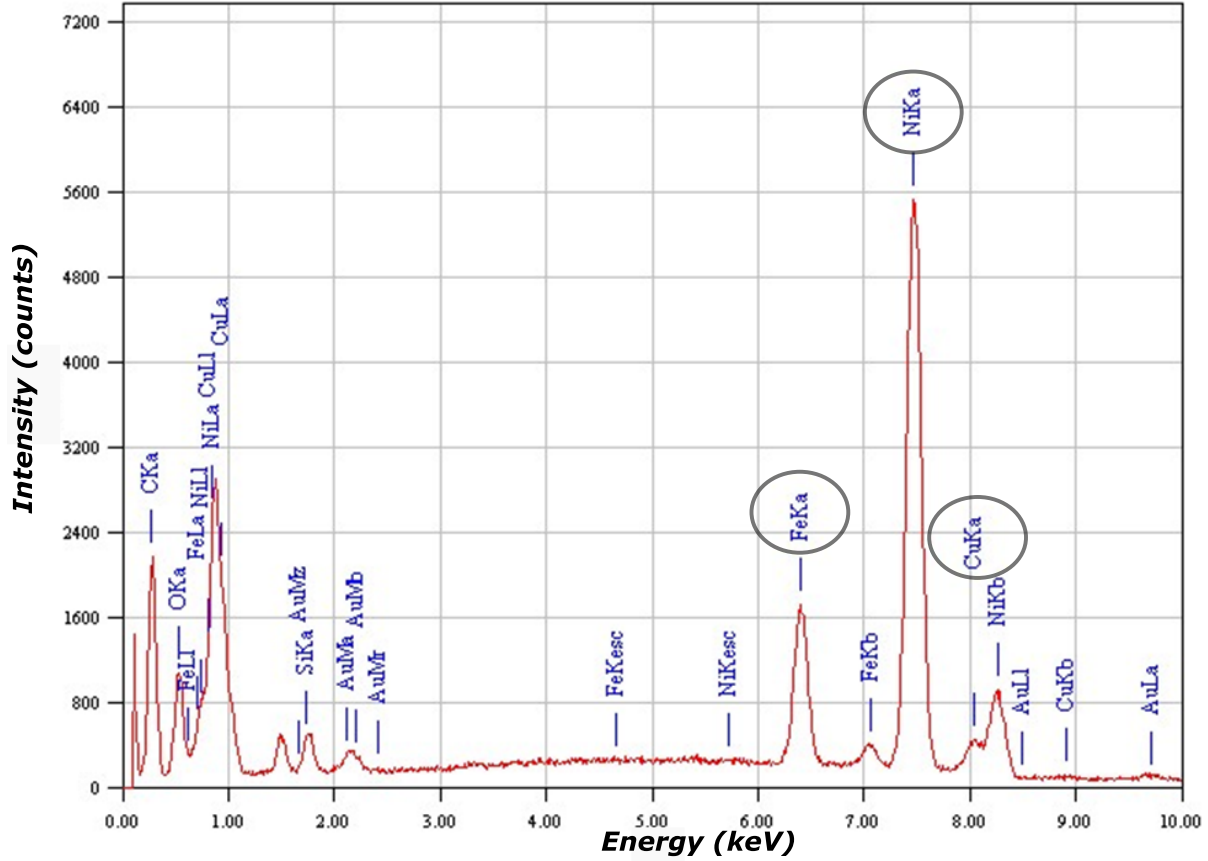


Figure 2.9: Energy dispersive X-ray spectrum of the 3D interconnected multilayered nanowire network made of Py/Cu. The peaks providing the main elements are framed in black.

Table 2.4: Atomic composition of the different homogeneous samples. The first four columns display the samples name together with the atomic percentages of the measured elements. The fit coefficients issued from the peaks evaluation are also provided. Finally, the last column shows the expected percentage ratio for the MLCNWs which present an excellent match with the desired compositions.

Label $Ni_xFe_{100-x}Cu$	Ni(%)	Fe (%)	Cu (%)	Fit coefficients	Ni_xFe_{100-x}
Ni ₆₀ Fe ₄₀ Cu	57.4	39.2	3.4	0.28	Ni ₅₉ Fe ₄₁
Ni ₇₀ Fe ₃₀ Cu	67.6	29.3	3.0	0.29	Ni ₆₇ Fe ₃₃
Ni ₈₀ Fe ₂₀ Cu	85.6	13.0	1.42	-	Ni ₈₇ Fe ₁₃
Ni ₉₃ Fe ₇ Cu	87.6	7.7	4.7	0.30	Ni ₉₂ Fe ₈

2.3 Magnetotransport and magneto-Seebeck characterization

The following section aims to describe the techniques allowing the measurements of the physical properties of the samples discussed in Chapter 3. As it is proved in this part, the unique geometry of the samples allow to perform macroscopic electrical and thermal measurements in the film plane while keeping the nanoscopic effects caused by the external magnetic field. The first part of this section briefly describes the transformation of the final electrodeposited nanowire network into a sample meeting the requirements for reliable measurements. Then, explanations about the set-up used for the determination of the resistance are provided. Finally, the configuration for the Seebeck coefficient determination is presented. The magnetic field going through the networks comes from external devices and can be oriented either in-plane (IP) direction or out-of-plane (OOP) direction with respect to the film plane. It can be noticed that the OOP measurement exhibits a unique direction with an angle of 25° whereas the IP directions are multiple and not well defined due to the rotation of 90° during the polymer bombardment.

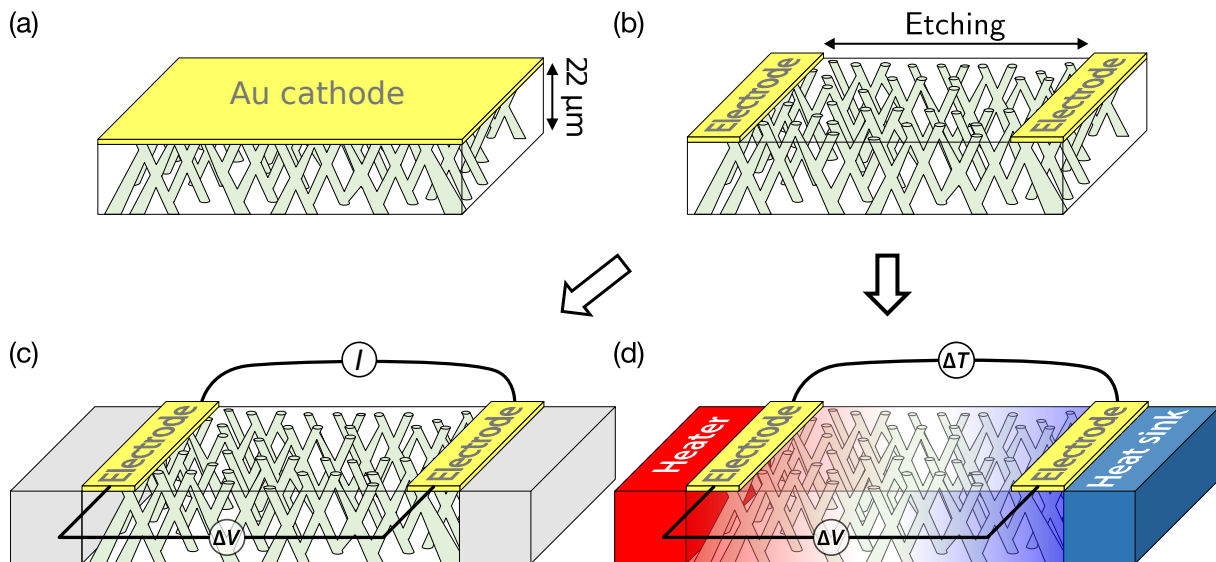


Figure 2.10: Schematics resume of the measurement configurations with (a) the raw sample transformed into (b) the appropriate sample to perform measurement after an appropriate etching. (c-d) The sample configurations to measure respectively the resistance and Seebeck coefficient. Figure from [21].

2.3.1 Sample preparation

At the end of the template-assisted electrodeposition, the final product is a 3D interconnected nanowire network film of $22\ \mu\text{m}$ coated with an Au layer as shown in Figure 2.10(a). In order to transport charges and heat only through the nanowire network, a part of the conductive Au cathode must be removed. An efficient solution is then to carry out a plasma etching. For this purpose, two strips of the circular sample are cut¹ and placed on a holder. Two masks at both ends of the strips are responsible for the

¹One strip could be sufficient to measure the sample but the devices have the ability to measure two strips so that variations due to factors as inhomogeneities are limited

selective etching giving rise to a two-probes electrodes as illustrated in Figure 2.10(b). Indeed, the Ar plasma disintegrates the whole cathode except the parts hidden by the masks. The etching is realized by a Plassys MP500S instrument, the Ar plasma being at a pressure of 5.10^{-3} Torr and accelerated with a power of 80 W. The time required depends on the materials but the etching rate has been calibrated to 12.6 nm/min for Au [21]. Considering our Cr(4.7nm)-Au(400nm) layers, the appropriate etching time is approximately 32 min. To avoid the overheating which may lead to NWs disconnection and thus a loss of conductivity, the etching is split in 2 times 10 min, 2 times 5 min and a final 2 min step with cooling breaks in between.

2.3.2 Magnetoresistance characterization

To carry out magnetoresistance measurements two systems were used. The first one serves to make simple but rapid measurements to characterize the quality of the multilayered samples thanks to the GMR ratio. The second one is able to determine precisely both the electrical resistance and the thermoelectric effect at different temperatures and for varying magnetic field. Only the first device is explained in this subsection since the other is described in Subsection 2.3.3. The configuration required for electrical resistance measurements is shown in Figure 2.10(c). It implies a preparation step leading to a pseudo four-probes system as displayed in Figure 2.11. It turns out that it is equivalent to a real four probes system since the contacts realized with Ag paint have resistances significantly smaller than the one of the interconnected nanowire network. The unetched ends are both connected by Cu wire to two pins allowing to measure the resistance and tension separately. A current is then applied from one electrode to the other, with the electrons passing through the interconnected nanowires. This current is generated by an alternating potential source passing through a resistance of several $k\Omega$, and thus larger than the contacts, which can be adapted depending on the resistance estimation of the sample. Thanks to the current direction changes created by the alternating potential, the signal-to-noise ratio is maximized. Since the tension and the current are known, the resistance of the network can therefore be determined at every moment. These measurements are performed while applying an external magnetic field with an electromagnet ranging from -8 kOe to 8 kOe. Thusly, the MLCNWs magnetoresistance mainly coming from GMR is estimated. It can be noticed that the cane on which lays the chip can be rotated by 90° to successively obtain the OOP and IP characterization.

2.3.3 Magneto-Seebeck characterization

The second system handled is more complex since it is composed of a thermal circuit in parallel with an electrical circuit as represented in Figure 2.10(d). This set-up is accordingly able to determine the Seebeck coefficient in addition to the electrical resistance for a temperature ranging from 10K-320K. In practice, precious information about the samples can be extracted at low temperature, as the RRR which is related to the quality of the crystal. However, the current must be limited to avoid the over-heating of the Pt. To reach such conditions, a cryogenic device composed of a helium (He) compressor is turned on in a chamber previously put under a high vacuum. A heating resistance is used to monitor the temperature by means of a Cernox sensor evaluating the temperature. A proportional-integral-derivative (PID) controller works in parallel to regulate the amount of power send through the heating resistance in order to stabilize the temperature. Despite

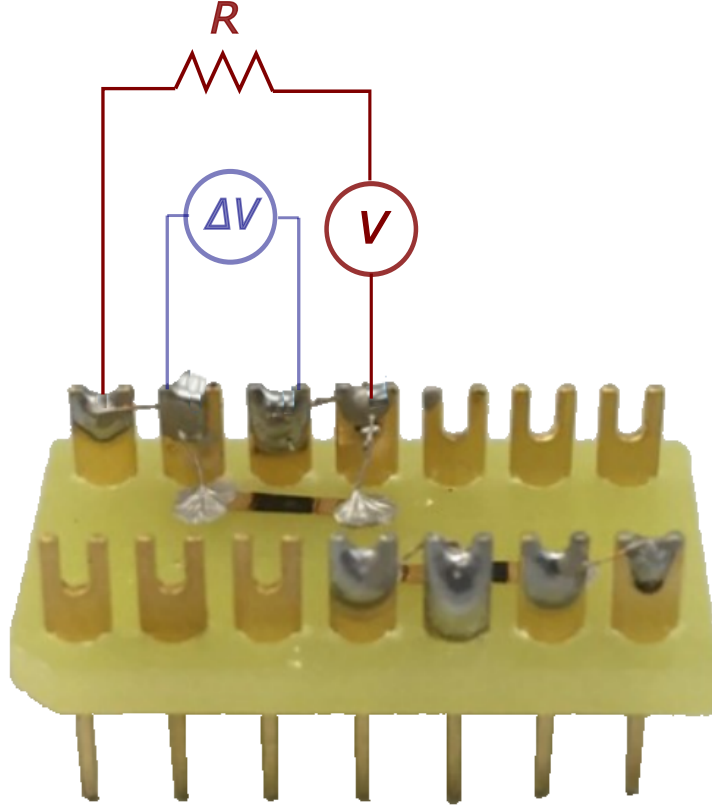


Figure 2.11: Picture of the chip. The two strips are on both sides with electrodes connected by Cu wire to two pins allowing to get a four/two-probe system. Therefore, the tension and the resistance are simultaneously measured. Contacts are realized with a conductive Ag paint.

the fact that there are in contact, a small temperature gap is created between the sample holder and the cold finger.

