PART II
THE NANOSTUCTURES
This chapter is dedicated to the study of FePt and Co nanostructures synthesized through colloidal crystal masks.

The morphology (SEM/AFM) of the dots is first discussed, followed by a crystallographic analysis (XRD) of the samples.

Finally, the magnetic properties are studied, both from a qualitative (MFM) and quantitative (SQUID/MOKE) points of view.
CHAPTER IV - Magnetic nanostructures

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1. Introduction

In recent years, patterned magnetic structures have attracted a huge interest due to their potential applications in many technological fields, such as magnetic information storage or non-volatile magnetic random access memory (MRAM). Indeed, the never-ending race towards miniaturization logically requires the storage of data in an ever-decreasing space, increasing therefore the recording density.

Although the components of a magnetic hard disk are multiple (read head, write head, etc.), this chapter focuses on the implementation and study of nanostructures fabricated by NSL, which could be used as magnetic recording media. In a first step, let us consider some issues and consequences of the shaping of ferromagnetic compounds at the nanoscale.

1.1 Bulk material or isolated magnetic particles... A difference?

Ferromagnetic materials exhibit a long-range ordering phenomenon at the atomic level, which causes the atomic magnetic moments to line up parallel with each other in a restricted region called a domain. Within the domain, the magnetization is intense, but in a bulk sample the material will usually be demagnetized because many domains will be randomly oriented with respect to each other.

When a magnetic field is applied (Figure IV - 1), the magnetization of the material increases until saturation ($M_s$). This process takes place in two different ways: (1) the growth of domains which are already aligned with field by shifting their walls, and (2) the coherent rotation of the domains to a direction parallel with the magnetic field. When the magnetic field is removed, a remnant magnetization ($M_r$) is maintained.

The magnetization will only relax back to zero under the application of a reverse magnetic field, called coercive field\(^*\) ($H_c$) and will reach saturation in the opposite direction ($-M_s$) by further increasing the field.

The full cycle of magnetization is obtained by changing the direction of the applied magnetic field and is complete when reaching again saturation.

The lack of retraceability in the magnetization curve is the property called hysteresis and is related to the existence of magnetic domains in the material. Once the magnetic domains are oriented, it takes some energy to turn them back again. A ferromagnetic material can possess a well-defined axis (the easy-axis) along which its magnetic moments will preferably align.

\* The coercive field, also called coercivity, of a ferromagnetic material is the intensity of the applied magnetic field required to reduce the magnetization of that material to zero after the magnetization of the sample has been driven to saturation. Coercivity is usually measured in oersted (Oe) or ampere/meter (A/m) units. However, due to a misuse of language, it is sometimes expressed in tesla (T), which is the unit of the magnetic induction B.
Several books\cite{1} may inform the reader seeking additional information on the basics of magnetism.

![Magnetization versus field (M-H loop) for a ferromagnetic material\cite{2}](image)

To begin, let us consider an unmagnetized sample (point 0).

(a) As the magnetic field strength is increased in the positive direction, the magnetization follows a non-linear magnetization curve (initial magnetization curve) and reaches the saturation level \((M_s)\), when all the magnetic domains are aligned with the direction of the field;

(b) If the magnetic field is relaxed to zero, the ferromagnetic material retains a degree of magnetization \((M_r)\);

(c) In order to drive the magnetization back to zero, the applied magnetic field must be reversed \((-H_i)\);

(d) If the reversed magnetic field is further increased, the saturation level in the opposite direction is reached;

(e) Reducing \(H\) to zero brings the sample to a level of residual magnetism equal to that achieved in point (b) but in the opposite direction \((-M_r)\);

(f) A magnetic field equal to the coercive field \((H_c)\) is needed to remove the magnetization.

The parameters described above \((H_o, M_s, M_r)\) play a major role in the selection of materials to be used in magnetic information storage. When the easy-axis is well defined (large remnant magnetization along the easy-axis in the absence of applied field) and if the field necessary to reverse the magnetic moment is large enough, the material will be called a permanent magnet and can be used to store information. Indeed, data is stored in the media based on the two stable magnetic configurations corresponding to \(M_r\) and \(-M_r\).

The stability of the media can be evaluated on the basis of the magnetic anisotropy of the used material. The anisotropy energy describes the amount of energy required to reverse the magnetization from one stable state to the other. This depends on several factors, most importantly the effective anisotropy constant \((K)\). The magnetic anisotropy is positively correlated with the coercivity, which is often used to provide a qualitative estimate of anisotropy of the material. The magnetic hardness parameter \((\kappa)\) is often used to classify materials by measuring the relative importance of anisotropy compared with magnetostatic effects.
Two main cases are apparent: magnetically soft samples, with a hardness parameter $\kappa \ll 1$, and magnetically hard samples, with larger values of $\kappa$.

$$\kappa = \frac{2K}{\mu_0 M_S^2} \quad \text{(Equation IV - 1)}$$

Parallel to the research on materials is the intense development of new-shaped structures such as magnetic nanoparticles as candidates for the media of future magnetic data storage systems. As illustrated in Figure IV - 1, bulk magnets are composed of many domains that form in an effort to minimize the magnetostatic energy of the material. The magnetostatic energy can further be reduced through the formation of closure domains, where the magnetization has a direction approximately parallel to the surface of the sample. A scheme of a simplified domain configuration is shown in Figure IV - 2.

![Figure IV - 2](image)

Simplified scheme of magnetic domain configuration in (a) Multi-domain and (b) single-domain particles.[3]

By reducing the particle size to the nanoscale, the transition from multi-domain to single-domain is reached, as the energy required to make a domain wall is larger than the decrease in magnetostatic energy resulting from dividing the grain into two domains.