All the measurements require the etching done during the preparation. The sample is again placed on a cane with an external magnetic field reaching ± 0.9 T either in IP or OOP direction. Concerning the resistance characterization, the same principle is applied than with the other device excepted that the current injected is unidirectional (DC). As regards the Seebeck coefficient measurements², the principle relies on the application of a thermal gradient between the two electrodes with a parallel quantification of the potential as schematically represented in Figure 2.12. The heat is only transported through the branched nanowires as the two ends are thermally isolated. The cold end is connected by Ag paint to a block of Cu serving as a sink. In the same way, the other end is connected to another Cu block rolled into a resistive element of 691Ω . A current ranging from 1 mA to 5 mA flows through this element releasing heat transferred to the Cu block and then to the electrode. This edge is called the oven. A thermocouple made of Chromel P/Constantan gives access to the temperature gap between the oven and the sink, typically between 1-3 K. The tension is measured independently from the temperature thanks to Chromel wires. Nevertheless, the contribution of these wires to the total thermoelectric power has to be removed so that the absolute value of the Chromel P S_{Crp} found in the literature is subtracted.

²The Peltier coefficient measurement works with the sample principle

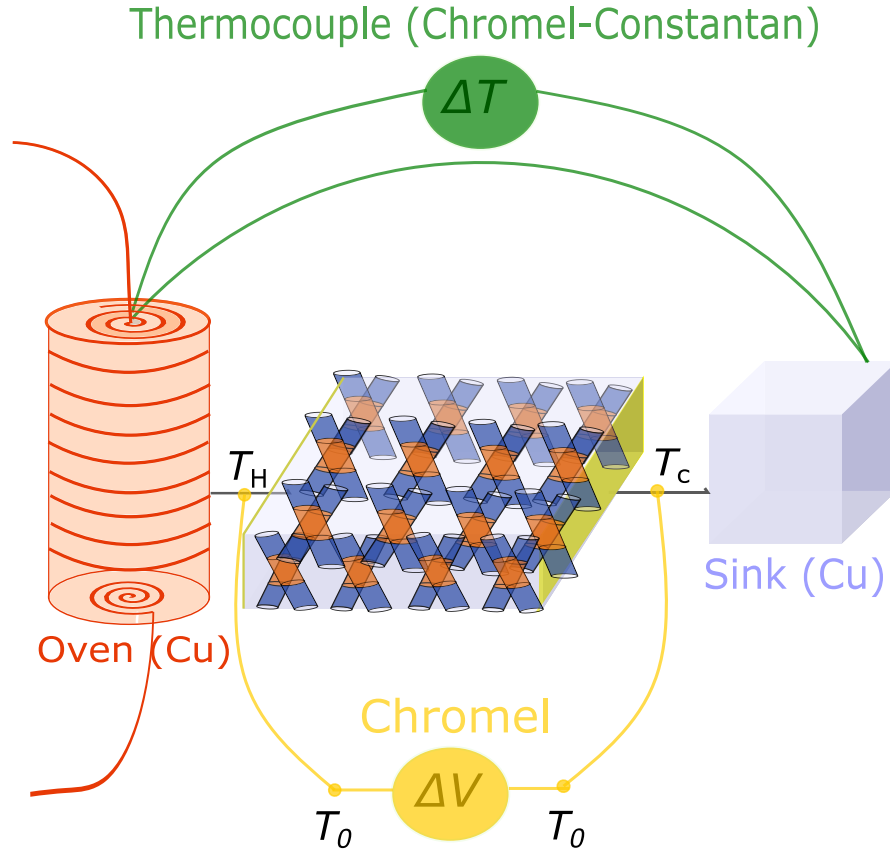


Figure 2.12: Schematic representation of the Seebeck-coefficient measurement based on the application of a thermal gap ΔT and a parallel determination of the tension ΔV . The thermocouple is made of Chromel P/Constantan while the tension probes are made of Chromel P only. At the left, the first electrode is connected to a Cu block called the oven, rolled with a resistive element of 691 Ω . A current ranging from 1 mA to 5 mA flows through this element releasing heat to reach the temperature T_H . At the right, the second electrode at temperature T_C is connected to another Cu block serving as a sink.

The Seebeck coefficient of the crossed nanowire network can, therefore, be computed from ΔV and ΔT respectively known thanks to the chromel P probe and the thermocouple. One gets:

$$S_{NW}(T_{av}) = S_{Crp}(T_{av}) - \zeta \frac{\Delta V}{\Delta T}, \quad (2.6)$$

with $T_{av} = (T_{sink} + 0.5\Delta T)$ and ζ the correction factor related to the fact that the real thermopower values are always a bit smaller than in the theory due to the relative position between the measurement of ΔV and ΔT . The correction factor has been estimated by minimizing the difference between the experimental Seebeck coefficients and the theoretical values found in the literature for classical materials. Results shown in Table 2.5 prove that $\zeta = 0.88$ is a reliable correction factor which is considered stable with the temperature.

Table 2.5: Comparison between the Seebeck coefficients found in the literature [109, 110] and the measured Seebeck coefficients of the samples S_{NW} with $\zeta = 1$ and $\zeta = 0.88$ being the factor minimizing the errors. All values are at RT and expressed in $\mu V/K$.

Material	S_{ref}	$S_{NW}(\zeta = 1)$	$S_{NW}(\zeta = 0.88)$
Py	-35	-45.4	-36.9
Ni	-20	-25.3	-19.6
Cu	1.7	0.7	3.2
Fe	15	14.0	15.0

Chapter 3

Results and discussions

This chapter aims to present the main results obtained with the multilayered samples $\text{Ni}_x\text{Fe}_{100-x}/\text{Cu}$ with $60 < x < 93$. The resistance and the Seebeck coefficient measurements in both P and AP arrangements emphasize the large magnetoresistance and magneto-Seebeck effects in this structure. From these results, the determination of $S_{\uparrow}$ and $S_{\downarrow}$ will be performed highlighting the interest of these alloys. In the meantime, the influence of the composition on the magnitude of these effects is analyzed while discussing the comparison with the homogeneous samples. Special attention is devoted to the quantification of the results uncertainty arising from signal noise during the resistance and temperature measurements. Therefore, some figures exhibit error bars corresponding to two times the standard deviation. In some cases, the signal-to-noise ratio was significant so that the uncertainty bars are negligible and not represented, in counterpart, numerical values are provided. This discussion is split in a first part dedicated to the magnetoresistance results while the second part focuses on the magneto-Seebeck analysis.

3.1 Magnetoresistance characterization of NiFe/Cu multilayered nanowire networks

The successful fabrication of MLCNWs made of NiFe/Cu allows to easily perform resistance measurements while injecting a current along the NWs axis and thereby perpendicular to individual layers. However, because of the nanowires inclination and their interconnections, the overall current is flowing in the plane of the 3D network film. All measurements were carried out by sweeping an IP (or eventually OOP at RT) external magnetic field from 8 kOe to -8 kOe and then back to 8 kOe. The normalized resistances for all the samples depending on the magnetic field are represented in Figure 3.1 for both the room-temperature (red curve) and a low temperature of 15K (blue curve).

At room temperature each alloy exhibits a bell shape with a maximal resistance at low magnetic field whereas the application of a stronger one leads to a dramatic resistance fall. The amplitude drop is variable ranging from 8% for $\text{Ni}_{70}\text{Fe}_{30}$ to 17% in the case of $\text{Ni}_{80}\text{Fe}_{20}$. From a given field, the saturation magnetization discussed in Figure 1.8 is reached so that the resistance does not evolve anymore. This plateau takes place below $H = 5$ kOe for all the alloys except for $\text{Ni}_{93}\text{Fe}_7$. Considering the low temperature of 15 K, the behavior is almost similar, though, the resistance drops are larger except for $\text{Ni}_{93}\text{Fe}_7$. For instance, $\text{Ni}_{80}\text{Fe}_{20}$ exhibits a resistance reduction above 35%. It can also be noticed that for $\text{Ni}_{93}\text{Fe}_7$ a slight slope subsists even for the highest magnetic field meaning that the saturation state is not reached at low temperatures.

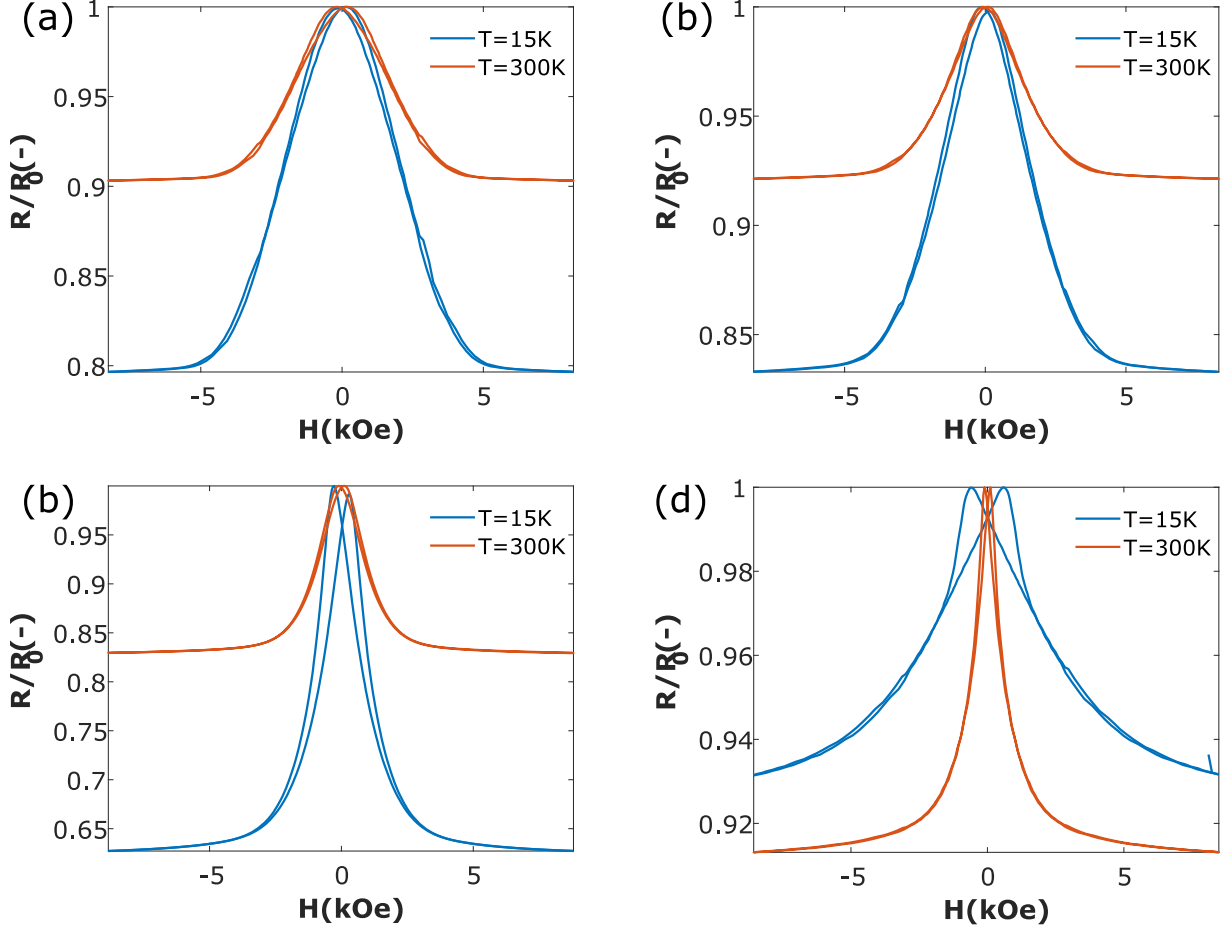


Figure 3.1: Normalized resistance at temperatures of 300 K and 15 K of NiFe/Cu samples for (a) $\text{Ni}_{60}\text{Fe}_{40}$, (b) $\text{Ni}_{70}\text{Fe}_{30}$, (c) $\text{Ni}_{80}\text{Fe}_{20}$, (d) $\text{Ni}_{93}\text{Fe}_7$. R_0 is the maximal resistance obtained near zero magnetic field. The resistance drop due to the switch from an AP to a P magnetization arrangement is easily discerned when applying $\mathbf{H}$.

The two distinguished parallel and antiparallel arrangements discussed in Subsection 1.2.3 can be easily observed with all the intermediate states in between. Hence for a 0 kOe magnetic field, the successive layers exhibit a natural antiparallel magnetization either coming from some dipolar coupling or due to the magnetization randomization. As previously seen in Equation 1.24, such configuration corresponds to the higher resistance state R_{AP} because both spin-up and spin-down electrons are partially scattered so that the conduction is limited. On the contrary, the application of a significant $\mathbf{H}$ enables to turn the layers magnetization parallel to the field, and then to each others. This configuration is characterized by the minimal resistance R_{P} , in which only majority electrons flow very well through the layers. The macroscopic saturation is reached when all the magnetic moments are aligned with the field. This is characterized by the flattening of the curve happening above a given amplitude of the magnetic field. All the samples depict this saturation except $\text{Ni}_{93}\text{Fe}_7$ at low temperature, despite, it exhibits a slight slope remaining even for the highest magnetic field. This could be ascribed either to a smaller response of the material to an external magnetic field, to a higher degree of inhomogeneity created during the electrodeposition, or to a higher saturation magnetization for this sample. However, these factors are difficult to quantify.

In addition, the thermal energy of the system is insufficient to counteract this magnetic induction reduction so that the system can not fully orient the domains in the field as discussed in Subsection 1.1.4. This deviation requires a special attention when interpreting results of this sample under the room-temperature since a full saturation would have led to a smaller resistance.

The graph also shows that at low temperature the resistance peaks do not exactly coincide with the zero magnetic field as it is almost the case at RT. This small shift is mainly observed for the Ni-rich samples emphasizing the relative softness of these materials. This remanence arises from some magnetic domains that do not relax when releasing the magnetic field, thereby the antiparallel state is not totally reached. To get a zero net magnetization, a small opposite direction magnetic field is required to reverse some additional magnetic moments. Remanence values together with coercive fields of the homogeneous and multilayered samples are displayed in Table 3.1. It confirms that even if the magnetic behavior is mainly dominated by the shape anisotropy, H_c increases with the Ni atomic percentage and with the temperature reduction due to the lack of thermal energy for magnetization reversal.