Like bulk ferromagnets, an array of single-domain magnetic nanoparticles can exhibit hysteresis in the M-H loop. However, the main difference between a bulk magnetic material and an array of magnetic nanoparticles lies in the mechanism by which the magnetization is cycled through the hysteresis loop. In a single-domain nanoparticle, domain wall movement is not possible and only coherent magnetization rotation can be used to overcome the effective anisotropy ($K$) of the particle. The behavior of uniformly magnetized, non-interacting single-domain particles was identified by Stoner & Wohlfarth.[4]

In the case of soft magnetic particles, a vortex arrangement of magnetic moments is favored in between the single- and multi-domain regimes. This type of magnetic domain will be further detailed with the study of Co nanostructures in section 3.3.2.

For particles of hard material, the vortex-domain state isn’t favored for any range of diameters. These magnetic domains are illustrated in Figure IV - 3.
The importance of particle size to its magnetic behavior becomes very apparent when one considers the coercivity as a function of particle size as shown in Figure IV - 4. Generally, a single-domain state is associated with a higher coercivity than the multi-domain state.

![Figure IV - 3](image)

Possible magnetic domains in a spherical magnetic particle
(a) Single-domain particle; (b) Multi-domain particle; (c) Vortex-domain particle.

![Figure IV - 4](image)

Schematic evolution of magnetic coercivity with size of particle, highlighting four regimes: (a) superparamagnetic (SPM) regime with 0<Diameter<D_{SPM}; (b) ferromagnetic single-domain particle with D_{SPM}<Diameter<D_0; (c) vortex-domain state for D_0<Diameter<D_1 (only for soft magnetic materials) and (d) multi-domain state for Diameter>D_1.

Taking into account only two possible spin arrangements, single-domain and two domains separated by a domain wall, the single-domain critical diameter ($D_{cr}^{SD}$) between these two regimes for a spherical particle is given by the following expression.

$$D_{cr}^{SD} = \frac{72 \sqrt{\mathcal{K}}}{\mu_0 M_s^2}$$

(Equation IV - 2)
In this expression, $A$ is the exchange stiffness constant, $K$ is the anisotropy constant, $M_s$ is the saturation magnetization and $\mu_0$ is the vacuum magnetic permeability.

For most magnetic materials, this diameter is in the range of 10-100 nm. However, the limit can reach several hundred nanometers for high-anisotropy materials.\[^5\]

However, if nothing is mentioned about the hardness of the material, the vortex state has to be considered. Brown has developed expressions for the critical diameters between the different regimes. The following equations report for the calculations of $D_0$ and $D_1$ mentioned in Figure IV - 4. $D_0$ represents the upper-limit of the single-domain configuration, while the critical diameter for a transition from vortex to multi-domain for a soft-magnetic material is given by $D_1$.

\[
D_0 = 7.211 \frac{2A}{\mu_0 M_s^2} \quad \text{(Equation IV - 3)}
\]

\[
D_1 = \frac{9.0584 \frac{2A}{\mu_0 M_s^2}}{1 - 2.8075 \frac{2K}{\mu_0 M_s^2}} \quad \text{(Equation IV - 4)}
\]

One should note that the values of the parameters that appear in the literature present a wide dispersion, reflecting the experimental uncertainty of some magnetic quantities, for example, in the estimate of the exchange stiffness constant $A$. Moreover, those models are based on spherical particles, which can explain the difference in case of particles with other shapes. However, it is obvious that the critical single-domain diameter increases with anisotropy (Figure IV - 5).

\[^5\] The *exchange constant* ($A$) describes the strength of the exchange interaction inside a ferromagnetic system. In solids, the electronic orbitals of neighboring atoms overlap, which leads to the correlation of electrons. This results in the interatomic exchange interaction that makes the total energy of the crystal depend on the relative orientation of spins localized on neighboring atoms. The exchange interaction is the largest magnetic interaction in solids ($\approx 1 \text{eV}$) and is responsible for the existence of parallel, i.e. ferromagnetic, and antiparallel, i.e. antiferromagnetic, spin alignment.
As the particle diameter further decreases, loss of data due to thermal instability (superparamagnetic effect) may arise. Superparamagnetism refers to the influence of thermal energy on a ferromagnetic nanoparticle. In the superparamagnetic size regime the moments of the nanoparticle fluctuate due to thermal energy. This fluctuation tends to randomize the moments of the nanoparticle unless a magnetic field is applied.

Considering an uniaxial single-domain magnetic particle, the two states of magnetization are separated from each other by an energy barrier, $K_V$, where $K$ and $V$ stand respectively for the anisotropy constant of the material and the particle volume. If the thermal energy, $k_B T$, becomes comparable to the barrier height, the magnetization is no longer stable and the particle is said to be superparamagnetic. This thermally activated switching follows the Arrhenius-Neel equation (Equation IV - 5) where $f$ is the frequency of switching between magnetization states, $\tau$ is the relaxation time and $f_0$ is the proportionality constant equal to $10^{-9}$ s$^{-1}$.

$$f = \frac{1}{\tau} = f_0 e^{\frac{KV}{k_B T}}$$

(Equation IV - 5)

By fixing $\tau$ to 100 s (which is roughly the time to measure the remanence of a sample), the superparamagnetic critical volume can be obtained ($V_{cr}^{SPM} = (25k_B T)/K$) and used to calculate the superparamagnetic critical diameter (Equation IV - 6).

$$D_{cr}^{SPM} = \left(\frac{6}{\pi} V_{cr}^{SPM}\right)^{1/3}$$

(Equation IV - 6)

Table IV - 1 gives some values of the single-domain critical diameter ($D_{cr}^{SD}$) and the superparamagnetic critical diameter for different spherical particles.

<table>
<thead>
<tr>
<th>Material</th>
<th>$D_{cr}^{SD}$ (nm)</th>
<th>$D_{cr}^{SPM}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>Fe</td>
<td>19</td>
<td>16</td>
</tr>
<tr>
<td>Ni</td>
<td>54</td>
<td>35</td>
</tr>
<tr>
<td>Co</td>
<td>96</td>
<td>8</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
<td>21</td>
<td>4</td>
</tr>
<tr>
<td>FePt</td>
<td>340</td>
<td>3</td>
</tr>
<tr>
<td>SmCo$_5$</td>
<td>1170</td>
<td>2</td>
</tr>
</tbody>
</table>

Moreover, the size and shape of a patterned thin film may also strongly influence its magnetic behavior.

Many methods can be used to synthesize magnetic structures from sub-micron scale to nanometer dimensions. Both top-down and bottom-up strategies have been reported in
the literature, forming either periodic structure (such as arrays of various shaped elements) or isolated single nanodots.

Due to the small size of the nanostructures, their magnetic characterization is not easy to perform and do require sensitive methods.

Among those materials, Co and FePt will be further studied through this thesis.

### 1.2. Studied Materials

#### 1.2.1 FePt

*Crystallographic structures and phase diagram of Fe-Pt alloys*

Recent reviews\(^6\), \(^7\), focused on the present reality and evolution of magnetic data storage, clearly highlighted that one of the most promising candidates for high-density magnetic recording was the face-centered tetragonal (fct) L1\(_0\) phase of FePt. For most applications, a permanent magnet should have not only optimised magnetic properties, but also appropriate nonmagnetic properties (electrical, mechanical, corrosion behavior etc.).

Modern permanent magnet materials are based on intermetallic compounds of rare earths and 3\(d\) transition metals with very high magnetocrystalline anisotropy, such as \(\text{Nd}_2\text{Fe}_{14}\text{B}\) and \(\text{SmCo}_5\). Distinct advantages of Fe-Pt alloys are, as opposed to the rare-earth-transition-metal-based compounds, that they are very ductile and chemically inert.\(^9\) Since the mid-1930s,\(^11\) Fe-Pt alloys are known to exhibit high coercivities due to high magnetocrystalline anisotropy of the L1\(_0\) FePt phase, but the high price prevented widespread applications of these alloys.

Depending on the Fe to Pt elemental ratio, iron-platinum alloys can display chemically disordered\(^\dagger\) face centered cubic (fcc) phase (A1, \(\text{Fm\dot{3}m}\)) or chemically ordered phases, such as (L1\(_2\), \(\text{Pm\dot{3}m}\)) for \(\text{Fe}_3\text{Pt}\), face centered tetragonal (fct) phase (L1\(_0\), \(\text{P4/mmm}\)) for FePt and (L1\(_2\), \(\text{Pm\dot{3}m}\)) for Pt\(_3\)Fe. The L1\(_2\) structure is a cubic phase that can form around a 1:3 stoichiometry. In \(\text{Fe}_3\text{Pt}\) (FePt\(_3\)), the Pt (Fe) atoms occupy the cube corners and the Fe (Pt) atoms occupy the face-centre positions.

The structure variations (Figure IV - 6) have dramatic effects on the magnetic properties of the alloys. For example, the \(\text{Fe}_3\text{Pt}\) material is paramagnetic, the FePt\(_3\) is antiferromagnetic, the FePt (A1) phase presents a very small magnetic anisotropy and displays soft magnetic properties while the FePt (L1\(_0\)) phase, which is made of an alternate stacking of Fe and Pt planes, has a large uniaxial magnetocrystalline anisotropy\(^{12}\) (\(K \approx 7 \times 10^6 \text{ J/m}^3\)) and shows strong ferromagnetic properties.

\(^\dagger\) Chemically *disordered* (versus chemically *ordered*) indicates that any atomic site in the unit cell has an equal chance of being occupied either by iron or platinum atom.
According to the Fe-Pt phase diagram (Figure IV - 7), an A1 solid solution (γ-Fe,Pt) is observed at high temperatures over the whole range of composition. At temperatures below 1300 °C, alloys close to the equiatomic concentration exhibit a disorder-order transition from the disordered A1 structure to the tetragonal L1₀ structure.

This phase change from cubic to tetragonal structure results in the breaking of the high symmetry of the cubic structure to the lower symmetry tetragonal structure, causing a preferential magnetic alignment along the c-axis.\textsuperscript{[14]}
The large anisotropy is caused by Fe and Pt interactions originating from spin-orbit coupling and the hybridization between Fe 3d and Pt 5d states. These Fe–Pt interactions further render the FePt nanoparticles chemically much more stable than the common high-moment nanoparticles of Co and Fe.[13]

The existence region of the L1₀ structure extends from approximately 35 to 55 atomic percent Pt. In Fe_{100-x}Ptₙ alloys deviating from the 35 ≤ x ≤ 55 stoichiometry, formation of the stable cubic superstructures Fe₃Pt (L1₂) and FePt₃ (L1₂) is expected at temperatures below 835 °C and 1350 °C, respectively.

**Synthesis of FePt nanoparticles**

Large-scale production of FePt-L1₀ nanoparticles is still a challenge. As we previously mentioned, the FePt-L1₀ is one of a relatively rare class of materials that have sufficient magnetocrystalline anisotropy to remain magnetically stable at room temperature with diameters of less than 4 nm.[6]

However, the use of FePt nanoparticles as a recording medium presents significant problems many of which remain to be overcome. Finding solutions to the difficulties associated with FePt nanoparticles manufacturing is an active area of research.

Currently, L1₀-FePt patterned nanostructures can be produced either by self-assembly of FePt nanoparticles[16] prepared by reduction of metal salts[17] and/or thermal decomposition of organometallic precursors[18] (solution chemistry) or by patterning FePt films using conventional expensive lithography techniques, such as electron beam-lithography[19] (Chapter I). Other methods for preparing patterned media for high-density recording are presented in Ref. [20]. However none of these methods can yet fulfill the requirement the manufacturing of low-cost and high throughput.