Table 3.1: Data of the normalized remanence M_r/M_s for homogeneous samples together with the experimental coercive field H_c for both homogeneous and multilayered samples. Data for HCNWs from [22]

Materials ($T=300\text{K}$)	M_r/M_s^{HCNWs} (-)	H_c^{HCNWs} (kOe)	H_c^{MLCNWs} (kOe)	$H_{c,T=15\text{K}}^{\text{MLCNWs}}$ (kOe)
Ni ₆₀ Fe ₄₀	0.65	0.30	0.17	0.17
Ni ₇₀ Fe ₃₀	0.75	0.34	0.11	0.16
Ni ₈₀ Fe ₂₀	0.85	0.40	0.13	0.32
Ni ₉₃ Fe ₇	-	-	0.10	0.64

The previous idea that the resistance drop between the P and AP arrangement is bigger at low temperature is confirmed by Figure 3.2(a) showing the temperature influence on the magnetoresistance for the four alloys. It appears that the MR ratio soars when the temperature is reduced except for Ni₉₃Fe₇. This tendency continues up to around 50 K. After that, a further temperature reduction leads to different behaviors depending on the composition. It can be seen that the Ni₈₀Fe₂₀ curve saturates whereas both Ni₇₀Fe₃₀ and Ni₆₀Fe₄₀ show a non negligible reduction of the magnetoresistance ratio. Regarding the Ni₉₃Fe₇ sample, it exhibits a truly different evolution with a gentle decrease just below RT followed by steady MR ratio.

The Ni₈₀Fe₂₀ line has a similar shape than classical magnetoresistance curves [111]. The origin of the growth when reducing the temperature is related to the extinction of the electron-phonon scattering events leading to a significant decline of the resistance. However, the difference $R_{\text{AP}} - R_{\text{P}}$ coming from the residual resistivity is generally not impacted by the temperature. All gathered, give a same difference between the two states, divided by a smaller value of R_{AP} and then a greater MR ratio. The plateau is reached around 50 K which is consistent with the resistivity behavior of thin Py film [112]. Indeed for this temperature, the ideal contribution tends to zero highlighting the constant residual resistivity. Thenceforth, the resistance uniquely depends on the geometry and the purity of the sample and does not change anymore with a further temperature decrease.

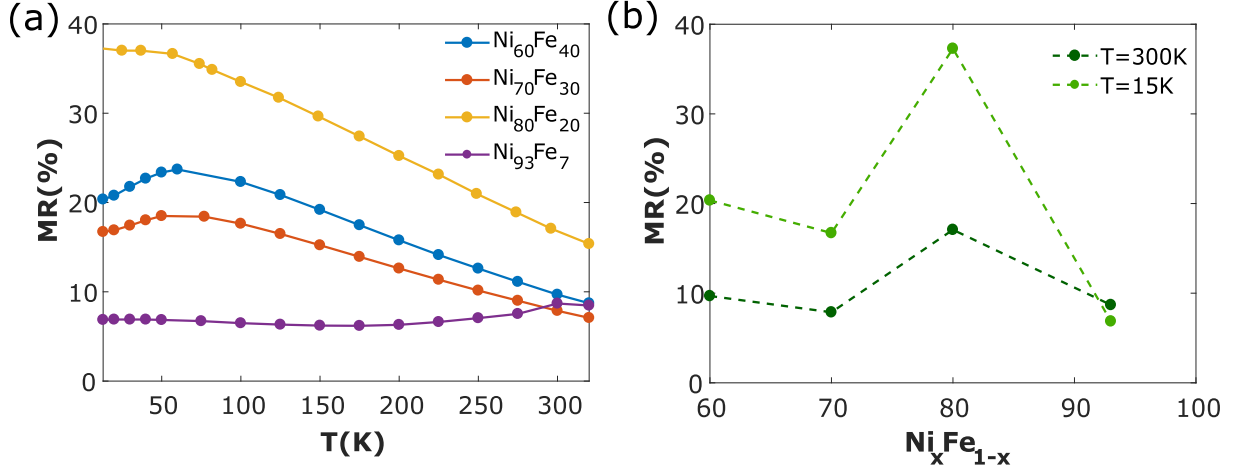


Figure 3.2: Evolution of the MR ratio with (a) the temperature for the four alloys and (b) the Ni atomic percentage at 300 K and 15 K. It appears that the MR ratio globally rises with the temperature reduction while its peak is observed for the Ni₈₀Fe₂₀ sample

Previous explanation over the magnetoresistance increase is also valid for Ni₆₀Fe₄₀ and Ni₇₀Fe₃₀. However, after the peak a moderate drop is surprisingly observed finding its origin in the decoupling of the R_P and R_{AP} curves at low temperature. In one side, R_P follows the conventional linear decline caused by the ideal resistivity reduction and ending by a saturation phase whereas R_{AP} decrease continuously so that the gap between the two states is gradually reduced. Some assumptions which may explain this phenomenon will be outlined later in this work. Finally, the evolution of Ni₉₃Fe₇ is difficult to interpret due to the lack of saturation at certain temperatures. All the MR ratio under 300 K are therefore underestimated, though an evolution without sharp variation is expected in agreement with the low magnetoresistance effect found for rich-nickel sample.

Figure 3.2(b) allows to have a closer look at the evolution of the MR ratio as function of the Ni atomic percentage for both 300 K and 15 K. Without any surprised, it can be seen that the maximal MR at room temperature is around 17% for the Ni₈₀Fe₂₀ confirming its great interest over the years. In addition, the composition variation leads to significant reduction of the magnetoresistance with MR values around 10% at room temperature.

The main magnetoresistance values are gathered in Table 3.2. It can be observed that MR at 15 K is more or less twice bigger than MR at room temperature except for Ni₉₃Fe₇. Besides, GMR values are always larger than MR ones since the gap of resistance is normalized by the smaller resistance R_P . Results of the Permalloy sample are faithful with the ones presented for arrays of parallel nanowires having GMR around 20% at room temperature [113]. From these similar results, it can be concluded that the magnetic behavior is dominated by the monodomain nanowires while the interconnections influence seems negligible. This is mainly related to the low porosity around 3% of this sample. The use of more porous membranes would lead to a higher impact of the interconnections on the network properties. Magnetic simulations would allow to understand the influence of the interconnections with more details. It should finally be noticed that the maximal uncertainty for the resistance measurement is always smaller than 80mΩ leading to a maximal error of 0.01% in the magnetoresistance determination.

Table 3.2: Summary of the main magnetoresistance values found for the four alloys at RT and $T=15\text{K}$.

	MR _{15K} (%)	MR _{RT} (%)	GMR _{15K} (%)	GMR _{RT} (%)
Ni ₆₀ Fe ₄₀	20.35	9.68	25.55	10.72
Ni ₇₀ Fe ₃₀	16.71	7.87	20.06	8.54
Ni ₈₀ Fe ₂₀	37.28	17.08	59.44	20.59
Ni ₉₃ Fe ₇	6.86	8.69	7.37	9.52

To come back on the decrease of Ni₇₀Fe₃₀ and Ni₆₀Fe₄₀ MR ratio under 50 K, Figure 3.3(a) displays $R(H)$ at different low temperatures for the Ni₆₀Fe₄₀ sample. It can be noticed that for a high magnetic field, the P states are almost overlapped meaning that the resistance does not change with the temperature. On the opposite, AP states are associated with different resistances, with an unusual drop of 40 Ω between 40 K and 15 K explaining the bump presence in the MR ratio. This decoupled behavior is depicted in Figure 3.3(b) describing the evolution of R_{AP} and R_P with the temperature. For these alloys, at low temperature the resistance gap slightly declines when approaching 15 K. The origin of the non-steady R_{AP} could be ascribed to a different degree of antiparallelism coming from pinned domain walls. By having a closer look at the nickel-iron phase diagram [114], it appears that below more or less 75% of Ni, there is a switch from a single NiFe₃ phase to a biphasic domain made of NiFe₃ and αFe phase called ferrite. This biphasic structure could prevent the rotation of some magnetic domains pinned in grain boundaries [115, 116] after the field relaxation so that the degree of antiparallelism is reduced. The energy barrier is inversely proportional to the size of the grains so that a higher deposition potential would theoretically decrease this phenomenon [117]. At higher temperature, the reduction of the ideal resistivity could mask this effect or the thermal energy could liberate the pinned magnetic domains leading to a classical behavior. In addition, in presence of a magnetic field, the additional Zeeman energy could overtake the energy barrier, explaining why the parallel state is not affected.

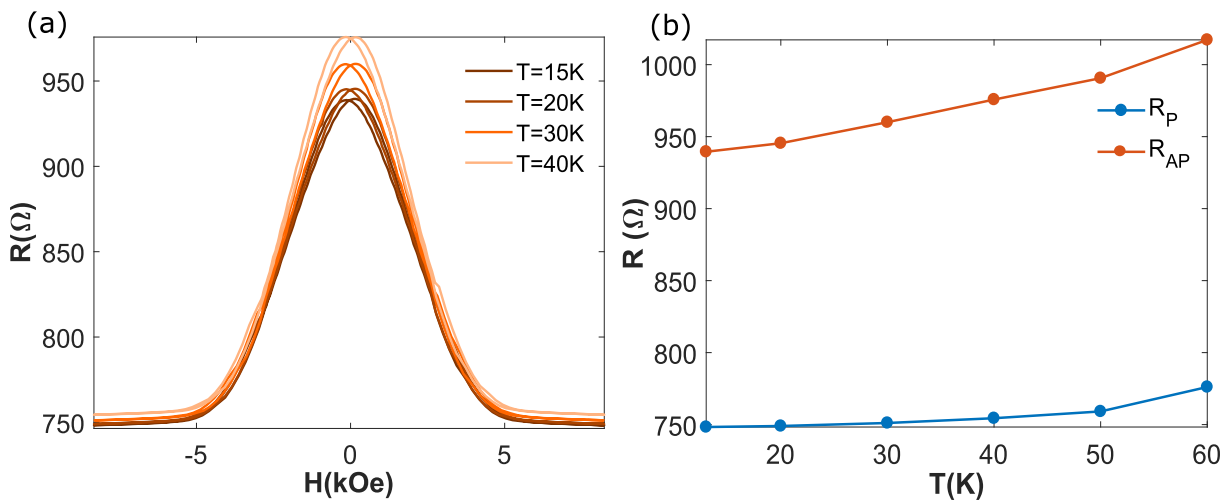


Figure 3.3: (a) $R(H)$ at different low temperatures for Ni₆₀Fe₄₀. (b) Evolution of R_P and R_{AP} with the temperature for Ni₆₀Fe₄₀. It appears that R_P follows the classical shape of the resistivity with a linear decrease and then a plateau whereas R_{AP} does not exhibit the saturation regime.

Up to now, results have only dealt with resistances which are extrinsic parameters. By knowing the geometry of the sample, it is possible to get the intrinsic resistivity. However, our knowledge of the section and the length is quite approximated. Therefore an alternative way to get rid of the sample geometry relies on a multilayered mathematical model computing resistances in series while taking into account the presence of interfaces [21]. Hence, the average resistivity in the parallel state $\bar{\rho}_P$ is expressed as:

$$\bar{\rho}_P (t_{\text{NiFe}} + t_{\text{Cu}}) \approx \rho_{\text{NiFe}} t_{\text{NiFe}} + \rho_{\text{Cu}} t_{\text{Cu}} + 2r_b, \quad (3.1)$$

with ρ_{Cu} and ρ_{NiFe} being respectively the resistivities of Cu and NiFe alloy, t_{Cu} and t_{NiFe} being the thicknesses and r_b being the interfaces resistance. To continue, the model requires three assumptions. Firstly, the interfaces resistance is not impacted by the temperature. Secondly, the measured $\text{RRR} = \rho_P^{295\text{K}} / \rho_P^{15\text{K}}$ is considered as the residual resistivity ratio of the 3D nanowire network in the parallel state. Finally the Mathiessen's rule seen in Equation 1.18 is used to distinguish the thermally activated scatterings arising from magnons and phonons, from the electrons scattered by static defects. Therefore, considering the room temperature and under the previous assumptions, the equation can be rewritten as:

$$\rho_P^{\text{RT}} = \rho_P^0 + \frac{\rho_{\text{iNiFe}}^{\text{RT}} t_{\text{NiFe}} + \rho_{\text{iCu}}^{\text{RT}} t_{\text{Cu}}}{t_{\text{NiFe}} + t_{\text{Cu}}}, \quad (3.2)$$

with ρ_P^0 the residual resistivity, $\rho_{\text{iNiFe}}^{\text{RT}}$ and $\rho_{\text{iCu}}^{\text{RT}}$ the ideal resistivity of respectively NiFe and Cu at RT. In this expression $\rho_P^0 = \rho_{\text{NiFe}}^0 + \rho_{\text{Cu}}^0 + 2r_b$ involving then the scatterings with the nanowires surface, the impurities, and the grain-boundaries of respectively NiFe and Cu as well as the scatterings within the interfaces.