Solution based chemical synthesis of FePt nanoparticles has many advantages including low-cost and narrow size distribution. The as-obtained particles are deposited onto a substrate by dip- or spin coating and are in a disordered fcc crystallographic phase. To use these materials as a recording medium the crystallographic phase must be converted to the high anisotropy L1₀ phase by an annealing treatment. However, temperatures up to 600°C are required before any significant phase transformation occurs and this leads to particle agglomeration and sintering. Subsequent progress in preventing particle aggregation was made by embedding the particles in a nonmagnetic matrix such as SiO₂ or Al₂O₃ but it is difficult to form arrays in this manner. Coating the particles with larger molecules such as polymers[21] or surfactants[22] containing long chain hydrocarbon, offers more efficient stabilization.

Furthermore, the functionalization of the substrate may work under appropriate conditions to form self-assembled layers. The research group of Prof. Sun is one the leading laboratories in the chemical synthesis and self-assembly of nanomagnets.[13, 14, 16, 23-25]
Although some papers have reported high-temperature annealing of FePt arrays with low visible aggregation, the magnetization dynamics of the particles have likely changed leading to particles that are no longer isolated.\[26\] Furthermore, the fine control over interparticle spacing, which is necessary for patterned media to be integrated into a hard disk design, is lost due to particle motion during annealing. These results seem to suggest that, for the self-assembled FePt nanoparticles, the temperature window for forming the desired L1\textsubscript{0} phase without significant particle aggregation is quite narrow.

The use of nanosphere lithography appeared to be obvious thanks to combining high efficiency associated with lithography in the top-down approach and low cost associated with the self-assembly in the bottom-up approach.

### 1.2.2 Co

Besides the study of such hard magnetic materials, the study of pure ferromagnetic elements (Co, Fe, Ni) is important to better understand the magnetic properties of such complex systems.

Co is a well-known ferromagnetic material, which is commonly used as an alloying element in permanent magnets. It exists in two forms (Figure IV - 8): hcp (hexagonal close-packed) and fcc (face-centered cubic). The hcp phase is the stable phase at room temperature, whereas fcc is stable at temperatures above 450 °C.\[27, 28\]

In a hexagonal close-packed (HCP) arrangement of atoms, the unit cell consists of three layers of atoms. The top and bottom layers contain six atoms at the corners of hexagon and one atom at the center of each hexagon. The middle layer contains three atoms nestled between the atoms of the top and the bottom layers, hence the name close-packed. Face-centered cubic structure is an arrangement of atoms in which the unit cell consists of eight atoms at the corners of a cube and one atom at the center of each of the six faces of the cube.

Figure IV - 8
Primary Metallic Crystalline Structures. (a) The face-centered cubic structure and (b) the hexagonal close-packed structure.\[29\]

Among the various kinds of metal nanoparticles, cobalt nanoparticles are of considerable interest due to their magnetic and catalytic properties.\[30\]
Indeed, Co particles display a wide range of interesting size-dependent structural, electrical, magnetic, and catalytic properties.[31] In particular, because of their large surface area, Co nanoparticles showed high chemical reactivity, which makes them suitable for catalysis.[32]

Future applications of Co nanoparticles in the fields of separation technology, catalysis, magnetic recording media and information storage systems[33-35] require the nanoparticles to be discrete, identical in size and shape, and uniform in composition and crystal structure.[36] However, formation of nanoparticles satisfying these requirements prove to be difficult due to their high surface energy, their intrinsic magnetic properties, and the inherent limitations of the available processes. In addition, there are also concerns regarding the reproducibility of the existing methods.

Moreover, cobalt nanoparticles can easily be oxidized upon exposure to air.[37] Cobalt oxide shows antiferromagnetic properties, which are not favorable. Therefore, besides shape control, another important concern in synthesis of cobalt nanostructures is the stability of these particles.

As for the synthesis of FePt nanoparticles, liquid-phase synthetic routes are used in the preparation of monodispersed Co nanoparticles. Examples of liquid-phase processes are metal salt reduction, reverse micelles, and thermal decomposition of organometallic precursor. Among these methods, direct metal salt reduction in solution is the simplest, fastest, and the least expensive, which are desirable for future attempts of large-scale production. However, in some cases, agglomeration of nanoparticles still occurred even in the presence of protective agents.[38]

In literature, cobalt nanostructures have been prepared by a variety of methods including, electron beam lithography,[39, 40] X-Ray lithography,[41] scanning probes techniques,[42] focused-electron-beam-induced deposition.[43]

Recently, Imperia et al.[44] reported the manufacturing of Co nanostructures by nanosphere lithography with polystyrene particles of 1710 nm diameter assembled with a methodology related to the preparation of Langmuir-Blodgett films. By reducing the size of the polystyrene nanospheres, we propose to reduce the size of the manufactured nanodots.

2. Experimental part

2.1 Colloidal mask preparation

Monodisperse PS nanospheres with a mean diameter of 490 nm and 250 nm were purchased from Bangs Laboratory as suspensions in water (concentration of about 10 % wt) in order to prepare single-layer colloidal crystal masks. Both masks were used to synthesize FePt nanostructures, while Co nanostructures have only been fabricated through the 490nm-PS masks. Before deposition, the aqueous nanospheres suspensions
were diluted ten times in a surfactant Triton X-100/MeOH mixture (1:400 by volume) and filtered through centrifugal filter units (porosity 0.65 μm) in order to eliminate aggregates of higher dimensions, which would disturb the formation of the monolayer. Suspensions were then vortexed during 2 minutes to ensure homogeneity.

Previous to spheres deposition, square (5x5 mm) quartz substrates (Crystal Gmbh) were treated to obtain a clean and hydrophilic surface. Each of them was separately cleaned by immersing in a piranha solution (1:3 30% H₂O₂/H₂SO₄) and sonicated for 1h. The substrates were rinsed repeatedly with ultrapure water (18.2 MΩ, Millipore Simplicity) and then sonicated for 1h in 5:1:1 H₂O (Milli-Q)/NH₄OH/30% H₂O₂. Finally, the substrates were copiously rinsed with water and stored in water until used. Before deposition, the substrates were flash-air dried at room temperature.