Under the assumption that the ideal resistivity of the nanowires corresponds to the bulk values as it has been proved in previous studies on Ni nanowires [118], and that the phonon/magnon scatterings are totally extinguished at 15K, ρ_P^{RT} can finally be estimated. Besides its evaluation allows to find $\rho_{\text{AP}}^{\text{RT}}$ as:

$$\rho_P^{\text{RT}} \approx \frac{\lambda \rho_{\text{iNiFe}}^{\text{RT}} + \rho_{\text{iCu}}^{\text{RT}}}{(1 + \lambda)(1 - \text{RRR}^{-1})} \quad \rho_{\text{AP}}^{\text{RT}} = \frac{\rho_P}{1 - \text{MR}}. \quad (3.3)$$

As explained in Subsection 2.1.3, some electrodeposition calibrations have enabled to target the desired thicknesses to $t_{\text{NiFe}} \approx t_{\text{Cu}}$ so that $\lambda \approx 1$ which seems to give sufficient quality multilayers. By using the ideal resistivities at room temperature found in Table 1.5, the values of ρ_P^{RT} and $\rho_{\text{AP}}^{\text{RT}}$ have been estimated and reported in Table 3.3. In addition, this table also provides the measured RRR as well as the residual resistivity in the parallel state ρ_P^0 which has been computed with Equation 3.2. It must be specified that a variation of λ does not lead to a severe alteration of ρ_P^{RT} , $\rho_{\text{AP}}^{\text{RT}}$, and ρ_P^0 as illustrated in Figure 3.4. In accordance with the theory, the conductivity decreases with λ due to the smaller thickness of pure Cu layers which is a better electrical conductor than NiFe alloys.

Despite the interfaces presence, the resistivity values of the multilayered samples are a bit smaller than the ones found in homogeneous nanowires [22, 119, 120]. This could be ascribed to the presence of the Cu layers which significantly improve the conduction. Nonetheless, these values stay larger than in the bulk materials due to the important defect density engendered by the electrodeposition process together with the numerous scatterings at the walls of the NWs. In particular, $\text{Ni}_{60}\text{Fe}_{40}$ and $\text{Ni}_{70}\text{Fe}_{30}$ exhibit a larger ρ_P^0 confirming the existence of precipitates and grain boundaries in the binary phase while $\text{Ni}_{80}\text{Fe}_{20}$ seems to be of higher quality.

It terms of purity, the measured RRR are slightly reduced when passing from homogeneous samples to multilayered samples due to the presence of layer interfaces. Hence a previous work has shown for homogeneous samples $\text{RRR}_{\text{Ni}_{60}\text{Fe}_{40}} = 2.08$, $\text{RRR}_{\text{Ni}_{70}\text{Fe}_{30}} = 2.10$, $\text{RRR}_{\text{Ni}_{80}\text{Fe}_{20}} = 2.27$, and $\text{RRR}_{\text{Ni}_{93}\text{Fe}_7} = 2.25$ [22].

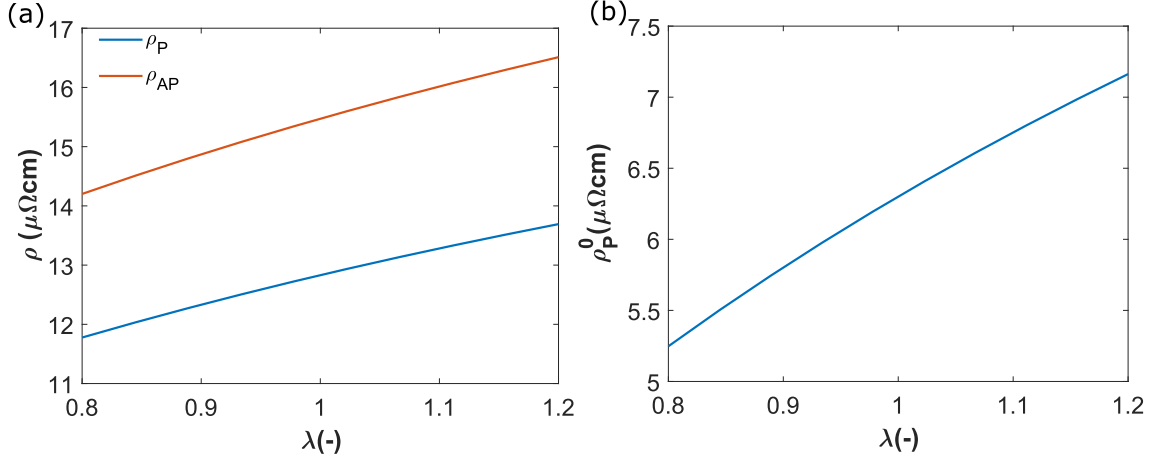


Figure 3.4: (a) Resistivity variations in AP and P configurations and (b) residual resistivity ρ_P^0 as a function of the thickness ratio $\lambda = t_{\text{NiFe}}/t_{\text{Cu}}$ for $\text{Ni}_{80}\text{Fe}_{20}$ sample at $T = 300\text{K}$. Resistivities increase with λ in accordance with the theory since Cu is a better conductor than NiFe alloys .

Table 3.3: Measured RRR ratio with the ideal resistivity of the bulk alloys and the resistivity of both the P/AP states at RT

	RRR (-)	$\rho_{\text{NiFe}}^{\text{RT}} (\mu\Omega\text{cm})$	$\rho_{\text{AP}}^{\text{RT}} (\mu\Omega\text{cm})$	$\rho_{\text{P}}^{\text{RT}} (\mu\Omega\text{cm})$	ρ_{P}^0
$\text{Ni}_{60}\text{Fe}_{40}$	1.70	16.76	24.72	22.32	13.09
$\text{Ni}_{70}\text{Fe}_{30}$	1.59	13.24	21.94	20.21	12.74
$\text{Ni}_{80}\text{Fe}_{20}$	2.03	11.32	15.46	12.82	6.31
$\text{Ni}_{93}\text{Fe}_7$	1.72	10.06	15.40	14.07	8.19

As far, all the analyzes of this thesis were performed by applying $\mathbf{H}$ in the plane of the layers. An almost isotropic behavior has been recorded when switching the field in the out-of-plane direction as proved in Figure 3.5 showing the normalized resistance depending on the magnetic field in both IP and OOP directions. For zero magnetic field, $\text{Ni}_{80}\text{Fe}_{20}$ and $\text{Ni}_{93}\text{Fe}_7$ exhibit almost similar peaks in both directions, though, for the other two samples a net difference of around 1% is observed. Then, it can be seen that the application of a magnetic field leads to a dramatic resistance drop followed by a flattening of the curve. This saturation is achieved for lower amplitude when the field is exerted in the OOP direction for all the alloys. Moreover, the associated resistance is higher so that the magnetoresistance effect is reduced.

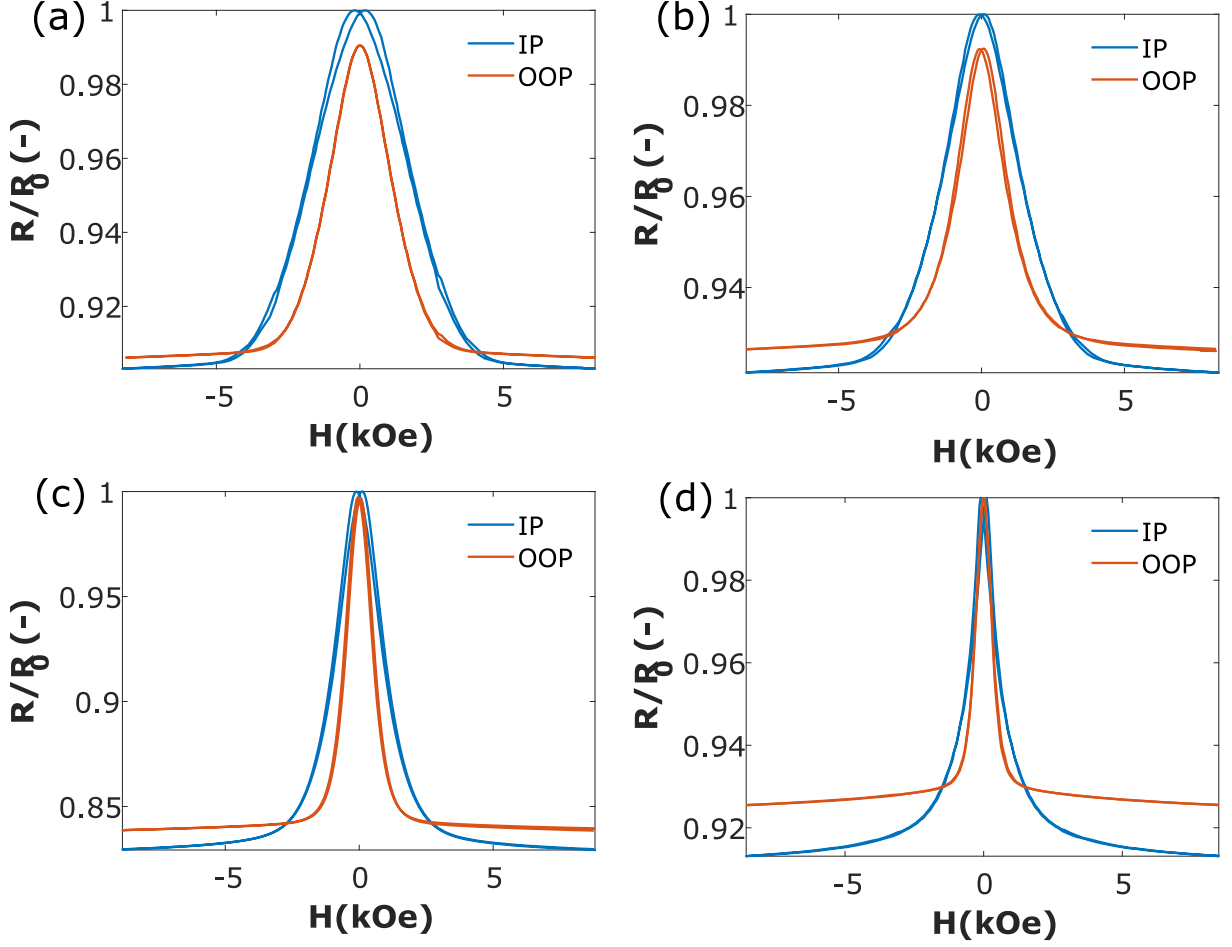


Figure 3.5: Normalized resistance at 300 K with $\mathbf{H}$ applied either in IP or OOP direction for (a) $\text{Ni}_{60}\text{Fe}_{40}$, (b) $\text{Ni}_{70}\text{Fe}_{30}$, (c) $\text{Ni}_{80}\text{Fe}_{20}$, (d) $\text{Ni}_{93}\text{Fe}_7$. The usual saturation difference as well as the AMR fraction gap in the parallel state are observed. Surprisingly, after removing the magnetic field, the IP-resistance and OOP-resistance do not perfectly match for the $\text{Ni}_{60}\text{Fe}_{40}$ and $\text{Ni}_{70}\text{Fe}_{30}$ samples.

The easier saturation in OOP as well as the resistance gap between the IP and OOP parallel state have already been reported in some papers [21, 22, 103]. The saturation amplitude difference finds its origin in the anisotropy. In contrast with magnetic films exhibiting the magnetization in the film plane, the nanowires magnetization is preferentially oriented along the axis due to the important shape anisotropy as explained in Subsection 1.1.4. Therefore, a lower magnetic field amplitude is required to align all the magnetic moments towards this direction. Regarding the difference of resistance in the parallel state, it is related to the angle between the magnetic field and the current flow. Indeed, for the IP configuration this angle is estimated to 65° which is larger than the 35° found when the magnetic field is applied in the OOP direction. This orientation is responsible for an additional anisotropic magnetoresistance in the parallel state, typically a fraction of the AMR ratio. This contribution is therefore larger for the IP direction which implies a magnetization with a bigger angle with respect to the current flow.

To our knowledge the presence of a small resistance shift between the IP and OOP resistance when interrupting the magnetic field after saturation has been met for the first time. This effect is perceptible for $\text{Ni}_{70}\text{Fe}_{30}$ and a bit amplified for $\text{Ni}_{60}\text{Fe}_{40}$. Even

if it could seem weak, this effect is in the same order of magnitude than the AMR ratio. Moreover, an amplitude difference of almost 3% being larger than the AMR [22] has been found at 15 K for $\text{Ni}_{60}\text{Fe}_{40}$. It can therefore be deduced that this effect is related to the giant magnetoresistance and more precisely to a different degree of antiparallelism. Again it could be explained by the biphasic structure of these samples, preventing the rotation of the pinned magnetic domains after the field relaxation so that the degree of antiparallelism is reduced. This phenomenon could be stronger in OOP given that it is an easy-direction favoring the magnetization compared to the IP direction. The amplitude enhancement when reducing the temperature could be related to the lack of thermal energy amplifying the pinning of the magnetic moments by the precipitates and the grain boundaries. In addition, this effect has also been observed with higher amplitude in a sample having a larger NiFe layers thickness. Consequently another origin of this smaller antiparallelism degree could arise from the form factor causing various dipolar coupling. Hence, as seen in Figure 1.11 an increase of t_{FM} leads to a reduction of the H_{dip} component in the plane in favor of the component along the axis, thereby the magnetic moments are more energetically advantaged to stay in that direction.

3.2 Magneto-Seebeck characterization of NiFe/Cu multilayered nanowire networks

This second part presents the magneto-Seebeck results. The measurements of these coefficients is challenging to perform due to the requirements for accurate temperature gradients and measurements of small voltages. Besides, all along the magnetic field cycling, the temperature gradient and the average temperature are difficult to stabilize and may fluctuate leading to smaller signal-to-noise ratio compared to the resistance measurements. However, as displayed in Figure 3.6, the influence of the external magnetic field over the temperature difference and average temperature is negligible. Indeed, $\Delta(\Delta T) < 5\text{mK}$ and $\Delta(T_{\text{av}}) < 20\text{mK}$ prove that fluctuations are negligible allowing then reliable Seebeck coefficient measurements. This affirmation has been confirmed for all the samples over the analyzed temperature range.