A 5 μL drop of the suspension was dispensed on the substrate with an Eppendorf pipette and led to instant wetting of the whole substrate surface. All the samples were prepared with the same spin-coating parameters (experiment 2 - Chapter III), characterized by a high rotation speed reached in a short time. The samples were accelerated to 1930 rpm (acceleration rate 643 rpm/s) for 2s and then spun at 2500 rpm (acceleration rate 190 rpm/s) for another 2s, followed by final spin at 6900 rpm (acceleration rate 1467 rpm/s) for 2s.

To remove the surfactant between the nanospheres (Chapter III - Section 3.3), all samples were submitted to an O₂ ion beam etching step during 30 s (P=300 W / O₂ flow = 50 sccm).

### 2.2 Deposition of nanodots & characterization

Metal films were deposited onto the nanosphere templates by Rf magnetron sputtering using an ultrahigh vacuum sputtering system (base pressure 2x10⁻⁶ mbar). All samples were kept rotating during deposition for getting uniform deposition on substrate.

A FePt composite target consisting of a platinum (99.99% - GoodFellow) disk overlaid with an open disk of iron (99.99% - GoodFellow) was used to sputter FePt films. The composition of the deposited alloy was determined by Energy Dispersive X-Ray Spectroscopy and was tuned by modulating the distance between the substrate and the target. The target-substrate distance was fixed at 15 cm to obtain equiatomic Fe₅₀Pt₅₀ alloys. The deposition rate was 3.3 nm per minute.

A cobalt target (99.99 % - GoodFellow) was used for the deposition of Co films. The target-substrate distance was fixed at 5 cm and the deposition rate was 16.08 nm per minute.

The deposition rates were calculated by measuring the thickness of films, corresponding to various deposition times, using a Dektak profilometer and AFM. Both methods were in good agreement.
To remove contaminants from the targets, pre-sputtering was done (20 W for 5 min) during which the substrates were kept away from the deposition zone. The sputtering pressure of high purity Ar gas was set at 5 mTorr, while the sputtering power was fixed at 40 W during deposition.

Four different deposition times were tested to evaluate the impact on the morphology of the FePt nanodots.

Removal of the polystyrene nanospheres was carried out by sonication twice in toluene for 1 min. The samples were rinsed with ethanol and finally flush-air dried.

In order to induce the formation of the desired L1₀-FePt hard magnetic phase, an annealing step was performed in a tubular furnace under Ar/H₂ (95/5 %) flow to prevent any oxidation of the samples. The evolution of crystal structure with annealing temperature and annealing time was investigated by grazing incident small angle x-ray diffraction (D8 Bruker).

Room-temperature quantitative magnetic characterizations were performed in a superconducting quantum interference device SQUID from Quantum Design. Both in-and out-of-plane hysteresis loops were measured. However, given the presence of defects (e.g. vacancies, dislocations or large uncovered areas) in the polystyrene template, each sample was composed of a mixture of thin film and nanodot areas.

The SQUID analysis delivered information about averaged magnetization from the whole sample. Therefore the use of local techniques such as focused-Moke was required. The Magneto-Optic Kerr Effect (MOKE) is the study of the reflection of polarized light by a material sample subjected to a magnetic field. This reflection can produce several effects, including 1) rotation of the direction of polarization of the light, 2) introduction of ellipticity in the reflected beam and 3) a change in the intensity of the reflected beam. The measured change in polarization is proportional to the magnetization of the material. More information about MOKE can be found in Ref. [45].

In order to highlight the patterning effect on the magnetic properties, both MOKE and SQUID hysteresis loops were measured from continuous thin films. All measurements were performed at room temperature.

Moke measurements on the FePt samples were carried out in the Paris Nanoscience Institute (Team “Nanostructures and Quantum devices” - Dr Catherine Gourdon). Magneto-optical images were obtained by Kerr microscopy. The optical setup was similar to a reflection polarizing microscope. Due to the high magnetic field required, most of all the magnetic components of the equipment were manufactured in non-magnetic material. The magnetic field was applied in a perpendicular way to the sample surface and the MOKE signal is therefore proportional to the perpendicular component of the sample magnetization. The samples were illuminated with light from a halogen lamp filtered at 632 nm. The detection system was a charge-coupled device CCD camera.
The spatial resolution was about one micron, which is far small enough to focus on homogeneous nanodots area. We performed data acquisition in field cycles, starting from high fields. Thanks to an automated procedure, images were taken after each field increment. The procedure to obtain the hysteresis cycles will be described in section 3.3.1.

Co samples were analyzed in the University of York (Department of Physics - Dr Jing Wu). In this case, the high resolution focused MOKE magnetometer consisted of a stabilized 5mW continuous HeNe laser of 635 nm wavelengths, a stack of focusing lenses. The focused laser spot size was measured to be 1μm in diameter. Measurements were performed in the longitudinal geometry, in which the incident laser beam is almost parallel to the sample surface and the Kerr effect is proportional to the in-plane magnetic moment.

The morphology and magnetic microstructure of the samples were examined by atomic force microscopy (AFM) and magnetic force microscopy (MFM) under ambient conditions using a Digital Instruments Nanoscope III microscope (Veeco).

The image acquisition was performed in tapping-lift mode with a high-resolution magnetic probe tip coated by Co-alloy (Team-Nanotech). This mode allows the sample topography to be separated from the magnetic structure; two passes are made over each scan line. In the first pass, the MFM cantilever is oscillated near its resonant frequency very close to the sample so that it lightly taps the surface. The oscillation amplitude is used as the feedback signal. The second pass is made with the feedback turned off and the computer repeating the topographic motion recorded during the first pass plus an added vertical offset. During this second pass the oscillation amplitude and phase of the cantilever can be monitored. The low moment of the tips as well as a tip-sample separation minimized distortions during imaging.

3. Results and discussion

The morphology (SEM/AFM) of the dots is first discussed, followed by a crystallographic analysis (XRD) of the samples. Finally, the magnetic properties are studied, both from a qualitative (MFM) and quantitative (SQUID/MOKE) points of view.

3.1 Morphological study of the nanodots

We will first talk about the FePt nanodots and the impact of the annealing treatment on their shape and size.

We then compare them with the Co nanodots.

Finally, we discuss the presence of defects in the samples and what this implies for the magnetic characterizations.
3.1.1 FePt

Two different sizes of PS spheres (diameters of 490 nm and 250 nm) were chosen for mask fabrication. The masks will be further referred as “PS 490 nm mask” and “PS 250 nm mask”.

As expected, the perpendicular evaporation through the 2D HCP polystyrene masks resulted in the formation of triangular nanoparticles.

SEM micrographs of the nanodots obtained with both masks are presented in Figure IV - 9 (a) and Figure IV - 10 (a). The samples were annealed during 2h at 700°C to induce phase transition to the L1₀ phase. Corresponding SEM micrographs are presented in Figure IV - 9 (b) and Figure IV - 10 (b). Insets in these figures are a zoom on a six fold symmetric structure. The evolution of the nanodots shape following annealing is striking.

The annealing not only modifies the edges of the particles but also increases their height. However, the triangular shape seemed to be preserved in most cases, which
could also be evidenced with the tilted SEM micrographs in Figure IV-11 (PS 490 nm mask) and Figure IV-12 (PS 250 nm mask).

Figure IV - 11
Tilted (30°) SEM micrograph of Fe₅₀Pt₅₀ nanodots synthesized through a PS 490 nm mask.
Scale bar is 1 μm.

Figure IV - 12
Tilted (30°) SEM micrograph of Fe₅₀Pt₅₀ nanodots synthesized through a PS 250 nm mask.
Scale bar is 1 μm.

Figure IV - 13 and Figure IV - 14 show 2D and 3D AFM views of Fe₅₀Pt₅₀ arrays of nanoparticles evaporated respectively through the PS 490 nm mask and the PS 250 nm mask, before and after annealing treatment.

In the not annealed samples (Figure IV - 13 (a) and Figure IV - 14 (a)), some polystyrene ring-like residues were found in the area of contact between the nanospheres and the substrate. They were attributed to incomplete lift-off process and can be removed by additional cleaning step. Due to the small amount of material, those residues could hardly be detected in secondary electron (SE) SEM mode.

Moreover, their low atomic numbers annihilated any chance of getting a usable phase contrast in back-scattered electron (BSE) SEM mode.
AFM micrographs of (a) as-obtained Fe$_{50}$Pt$_{50}$ nanostructure, manufactured through the PS 490 nm mask, showing the presence of PS residue in-between triangular nanoparticles and (b) annealed sample (2h - 700°C).

2D (resp. 3D) views are shown on left (resp. right) sides. Scale bars in 2D view are 1 μm.
AFM micrographs of (a) as-obtained Fe50Pt50 nanostructure, manufactured through the PS 250 nm mask, showing the presence of PS residue in-between triangular nanoparticles and (b) Annealed (2h - 700°C) sample. 2D (resp. 3D) views are shown on left (resp. right) sides. Scale bars in 2D view are 1 μm.
The maximum size of the structures (Figure IV - 15) obtained by nanosphere lithography is spatially limited by the aperture size between the nanospheres. Moreover, the amount of space between the spheres is decreasing progressively, due to deposition of incoming material on the edges of the aperture.

![Figure IV - 15](image)

Evolution of (a) the aperture size (black) between the nanospheres (white) during deposition (top-view) and (b) the corresponding out-of-plane height (H_{OP}) showing increasing thickness (T).[47]

Four deposition times were tested on the PS 490 nm mask: 20 min, 40 min, 60 min & 100 min corresponding respectively to thicknesses of 75 ± 5 nm, 135 ± 5 nm, 223 ± 5 nm & 345 ± 5 nm. Only one deposition time was tested on the PS 250 nm mask. Out of plane heights (H_{OP}) on both as-deposited and annealed nanodots were measured by AFM and are listed in Table IV - 2.

<table>
<thead>
<tr>
<th>Deposited thickness (nm)</th>
<th>H_{OP} As-deposited (nm)</th>
<th>H_{OP} Annealed (nm)</th>
<th>H_{OP} As-deposited (nm)</th>
<th>H_{OP} Annealed (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS 490 nm mask</td>
<td>75 ± 5</td>
<td>22 ± 2</td>
<td>30 ± 5</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>135 ± 5</td>
<td>25 ± 3</td>
<td>37 ± 5</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>223 ± 5</td>
<td>24 ± 4</td>
<td>35 ± 5</td>
<td>25 ± 3</td>
</tr>
<tr>
<td></td>
<td>345 ± 5</td>
<td>26 ± 5</td>
<td>36 ± 5</td>
<td>/</td>
</tr>
<tr>
<td>PS 250 nm mask</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

As predicted by the SEM micrographs (Figure IV - 9 & Figure IV - 10), the annealing treatment resulted in an increase in the out-of-plane height of the dots (≅ 24-35 %) prepared with both masks.
Regarding the evolution of the height with the deposited thickness (only for the PS 490 nm mask), it seems that the $H_{0P}$ is rather similar from one sample to another, no matter what the deposited thickness is. However, a very slight difference is evidenced for the smallest deposition time. AFM 3D views (Figure IV - 16) of the as-obtained nanodots do reveal a sharper profile for the longest deposition times, which reminds the evolution presented in Figure IV - 15 (b).

![Figure IV - 16](image)

3D AFM micrographs (with the same z-scale) of a sixfold Fe_{50}Pt_{50} nanostructure (before annealing) obtained after deposition thickness of: (a) 75 nm & (b) 223 nm through the PS 490 nm mask.

Based on geometric considerations\cite{48} (Figure IV - 17) the in-plane height ($H_{IP}$) and the lateral size ($L_S$) of the expected triangles were calculated with the following equations, which are demonstrated in appendix C.