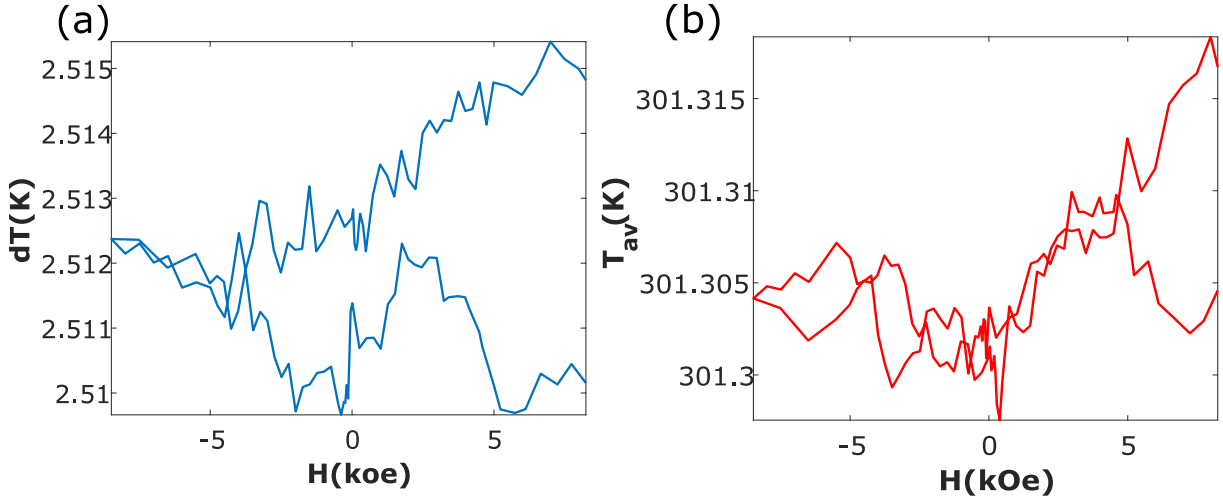


Figure 3.6: Fluctuation of (a) the temperature gradient, and (b) the average temperature in the system depending on the external magnetic field applied during the characterization of $\text{Ni}_{70}\text{Fe}_{30}$ sample at RT. This proves the temperature stability and then the reliability of the results.

The first topic analyzed concerns the magnitude of the Seebeck coefficient in the parallel state which has been plotted as function of the temperature for the four alloys in Figure 3.7(a). It appears that the absolute Seebeck coefficient values of all alloys are enhanced with the temperature increase through an almost linear regime up to reach a saturation around 300 K. $\text{Ni}_{80}\text{Fe}_{20}$ and $\text{Ni}_{93}\text{Fe}_7$ exhibit a similar curve with S around $-25 \mu\text{V/K}$ at room temperature. On the other hand, $\text{Ni}_{70}\text{Fe}_{30}$ presents a slight improvement of S while $\text{Ni}_{60}\text{Fe}_{40}$ reaches an important ceiling value around $-34 \mu\text{V/K}$ at room-temperature. It can be seen that at 70 K the four curves converge to very low Seebeck coefficient amplitude and approach $0 \mu\text{V/K}$ when tending toward 0 K.

The linear regime when increasing the temperature is related to the Mott Expression 1.35 linking the electrical conductivity to the diffusion thermopower. Hence, the curve shapes confirm the dominance of this contribution for the 3D multilayered nickel-iron samples. Physically the improvement of the Seebeck coefficient with the temperature can be explained by a larger broadening of the Fermi function so that a larger flux of

electrons flows from the hot side to the cold side creating a larger $\mathbf{E}$ in an open circuit. On the opposite, the plateau observed above the room temperature finds its origin in the increase of the electron-phonon scatterings as well as the higher efficiency of their collisions [31]. Indeed, these collisions become more numerous and resistive at higher temperature counteracting the increase of electron flux so that the thermopower does not evolve anymore. It should be precised that a small shift around 70 K is observed coming from a variation in the measurement technique, since below this point the temperature is not directly controlled during the measurement. Finally, an additional thermopower may arise from a magnon-drag contribution, overall at low temperature, but the importance of this contribution is still discussed in the scientific world.

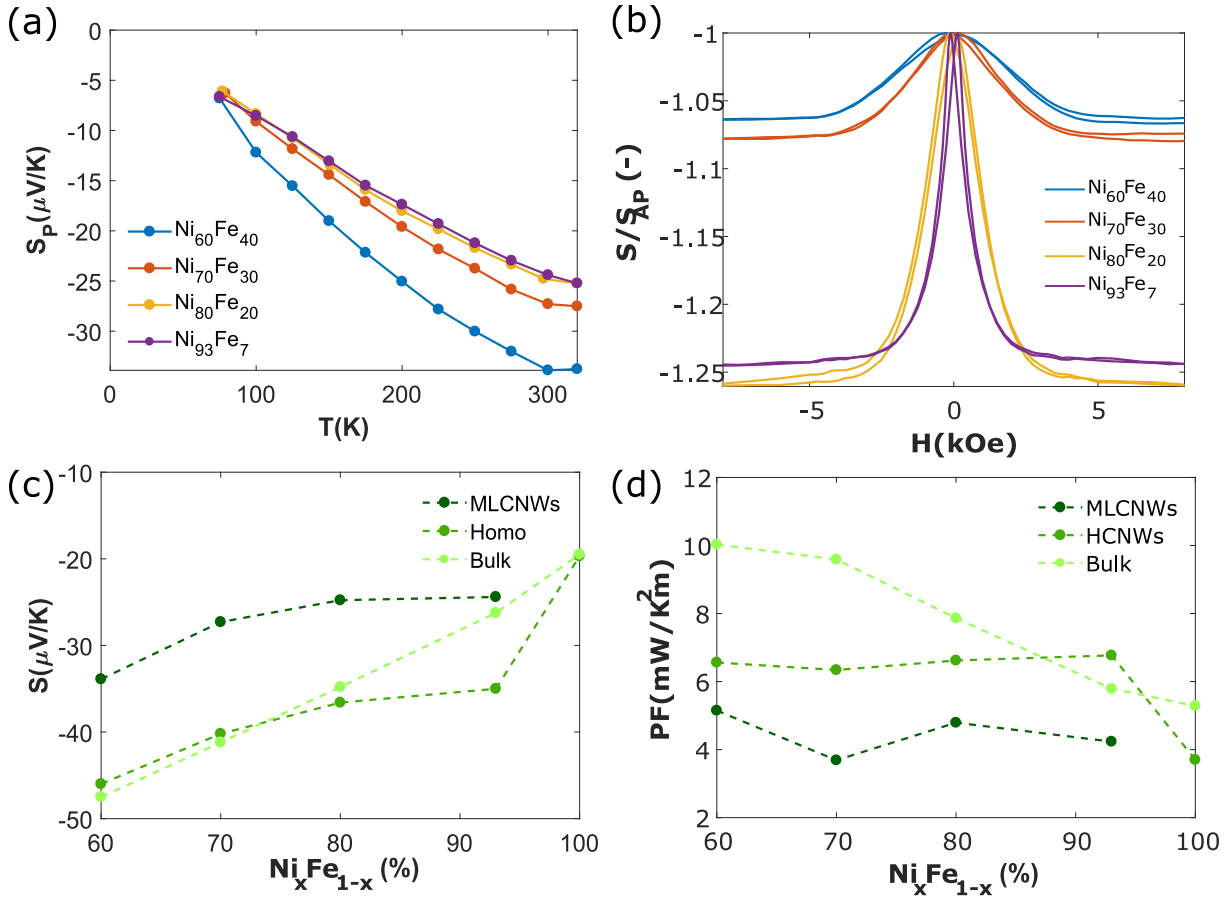


Figure 3.7: Evolution of (a) the Seebeck coefficient in the parallel configuration depending on T for the four alloys, and (b) the Seebeck coefficient depending on $\mathbf{H}$ normalized by its value in the antiparallel configuration. Images (c) and (d) represent respectively the Seebeck coefficients and the power factors as function of the Ni atomic percentage for the MLCNWs, HCNWs and bulk alloys. Data concerning the bulk materials come from [45, 70]

By analogy to the resistance, the Seebeck coefficient is influenced by the application of an external magnetic field. This influence is illustrated in Figure 3.7(b) depicting the evolution of the normalized Seebeck coefficient with the magnetic field for the four alloys at room temperature. The normalization has been carried out with the Seebeck coefficient in the antiparallel state. Again, the curves exhibit a bell shape with a smaller Seebeck value in the antiparallel state since the electrons responsible for the thermopower are

highly scattered in this configuration. The magnetic field application leads to a moderate enhancement of S in the case of $\text{Ni}_{70}\text{Fe}_{30}$ and $\text{Ni}_{60}\text{Fe}_{40}$ while a severe rising of more than 20% is observed for $\text{Ni}_{80}\text{Fe}_{20}$ and $\text{Ni}_{93}\text{Fe}_7$. This last sample has the particularity to switch from the S_{AP} to S_{P} value with a magnetic field of only 2 kOe, making then an extremely sharp transition compared to the other alloys. After this change of configuration, the Seebeck coefficient does not evolve anymore with the magnetic field as all the magnetic moments are aligned with the field.

In the following, the impact of the multilayers on the Seebeck coefficient has been considered. In this purpose, Figure 3.7(c) shows a comparison of the multilayered Seebeck coefficients in the parallel state with both the homogeneous samples and the bulk nickel-iron alloys Seebeck coefficients at RT. The global trends shows a decrease of S when increasing the Ni atomic percentage. Moreover, it can be seen that S is smaller for the multilayered samples while the homogeneous and the bulk samples have a pretty similar trajectory ranging from $-45 \mu\text{V/K}$ to $-20 \mu\text{V/K}$ for pure nickel. The shift observed for the $\text{Ni}_{93}\text{Fe}_7$ point may originate from deviations of the form factor, the composition, or the bulk alloy data [45, 70]. The match between the bulk and the homogeneous samples is legitimate since S is an intrinsic property which does not vary with the sample geometry. It also proves that no quantum phenomenon takes place for these dimensions. However, the addition of the Cu layers to produce multilayered samples leads to a significant fall down of the Seebeck coefficient coming from the small positive contribution of the copper $S_{\text{Cu}} = 1.6 \mu\text{V/K}$. The impact of the interfaces could also cause additional scatterings reducing the thermopower. As regards the decrease of S for a Ni enrichment, it is in agreement with the theory stating that alloys can exhibit large variation of the DOS near the Fermi level inducing an large first derivative and then an improvement of the electron diffusion thermopower. In particular, Ni and Fe are ferromagnetic materials with quite sharp densities of states [21, 32].

An alternative way to characterize the thermoelectric power output is the PF linking the Seebeck coefficient and the electrical conductivity. The evolution of the room-temperature PF depending on the composition has been plotted in Figure 3.7(d) for the multilayered, homogeneous, and bulk samples. The graph highlights a larger PF value for the bulk materials than for the nanowires. Besides, it can be seen that the addition of the multilayers within the nanowires further decrease this ratio as testify the smaller values reached for the multilayered nanowires. Despite the unchanged value of S , this time there is a differentiation of the HCNWs and the bulk curves caused by an increase of residual resistivity due to the scattering with the NWs walls. As regards the MLCNWs, they combine this increase of resistivity together with a diminution of S leading to a further reduction of PF which reaches values around $4\text{-}5 \text{ mWK}^{-2}\text{m}^{-1}$. Furthermore, a greater PF value is observed for Fe richer samples even if this trends is less clear for the NWs. Although the diminution of impurities enables to decrease the resistivity, it causes a simultaneous reduction of S which is more determinant in the expression so that PF is reduced. However, the evaluation of this parameter relies on the determination of ρ for the samples which is based on inaccurate values and approximations. Consequently, carefullness is required when interpreting the results.

Although an important Seebeck coefficient is essential, the key factor for the magnetic Seebeck control arises from the MTP ratio quantifying the normalized difference between the AP and P configurations. This factor is analyzed in Figure 3.8(a) displaying the temperature influence on the opposite of MTP for the four alloys. It can be seen that the behavior is relatively similar to the MR ratio. At room temperature, alloys have a MTP ranging from 26% for $\text{Ni}_{80}\text{Fe}_{20}$ to 8% for $\text{Ni}_{70}\text{Fe}_{30}$ and $\text{Ni}_{60}\text{Fe}_{40}$. Globally, the magneto-thermopower varies oppositely to the temperature except for $\text{Ni}_{93}\text{Fe}_7$. This tendency accelerates at low temperature to reach values more or less three time larger than at room temperature. However, $\text{Ni}_{93}\text{Fe}_7$ exhibit a totally different behavior with a decrease of MTP all along the temperature reduction.

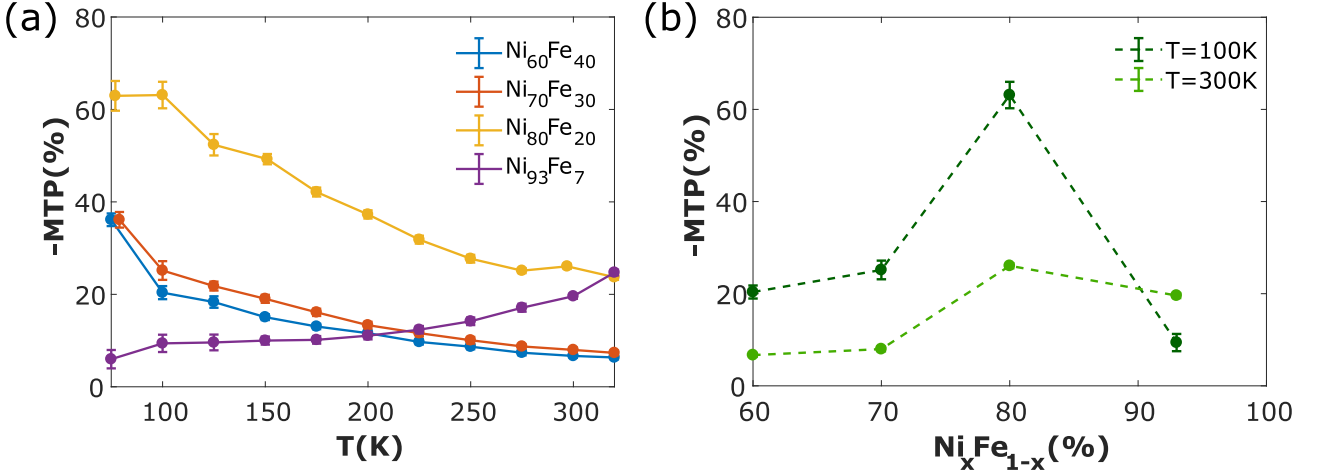


Figure 3.8: Evolution of MTP depending on (a) the temperature for the four alloys and (b) the composition at 100 K and 300 K. The MTP ratio globally rises up when decreasing the temperature except for $\text{Ni}_{93}\text{Fe}_7$ which displays an opposite behavior. The maximal value is found for the composition $\text{Ni}_{80}\text{Fe}_{20}$ exhibiting a magneto-thermopower of 60% at room temperature.