![Figure IV - 17](image)

\begin{align}
    H_{IP} &= \frac{3D}{2} x \left( \sqrt{3} - 1 - \frac{1}{\sqrt{3}} \right) \\
    L_S &= \sqrt{\frac{4}{3} H_{IP}^2}
\end{align}

(Equation IV - 7)

(Equation IV - 8)
We measured lateral size of the triangles by SEM and used these values to deduce the in-plane heights. Table IV - 3 summarizes all these values.

<table>
<thead>
<tr>
<th></th>
<th>PS 490 nm mask</th>
<th>PS 250 nm mask</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lₜ</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated (nm)</td>
<td>131</td>
<td>67</td>
</tr>
<tr>
<td>Measured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-deposited (nm)</td>
<td>114 ± 3</td>
<td>65 ± 3</td>
</tr>
<tr>
<td>Measured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealed (nm)</td>
<td>123 ± 6</td>
<td>73 ± 3</td>
</tr>
<tr>
<td><strong>H_{IP}</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated (nm)</td>
<td>114</td>
<td>58</td>
</tr>
<tr>
<td>Measured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-deposited (nm)</td>
<td>99</td>
<td>56</td>
</tr>
<tr>
<td>Measured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealed (nm)</td>
<td>106</td>
<td>63</td>
</tr>
</tbody>
</table>

Obviously, calculated values should only be compared with the *as-deposited* measured values. Indeed, as it was already reported in Table IV - 2, the annealing treatment induced an increase in the out-of-plane dot size. In-plane dot size also increases but in a lesser extent (≈ 8 -12 %). This could be due to a pinning effect that hinders the lateral expansion of the dots.

For the PS 250 nm mask, the calculated data and the *as-deposited* measured values agree, while for the PS 490 nm mask the calculated values were above the measured ones.

As depicted in Figure IV - 17, the size of the dots is highly dependent on the aperture size between the nanospheres, which is directly related to the contact area between the spheres in the mask. Annealing (heating-plate, microwave irradiation etc.) or plasma etching (Chapter III) are means to modify the shape of the masks.

Both *PS 490 nm mask* and *PS 250 nm mask* were submitted to the same O₂ plasma-etching step during 30 s. Consequently, it could be assumed that, being of smaller size, the *PS 250 nm mask* was eroded more significantly.

### 3.1.2 Co

We synthesized cobalt triangular nanostructures through the PS 490 nm masks. We only tested one deposited thickness (300 nm). As with FePt alloys, we also obtained triangular nanodots. However, due to the lack of contrast, we didn’t manage to measure
precisely the dimensions of the nanodots. Nevertheless, we expect that the out-of-plane height measurement is quite accurate and we evaluated to be $25 \pm 4$ nm.

SEM and AFM micrographs of the as-deposited Co nanodots are presented in Figure IV - 18 and Figure IV - 19, respectively. A ring-like polymer residue was again evidenced by AFM analysis. Compared with the as-deposited Fe$_{50}$Pt$_{50}$ nanodots (Figure IV - 13 (a)), the Co nanodots seemed to be of a bigger size, which could be due to the shorter target-sample distance.

![Figure IV - 18](image1.png)

**Figure IV - 18**
As-deposited Co nanoparticles made through a PS 490 nm mask. Inset is a zoom on sixfold structure.
The main scale bar is 1 $\mu$m. The inset scale bar is 100 nm.

![Figure IV - 19](image2.png)

**Figure IV - 19**
AFM micrographs of (a) as-obtained Co nanostructure, manufactured through the PS 490 nm mask, showing the presence of PS residue in-between triangular nanoparticles.
2D (resp. 3D) views are shown on left (resp. right) sides. Scale bar in 2D view is 1 $\mu$m.
3.1.3 Defects

The presence of defects in the masks led to different architectures (Figure IV - 20 & Figure IV - 21). Due the lack of polystyrene nanosphere covering in some areas, nanodots areas were interspersed with plain thin film areas. Although the height of the dots was almost insensitive to the total deposited thickness, the height of these plain thin films is equal to the deposited thickness. This information will have a major impact in the magnetic characterization of the samples.

**Figure IV - 20**
Tilted (30°) SEM micrographs showing the coexistence of nanodots and a thin film area due to the lack of nanospheres in the colloidal mask.
Scale bar is 1 μm.

**Figure IV - 21**
3D AFM micrograph highlighting the coexistence of plain thin film and nanodots areas.

3.2 Crystallographic study (DRX)

In order to be used as potential magnetic information storage media, we need to know the crystallographic information of the samples.

The impact of annealing temperature and time on the crystallographic properties of FePt is first broached and we then discuss the Co samples.

3.2.1 FePt

The corresponding XRD diffraction peaks in Figure IV - 22 were assigned to the various FePt crystallographic phases with JCPDS-ICDD PDF-4+ files as a reference base (FePt L1₀ N° 00-043-1359 / FePt A1 N° 00-029-0718 / Fe₃Pt N° 01-071-8364 / FePt₃ N° 01-071-5031).

Both structure and magnetic properties of the FePt material are sensitive to its composition. Many studies\(^{[9, 49, 50]}\) demonstrated that FePt alloys close to the equiatomic composition are better candidates for magnetic recording applications.

We therefore performed preliminary works to tune the alloy composition by varying the target-substrate distance.
The target-substrate distance was then fixed at 15 cm to deposit Fe₅₀Pt₅₀ alloys.

The XRD patterns of the as-deposited and post-annealed Fe₅₀Pt₅₀ nanodots array prepared with the PS 490 nm mask are presented in Figure IV - 22. Samples were annealed at 600°C or 700 °C for 1h or 2h.

![XRD patterns](image)

**Figure IV - 22**

XRD patterns of the as-deposited and post-annealed Fe₅₀Pt₅₀ nanodots array obtained through the PS 490 nm mask. The indexation corresponds to (hkl) indices of the L₁₀ phase.