As a matter of fact, this ratio is related to $S_{\text{AP}} - S_{\text{P}}$ which is usually only slightly impacted by the temperature reduction while the denominator significantly drops explaining the dramatic increase of MTP. Moreover, under 70 K S is getting closer to zero explaining the sudden acceleration. The particular $\text{Ni}_{93}\text{Fe}_7$ curve originates from the variation of $S_{\text{AP}} - S_{\text{P}}$. At low temperature these values are almost similar and they slowly diverge with the temperature increase. More details about this evolution will be provided in the next. Figure 3.8(b) highlights the magnitude of MTP depending on the Ni atomic percentage for both 100 K and 300 K. It confirms both idea than a temperature decline has a positive influence on MTP, with an important peak for the Py sample which exhibits a magneto-thermopower up to 60% at 100 K. It should be precised that the maximum uncertainty over the S measurement is evaluated around 10^{-8} V/K leading to errors about 3% at low temperature for the MTP determination.

A parallelism can be done between the MR ratio in Figure 3.2 and the MTP value in Figure 3.8. Previous works have shown that for an unknown reason, these two values were intimately related [21, 22]. This relation is confirmed for $\text{Ni}_{80}\text{Fe}_{20}$, but a slight decoupling occurs for $\text{Ni}_{70}\text{Fe}_{30}$ and $\text{Ni}_{60}\text{Fe}_{40}$ at low temperature. Besides, $\text{Ni}_{93}\text{Fe}_7$ runs opposite to this relation since MR is mainly stable all along the temperature reduction whereas MTP significantly declines. Results of the ratio between the opposite of MTP and MR are displayed in Table 3.4. It can be observed that this ratio increases with the Ni atomic percentage, therefore an Ni enrichment enables to exhibit a large magneto-thermopower while maintaining a giant magnetoresistance relatively low.

Table 3.4: Ratio of the opposite of MTP and MR values for all the samples at a temperature of 300K

$T = 300 \text{ K}$	-MTP (%)	MR (%)	-MTP/MR _{300K} (-)
Ni ₆₀ Fe ₄₀	6.67	9.68	0.69
Ni ₇₀ Fe ₃₀	7.98	7.87	1.01
Ni ₈₀ Fe ₂₀	26.06	17.08	1.53
Ni ₉₃ Fe ₇	19.60	8.69	2.26

Up to now, the magnetoresistance and the magneto-Seebeck effects have been quantified distinctly. Nevertheless, both contributions are gathered in the MPF ratio which can alternatively be defined as:

$$\text{MPF} = \frac{(1 - \text{MTP})^2}{1 - \text{MR}} - 1 \quad (3.4)$$

This factor is depicted as function of the temperature in Figure 3.9(a). It reveals the possibility to have a very large magnetic control of the thermoelectric output power density. This graph shows a similar shape to the MTP one with Ni₆₀Fe₄₀ and Ni₇₀Fe₃₀ rising when decreasing the temperature as well as Ni₈₀Fe₂₀ with a bigger amplitude. Once again, Ni₉₃Fe₇ describes an opposite behavior. This evolution proves that the MPF shape is mainly dominated by MTP, despite the presence of MR in the expression which has rather an influence over the amplitude at low temperatures. The factors favoring this important MPF ratio are the importance of the resistivity drop as well as the amplitude of the Seebeck coefficient jump in presence of a magnetic field. The growth when decreasing the temperature is ascribed to the decline of the resistivity improving the MR ratio together with the drop of S enhancing MTP so that the MPF value is boosted. Figure 3.9(b) displays the evolution of MPF ratio with the Ni atomic composition for both 300 K and 100 K. It confirms the rise of MPF at low temperatures. The effect is particularly outstanding for Ni₈₀Fe₂₀ which describes a jump from 91% at room temperature up to 300% at 100 K. It must be noticed that the behavior of Ni₉₃Fe₇ is a bit biased since the MR ratio is underestimated under 300 K due to the lack of magnetic saturation. Consequently, for larger H , it would lead to higher MPF ratio for this sample. The maximal MPF uncertainty is estimated at 12% at low temperature for Py while it is kept under 4% for other alloys. A summary of the thermoelectric parameters and spin-dependent ratios is presented in Table 3.5.

Table 3.5: Seebeck-coefficients S and power factors PF for the four alloys at room-temperature. This table discerns the values in parallel arrangement from the antiparallel arrangement at room-temperature and for $\lambda \approx 1$. It also provides the factors allowing to quantify the spin-dependence as MTP characterizing the Seebeck-coefficient variation and MPF expressing the power factor difference.

$T=300 \text{ K}$	$S_{\text{AP}}(\mu\text{V/K})$	$S_{\text{P}}(\mu\text{V/K})$	MTP(%)	PF _P (mW/K ² m)	PF _{AP} (mW/K ² m)	MPF(%)
Ni ₆₀ Fe ₄₀	-31.78	-33.90	-6.67	5.15	4.09	26.00
Ni ₇₀ Fe ₃₀	-25.28	-27.30	-7.98	3.69	2.91	26.56
Ni ₈₀ Fe ₂₀	-19.66	-24.78	-26.06	4.79	2.50	91.61
Ni ₉₃ Fe ₇	-20.41	-24.40	-19.60	4.23	2.70	56.64

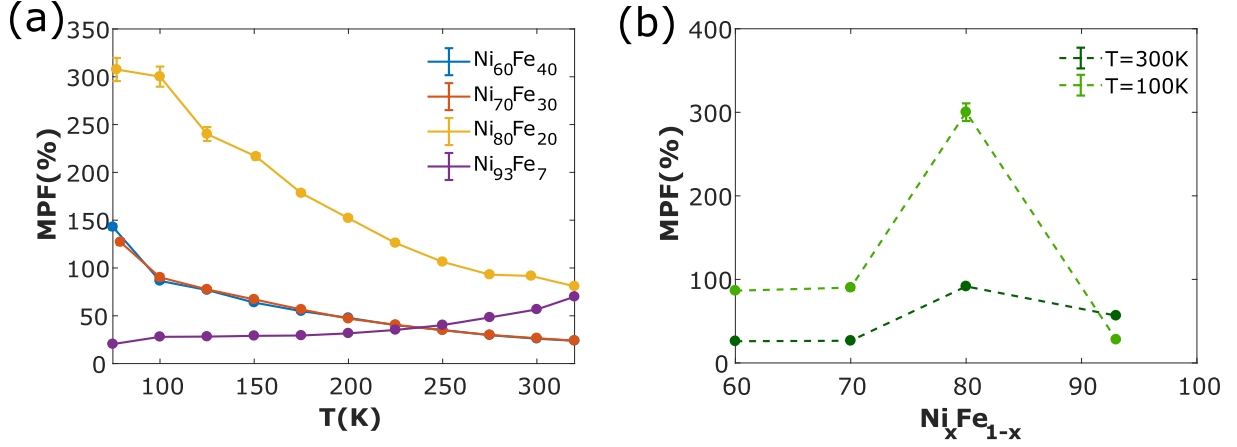


Figure 3.9: Evolution of MPF depending on (a) the temperature for the four alloys and (b) the atomic composition for 300 K and 100 K. This ratio follows a similar shape with respect to MTP curve and confirms the large magnetic dependence of the output power factor PF.

To sum up Ni₆₀Fe₄₀ has the advantage to exhibit the largest thermopower at room-temperature leading to a power factor of 5 mW/K²m comparable with famous thermoelectric bulk materials as BiSbTe [121], even if a recent paper has achieved a record value of 53.8 mW/K²m at 300K for this material after an appropriate treatment [122]. However, Ni₆₀Fe₄₀ also displays low MTP and MPF ratios making the magnetic control difficult. Ni₇₀Fe₃₀ has more or less the same characteristics with slightly lower thermopower values. The properties of Ni₈₀Fe₂₀ are significantly different. This alloy exhibits a large alteration of its Seebeck-coefficient and power factor when switching from an antiparallel to a parallel configuration. Despite a further decrease of S magnitude, the MTP reaches a large value of 26% while the MPF ratio attains 92% at room-temperature, confirming the ability to magnetically control the thermoelectric properties of this sample. Finally, Ni₉₃Fe₇ has approximately the same thermopower than Ni₈₀Fe₂₀, though, its spin-dependence is a bit smaller while remaining fairly high.

In the perspective to create magnetic interrupters for thermoelectric devices, this work aims to maximize the gap between $S_{\uparrow}$ and $S_{\downarrow}$. As reminder, our working system is well adapted for the extraction of these spin-dependent Seebeck coefficients. Hence, as previously seen in Subsection 1.3.3, under the two current models and the limit of no-spin relaxation:

$$S_{\uparrow} = \frac{1}{2}[S_{AP}(1 - \beta^{-1}) + S_P(1 + \beta^{-1})] \quad S_{\downarrow} = \frac{1}{2}[S_{AP}(1 + \beta^{-1}) + S_P(1 - \beta^{-1})], \quad (3.5)$$

with $\beta = \sqrt{MR}$. By solving this system with the values found for MR, S_{AP} , and S_P , one can access to both $S_{\uparrow}$ and $S_{\downarrow}$. Results as function of the temperature are shown in Figure 3.10 together with the S_{AP} and S_P curves. It appears that the difference $S_{\uparrow} - S_{\downarrow}$ is always larger than $S_{AP} - S_P$. Mathematically, it comes from the spin asymmetry coefficient β being always smaller than 1 for nickel-iron alloys. The extreme case of $\beta = 1$ leads to $S_{\uparrow} = S_P$ and $S_{\downarrow} = S_{AP}$ but is impossible since as shown with the Equation 1.23 it would implies an infinite α and then a current totally spin-polarized. By having a closer look at both Figure 3.10(a) and (b) respectively for Ni₆₀Fe₄₀ and Ni₇₀Fe₃₀, it can be noticed that they exhibit an almost similar behavior. As for the classical Seebeck coefficient, the

saturation regime above the room-temperature and the amplitude decline when cooling down the sample are observed. Furthermore, these two alloys show equivalent slopes between the AP and P configurations leading to a stable gap $S_{AP} - S_P$ over the whole set of temperatures and consequently a steady $S_{\uparrow} - S_{\downarrow}$. On the contrary, $\text{Ni}_{80}\text{Fe}_{20}$ sample in Figure 3.10(c) exhibits a slight slope variation leading to a difference $S_{AP} - S_P$ increasing with the temperature. This effect is also observed at a larger scale for $S_{\uparrow} - S_{\downarrow}$. Finally, $\text{Ni}_{93}\text{Fe}_7$ in Figure 3.10(d) is the most interesting sample. At low temperature all the curves converge to the same value, closing the difference between $S_{\uparrow}$ and $S_{\downarrow}$. This trajectory is responsible for the significant reduction of the MTP ratio with the temperature. On the other hand when increasing the temperature, S_{AP} diverges from S_P because of a smaller slope. Therefore, the difference grows with the temperature up to 300 K. Surprisingly above this point, S_P and S_{AP} even start to evolve in opposite directions exhibiting an opening. The behavior for the majority and minority Seebeck coefficients follows the same pattern amplifying the difference. Consequently at low temperature, this alloy reveals an almost imperceptible gap between $S_{\uparrow}$ and $S_{\downarrow}$ which is continuously enhanced with the temperature and become very large, $S_{\uparrow}$ being twice bigger than $S_{\downarrow}$ at room-temperature. Above this point, the opposite slopes result in a large opening gap.

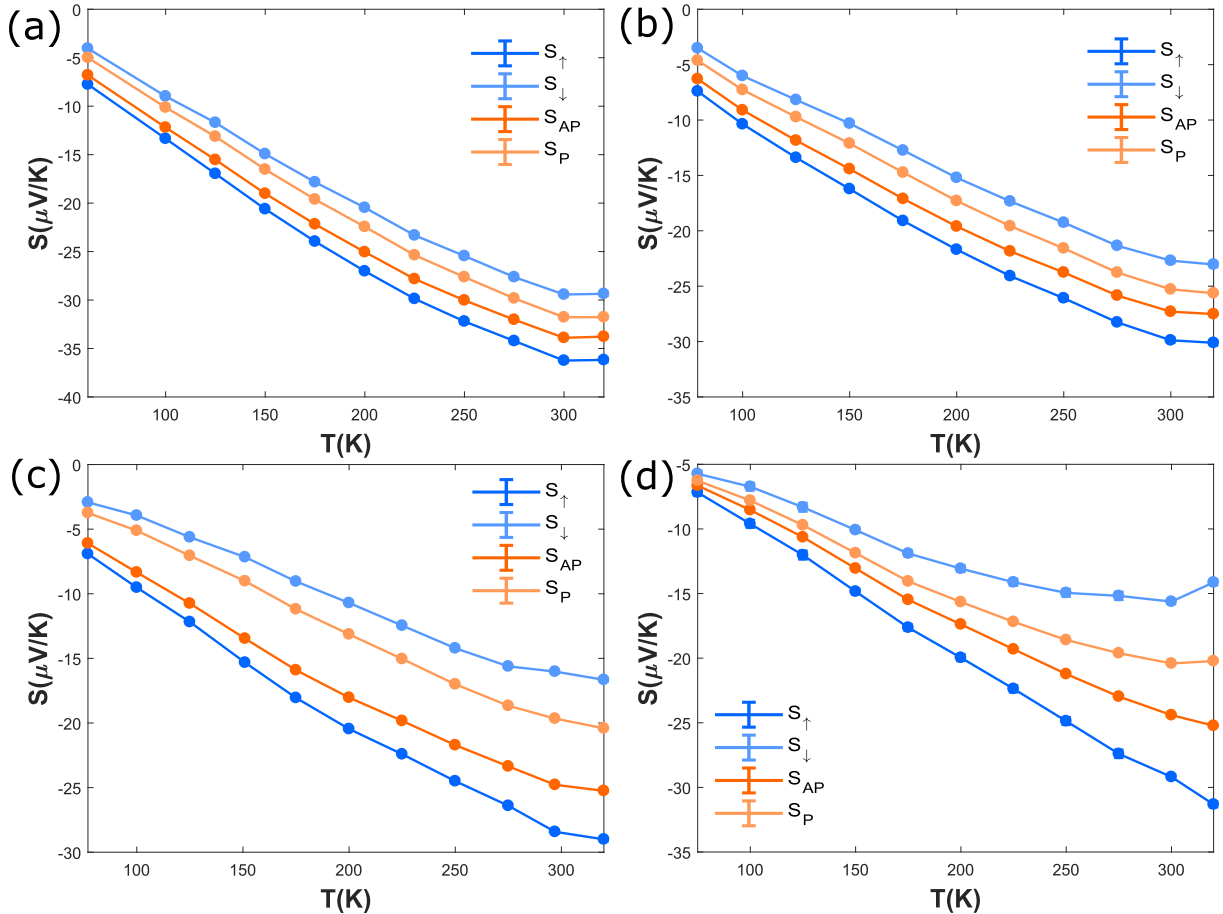


Figure 3.10: Evolution of S_{AP} , S_P , $S_{\uparrow}$ and $S_{\downarrow}$ depending on the temperature for (a) $\text{Ni}_{60}\text{Fe}_{40}$, (b) $\text{Ni}_{70}\text{Fe}_{30}$, (c) $\text{Ni}_{80}\text{Fe}_{20}$ and (d) $\text{Ni}_{93}\text{Fe}_7$. Sample (a) and (b) exhibit curves with almost similar slopes while (c), but overall (d) present another behavior with an opening gap for high temperature.

From now, the attention will be focused on the quantification of the $S_{\uparrow} - S_{\downarrow}$ gap. This difference has been plotted in Figure 3.11(a) as function of the temperature for the four alloys. Once again, $\text{Ni}_{60}\text{Fe}_{40}$ and $\text{Ni}_{70}\text{Fe}_{30}$ have a similar gap slightly increasing with the temperature while remaining under $-7 \mu\text{V/K}$. $\text{Ni}_{80}\text{Fe}_{20}$ starts at the same level at 70 K but exhibits a larger slope so that it finally reaches a gap around $-12 \mu\text{V/K}$. In regards to $\text{Ni}_{93}\text{Fe}_7$ it begins with a gap of only $-1 \mu\text{V/K}$, however, it has a severe slope so that it exceeds $\text{Ni}_{60}\text{Fe}_{40}$ and $\text{Ni}_{70}\text{Fe}_{30}$ after 200 K. Moreover, it continues to grow crossing $\text{Ni}_{80}\text{Fe}_{20}$ around 250 K. Finally, it displays a value of around $-14 \mu\text{V/K}$ at room-temperature. Besides, it can be noticed that above this point, the difference climbs up to $-17 \mu\text{V/K}$ at 320 K. Therefore, it can be concluded that the optimal gap is displayed by $\text{Ni}_{80}\text{Fe}_{20}$ up to 250 K while $\text{Ni}_{93}\text{Fe}_7$ outperforms the others above this point.

This reverse of performances with temperature is confirmed in Figure 3.11(b) showing the evolution of the gap as function of the atomic composition for 100 K, 300 K, and 320 K. At low temperature the gap does not much vary with the composition except for $\text{Ni}_{93}\text{Fe}_7$ which shows a lower value. At higher temperatures of 300 K and 320 K, the curves are similar with a common enhancement of the gap up to the $\text{Ni}_{80}\text{Fe}_{20}$ sample. Nonetheless for the richer Ni sample, curves are decoupled with the gap only evolving slightly at 300 K whereas this alloy jumps over $-17 \mu\text{V/K}$ at 320 K. Some results are reported in Table 3.6 which also contains the spin asymmetry coefficient for Seebeck values η . This factor is defined as:

$$\eta = \frac{S_{\uparrow} - S_{\downarrow}}{S_{\uparrow} + S_{\downarrow}}. \quad (3.6)$$

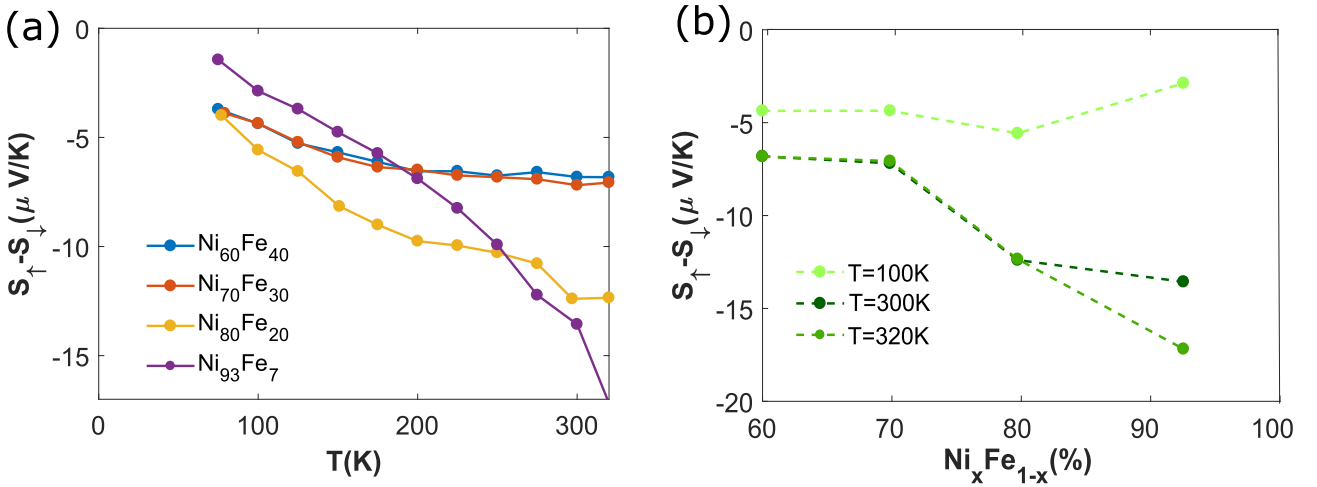


Figure 3.11: Evolution of $S_{\uparrow} - S_{\downarrow}$ depending on (a) the temperature for the four alloys (b) the atomic composition for 100 K, 300 K, and 320 K. It appears that under 250 K, the optimal $S_{\uparrow} - S_{\downarrow}$ is found for $\text{Ni}_{80}\text{Fe}_{20}$, however, above this temperature $\text{Ni}_{93}\text{Fe}_7$ exhibits the highest gap.

Table 3.6: Room-temperature spin-dependent Seebeck coefficients together with their gap as well as the spin asymmetry coefficient for Seebeck values η . The gap at 320 K is also provided.

T=300K	$S_{\uparrow}(\mu\text{V/K})$	$S_{\downarrow}(\mu\text{V/K})$	$S_{\uparrow} - S_{\downarrow}(\mu\text{V/K})$	$\eta(-)$	$S_{\uparrow}^{320\text{K}} - S_{\downarrow}^{320\text{K}}(\mu\text{V/K})$
$\text{Ni}_{60}\text{Fe}_{40}$	-36.24	-29.43	-6.81	-0.10	-6.82
$\text{Ni}_{70}\text{Fe}_{30}$	-29.89	-22.69	-7.19	-0.14	-7.07
$\text{Ni}_{80}\text{Fe}_{20}$	-28.42	-16.02	-12.40	-0.28	-12.35
$\text{Ni}_{93}\text{Fe}_7$	-29.19	-15.62	-13.57	-0.30	-17.18

As seen in Subsection 1.3.2, the thermopower origin in this unique architecture is suspected to be dominated by electron diffusion. Additional evidences are exposed in Figure 3.12 where the inverse linear relationship of Equation 1.44 is plotted for several temperatures. The existence of a fair agreement between the dots, corresponding to experimental values, and the solid lines, showing the theoretical diffusion thermopower can be seen. This linear match confirms the expectations about the diffusion thermopower and explains the similar patterns obtained for both the magnetoresistance and magneto-Seebeck curves. In addition, the temperature seems to have no significant influence over the electron diffusion dominance. Some dispersion may possibly comes from magnon drag but this contribution is still debated in the scientific world.

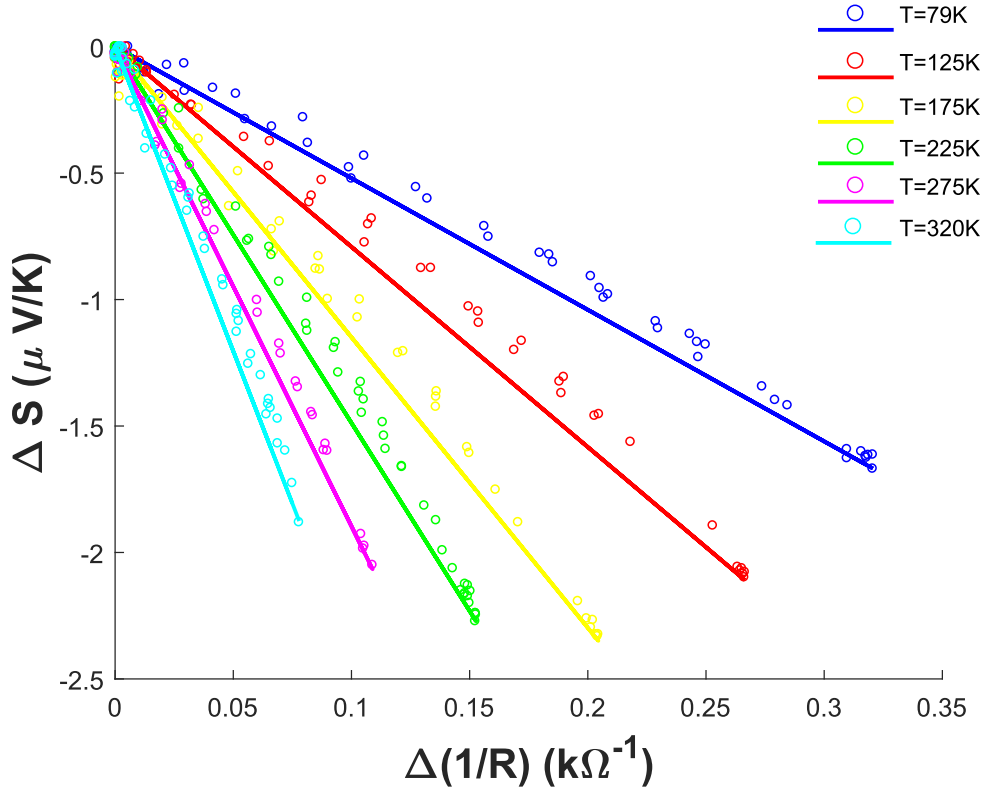


Figure 3.12: Linear relation of $\Delta S(H) = S(H) - S_{\max}$ vs. $\Delta(1/R(H)) = 1/R(H) - 1/R_{\max}$ for $\text{Ni}_{70}\text{Fe}_{30}$ sample over the temperature range investigated. Data fits with the solid lines corresponding to the theoretical relation, confirming the dominance of the diffusion thermopower.

The Seebeck measurements of the 3D multilayered crossed nanowires networks made of NiFe/Cu with the alloy layers varying from 60% to 93% of Ni allows to get some precious information over the spin-dependent Seebeck coefficients. Although $\text{Ni}_{60}\text{Fe}_{40}$ and $\text{Ni}_{70}\text{Fe}_{30}$ have a large thermopower, they do not exhibit a significant gap $S_{\uparrow} - S_{\downarrow}$ so that they do not meet the main objective. Moreover a further decrease of the Ni content should not reveal great spin-dependence property performances. $\text{Ni}_{80}\text{Fe}_{20}$ which is an already well known alloy exhibits interesting characteristics with gap $S_{\uparrow} - S_{\downarrow}$ of $12.3 \mu\text{V/K}$ in absolute value, which is almost three times greater than the values found for nanopilars made of this alloy [123].

Finally, $\text{Ni}_{93}\text{Fe}_7$ has been revealed very interesting since this alloy exhibits a gap $S_{\uparrow} - S_{\downarrow}$ reaching an absolute value of $17.18 \mu\text{V/K}$ at 320K together with a sharp switch from the AP configuration to the P configuration for a low magnetic field of 2 kOe . This high Seebeck coefficient spin-dependence arises from the large Ni concentration and could even be improved by a further enrichment. As a matter of fact, a previous study has predicted that nickel sample could exhibit $S_{\uparrow}$ of $-43 \mu\text{V/K}$ and $S_{\downarrow}$ of $+20 \mu\text{V/K}$ [75]. This tremendous gap originates from the DOS of the d band at the Fermi level shown in Figure 3.13. As a reminder $S_d \propto \mathcal{D}'_d(\epsilon_F)/\mathcal{D}_d(\epsilon_F)$, meaning that the first derivative of the DOS is related to the sign and the amplitude of the spin-diffusion thermopower while the DOS amplitude has a negative influence on it. Specifically, the first derivative of the spin-down band is largely positive while the amplitude reaches a significant value justifying the $S_{\downarrow}$ of $+20 \mu\text{V/K}$. In contrast the spin-up band has a small negative first derivative associated with a small DOS leading to a negative $S_{\uparrow}$ of around $-43 \mu\text{V/K}$. The high spin Seebeck coefficient difference observed in $\text{Ni}_{93}\text{Fe}_7$ could then arise because the composition is getting closer to the pure nickel. It could be really interesting to investigate the behavior when targeting higher Ni content to observe if one could obtain a larger gap with maybe $S_{\uparrow}$ and $S_{\downarrow}$ being of opposite signs. However, it should be precised that the dilution of a few percentage of impurities drastically alters the DOS at the Fermi level due to the creation of virtual bound states [75], making results difficult to forecast. Besides, samples at this composition are challenging to deposit but will be one of the work focus of Luc Piriaux's researcher team in the future.

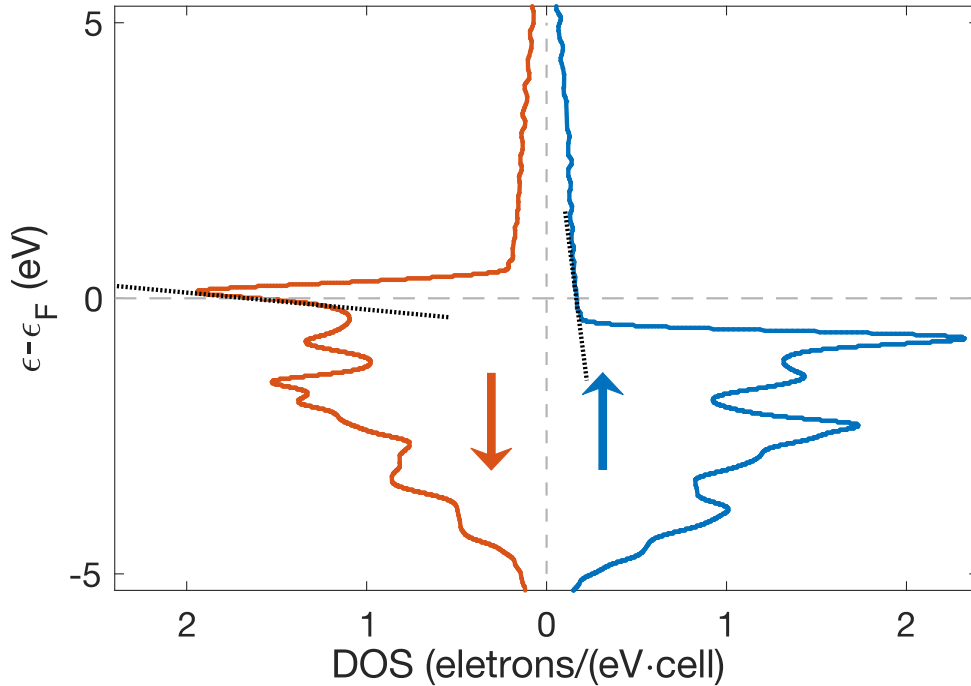


Figure 3.13: Simulated spin-up and spin-down density of states for pure nickel containing the first derivative in black dots indicating the sign of the electron diffusive thermopower. Figure adapted from [21]

Conclusion and future perspectives

This work has investigated the magnetotransport properties of 3D interconnected multi-layered nanowire network made of ferromagnetic NiFe alloys spaced by Cu layers. The study has been performed on 4 different alloys with a set of composition ranging from 60% to 93% of Ni. Track-etched polymer membranes with crossed nanochannels have been proved successful templates for the fabrication of such samples through the growth of nanowires inside the template pores by metallic electrodeposition from a single electrolyte bath. This technique has been proved reliable, versatile, and cheap. Besides, it has enabled to produce unique nanowire structures while keeping an accurate control over the morphology, the material composition as well as the density of nanowires. This innovative interconnected architecture combines mechanical stability and electrical conductivity within the self-supported sample together with flexibility and thermal stability provided by the polycarbonate template. The electrons flow along the nanowires axis while the global transport of heat and charges takes place in the film plane measuring some centimeters. From this configuration results the possibility to perform suitable macroscopic electrical and thermal measurements after removing a part of the cathode by ions sputtering to create a two-probe design.

The successive layers formed respectively from a ferromagnetic (NiFe) and a non-magnetic (Cu) materials have led to an antiparallel configuration in the absence of external magnetic field arising either from some antiferromagnetic coupling or the randomization of the magnetic moments within the magnetic layers. On the other hand, the application of an external magnetic field has ensured to align all the magnetic moments with the field, and thereby parallel to each others. These two arrangements give rise to different behavior of spin-up and spin-down electrons resulting in an alteration of the transport properties when switching from one magnetization state to the other. An appropriate external magnetic field is therefore at the origin of a relatively tunable electrical resistance and Seebeck coefficient characterizing the thermoelectric power. Measurements have demonstrated various giant magnetoresistance and magneto-thermopower depending on the alloy composition. Results concerning $\text{Ni}_{60}\text{Fe}_{40}$ and $\text{Ni}_{70}\text{Fe}_{30}$ can be analyzed simultaneously since they exhibit approximately the same properties. In term of magnetoresistance, these alloys have exhibited relatively low GMR around 10% at room temperature. Moreover, a temperature drop has led to a peak around 50 K followed by a particular decline observed for the first time. This tendency could be related to the biphasic structure depicted for these compositions responsible for magnetic domains pinning in absence of sufficient thermal and Zeeman energies so that the antiparallelism degree is reduced. This phenomenon, together with the shape anisotropy could also be at the origin of the resistance peak shift observed when relaxing the magnetic field after a saturation in IP and OOP. Indeed after a magnetic saturation, a larger part of the magnetic domains would be pinned in the OOP direction compared to the IP one, since it is an easy axis favoring the magnetization.

In regards of the thermoelectric performances, these alloys exhibit very large Seebeck coefficients and power factor values reaching respectively $-34 \mu\text{V/K}$ and $5.15 \text{ mW/K}^2\text{m}$ for 60% of Ni which is a power factor comparable with bulk bismuth telluride alloy [124]. Nevertheless, these alloys are associated with low magneto-thermopowers so that the gaps between the spin-dependent Seebeck coefficients $S_{\uparrow} - S_{\downarrow}$ have been evaluated only around $-7 \mu\text{V/K}$.

The transport properties of $\text{Ni}_{80}\text{Fe}_{20}$ has been proven quite different. This sample has shown a significant GMR ratio of 20% at room-temperature rising up to 60% at 15 K. Moreover, it has demonstrated a very large thermopower spin-dependence with magneto-thermopower evaluated at 26% and 60% respectively at room-temperature and 70 K. This comes from large spin-dependent Seebeck coefficient $S_{\uparrow} - S_{\downarrow}$ reaching $-12.4 \mu\text{V/K}$ at room-temperature outperforming three times recent values found in permalloy nanopillars [123]. Finally $\text{Ni}_{93}\text{Fe}_7$ has displayed quite small magnetoresistance values together with difficulties to be magnetically saturated below the room-temperature. This may originate from important inhomogeneities in the microstructure. Consequently, the magnetoresistance values under 300 K are slightly underestimated. On the opposite, this alloy exhibits attractive magneto-Seebeck effect at room-temperature with an interesting opening of the curve representing the spin-dependent gap. Measurements of $S_{\uparrow} - S_{\downarrow}$ equal to $-13.6 \mu\text{V/K}$ have been achieved at room temperature while a spectacular value of $-17.2 \mu\text{V/K}$ has been reached for a temperature of 320 K. Besides, to switch from an antiparallel arrangement of the magnetic layers to a parallel configuration the system only requires an external magnetic field of around 2 kOe making it quite sensitive.

The main application of these particular transport properties consist in the production of a macroscopic active cooling device made of interconnected nanowire networks embedded into a polymer membranes as illustrated in Figure 3.14. The units of this flexible system are legs made of n-type and p-type material merging their effect to produce a larger cooling. Moreover, these thermoelectric legs can be gathered and connected electrically in series and thermally in parallel to improve their efficiency. The material choice is a key point to obtain a powerful cooling and factors such as high power factors and high thermal conductivity are essential. Currently, homogeneous crossed nanowires of Co (n-type) and Fe (p-type) have been selected (with power factor values of respectively $11 \text{ mW/K}^2\text{m}$ and $2 \text{ mW/K}^2\text{m}$ as well as thermal conductivity of 100 W/Km and 60 W/Km). A previous study has demonstrated an heat evacuation 10 times larger compared to passive cooling with $\Delta T = 1 \text{ K}$ [21] which opens the possibility to embed such p-n junctions inside electronic circuits to cool down the components. Moreover, given the recent results it could be considered to replace the homogeneous n-type material by a nickel-iron/copper interconnected multilayered nanowire network ensuring an additional magnetic control over the cooling power. Thus, the application of a small magnetic field could locally drive the cooling of large electronic devices without any contacts. As there is no sample size limitation, networks could be easily extended into larger dimensions. Finally, these networks could also find attractive applications in power generation for wireless sensors and wearable electronic devices [125–127].

The future will then be dedicated to the improvement of the transport properties within this unique architecture aiming to further develop the Peltier active cooling or to emerge on new innovative applications. In this purpose the challenge is to combine the large

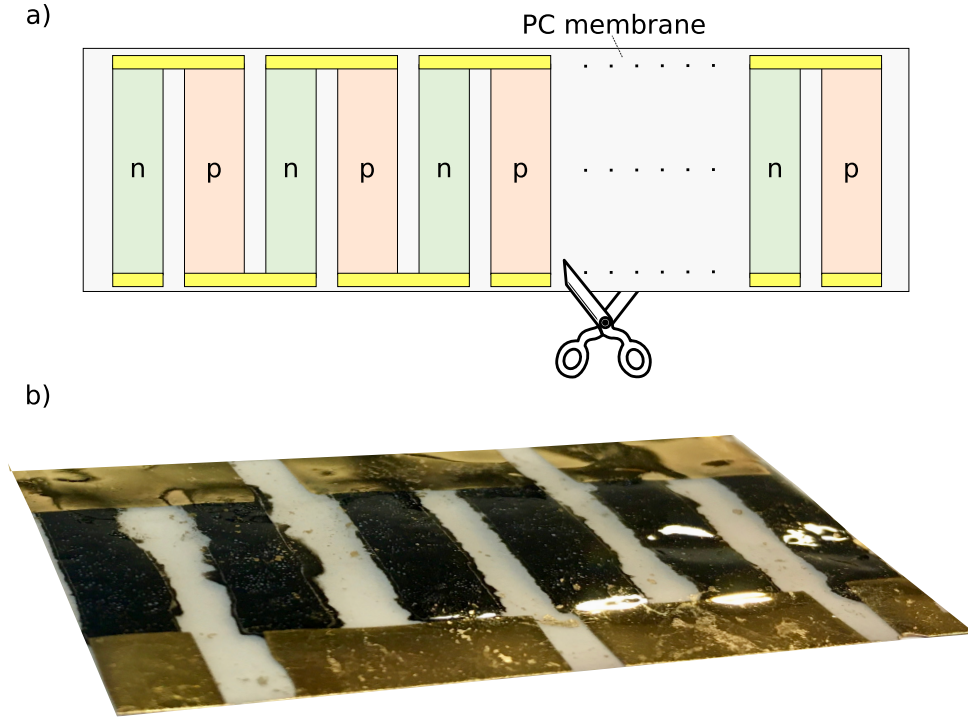


Figure 3.14: Active Peltier cooling with (a) schematic p-n junction architecture, and (b) an experimental p-n junction with 6 legs made of 3D interconnected nanowires network. Adapted from [21]

magnetic control arising from the multilayers while continuing to enhance the power factors and thermal conductivity which has been revealed satisfactory for homogeneous nanowire networks. $\text{Ni}_{93}\text{Fe}_7$ could be a potential candidate, however, theory suggests than the properties could be even greater for a further Ni enrichment. Indeed, nickel dilute alloy could exhibit an opposite sign of spin-up and spin-down Seebeck coefficient due to the strong derivative difference in the density of states resulting in a tremendous gap [75]. The idea to fabricate samples with a composition approaching the pure Ni is exciting but challenging since high quality multilayered nanowires are difficult to deposit for this Ni concentration. Moreover to be efficient, the network needs to maintain a sufficiently large Seebeck coefficient. Despite these difficulties, $\text{Ni}_{93}\text{Fe}_7$ sample has confirmed the good direction taken and allows to maintain good hopes in regards of this highly rich nickel sample and then on the realization of a cost-effective, viable, and efficient active cooling. Among the avenues for future researches, the fabrication of pure bismuth or bismuth-telluride alloys nanowires is considered. Although the bismuth is an heavy metals, no human body harmful effects have been demonstrated so far [128]. This alloy has the particularity to show a transition from a p-type to a n-type material as a result of high-energy ball milling [129]. Moreover, it has already been revealed successful for the electrodeposition of nanowires [130]. In particular, previous results have reported Seebeck coefficient values of $260 \mu\text{V/K}$ for $\text{Bi}_{46}\text{Te}_{54}$, meaning 60% greater than for the bulk value [131]. Besides, it has been shown that bismuth could also display important MTP in the range of 20% at room-temperature [132], it could be interesting to investigate if the incorporation of Te would alter this ratio. Finally the only drawbacks could be ascribed to the very bad thermal and electrical conductivity of this material.

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