The as-deposited Fe₅₀Pt₅₀ nanodots revealed a chemically disordered A₁ (fcc) structure. After 600 °C annealing, some characteristic reflections of the L₁₀ ((001), (002), (201), (112), and (202)) appeared as the result of the phase transition.

As illustrated in section 3.1.3, the samples are composed of both nanodots and thin film areas. As the XRD analysis will give average information from the whole diffraction volume, the obtained results may not be representative of the nanodots. However, there is no a priori reason why the particles with approximate diameters of 150 nm would be amorphous, if the average signal corresponds to a crystallized phase. The micro X-ray Diffraction (μXRD) could allow the examination of very small sample areas (spatial resolution from several hundred microns to several millimeters), but the best way would be to analyze a nanodot by electron diffraction in a TEM.
CHAPTER IV
Magnetic nanostructures

After annealing at a temperature of higher than 700 °C for 1 h, all of the L1₀ peaks became clear, indicating that the nanodots converted into a fully ordered L1₀ phase. Samples annealed at 700°C displayed more intense and sharper diffraction peaks, sign of increasing crystallinity.

We normalized the intensities of the four most intense peaks of the annealed samples and compared them with values of the JCDPS files. No drastic change is observed from one sample to another (Table IV - 4). We concluded to a major random orientation of the samples.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>2θ</th>
<th>Theoretical intensity</th>
<th>Experimental intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Annealed 1h 600°C</td>
</tr>
<tr>
<td>(001)</td>
<td>23,967</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>(100)</td>
<td>32,840</td>
<td>28</td>
<td>25</td>
</tr>
<tr>
<td>(111)</td>
<td>41,050</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(200)</td>
<td>47,124</td>
<td>33</td>
<td>24</td>
</tr>
</tbody>
</table>

The tetragonal L1₀ phase is characterized by a c/a (Figure IV - 6 (c)) ratio of 0.96. From the diffractograms of the nanodots, we calculated the lattice parameters of the annealed samples with the following equation:

\[
\frac{1}{d_{hkl}} = \left( \frac{h^2+k^2 + l^2}{a^2} \right) \quad \text{(Equation IV - 9)}
\]

The four calculated ratios (Table IV - 5) are close to the theoretical value.

<table>
<thead>
<tr>
<th>Annealed 1h 600°C</th>
<th>Annealed 2h 600°C</th>
<th>Annealed 1h 700°C</th>
<th>Annealed 2h 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>c/a</td>
<td>0.963</td>
<td>0.965</td>
<td>0.965</td>
</tr>
</tbody>
</table>
The Fe<sub>50</sub>Pt<sub>50</sub> fabricated through the PS 250 nm masks were annealed during 2h at 700°C. The XRD patterns before and after annealing (Figure IV - 23) highlighted the same structural characteristics as for the nanodots fabricated through the PS 500 nm masks.

However, as mentioned in chapter III, the small dimensions of the well-ordered hcp domains resulted in the increase of deposited material in plain thin film, leading therefore to less noise in the XRD patterns.

![XRD patterns of the as-deposited and post-annealed Fe<sub>50</sub>Pt<sub>50</sub> nanodots array obtained through the PS 250 nm mask.](image)

We also synthesized a 35 nm-thick Fe<sub>50</sub>Pt<sub>50</sub> plain thin film (same height as the nanodots) to compare with the patterned samples. As expected, as-deposited and annealed films were in the A1 and the L<sub>10</sub> phase, respectively (Figure IV - 24).

However, we observed an increased relative (001) intensity (Table IV - 6) compared with the results obtained on the patterned samples (Table IV - 4). Breitling et al.[51] also evidenced this difference of crystallographic structure for different film thicknesses.

We will further discuss the impact of these results on the magnetic properties of the samples in section 3.3.1.
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Magnetic nanostructures

Figure IV - 24
XRD patterns of the as-deposited and post-annealed Fe$_{50}$Pt$_{50}$ plain thin films.

Table IV - 6
Normalized experimental intensities of the four most intense diffraction peaks of the L1$_0$ phase in the 35 nm thick film compared with the intensities extracted from the JCPDS file (PDF #00-043-1359).

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>2θ</th>
<th>Theoretical intensity</th>
<th>Experimental intensity</th>
<th>Annealed 2h 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>23.967</td>
<td>30</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>(100)</td>
<td>32.840</td>
<td>28</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>41.050</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>(200)</td>
<td>47.124</td>
<td>33</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>
3.2.1 Co

X-ray diffraction (XRD) results for Co nanodots are shown in Figure IV - 25, which match with the hexagonal phase of standard Co powder pattern (PDF #04-001-3273). The strongest peak (002) indicates that the most dominant planes are (00l) planes (Table IV - 7).

![XRD pattern](image)

**Table IV - 7**

Normalized experimental intensity of the diffraction peaks detected in the XRD pattern of the Co nanodots (obtained through the PS 490 nm mask) compared with the intensities extracted from the JCPDS file of the hexagonal Co phase (PDF#04-001-3273).

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>2θ</th>
<th>Theoretical intensity</th>
<th>Experimental intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>41.56</td>
<td>27</td>
<td>64</td>
</tr>
<tr>
<td>(002)</td>
<td>44.501</td>
<td>28</td>
<td>100</td>
</tr>
<tr>
<td>(101)</td>
<td>47.424</td>
<td>100</td>
<td>42</td>
</tr>
<tr>
<td>(102)</td>
<td>62.516</td>
<td>11</td>
<td>/</td>
</tr>
<tr>
<td>(110)</td>
<td>75.830</td>
<td>10</td>
<td>33</td>
</tr>
</tbody>
</table>

3.3 Magnetic study

Due to their small volume, the analysis of magnetic nanodots is not simple and therefore requires sensitive methods. Depending on the desired information, various techniques can give us help in understanding the magnetic behavior of such nanostructures.

We first tried to measure the hysteresis loops by Vibrating Sample Magnetometer (VSM). However, after several attempts, this method turned out to be not sensitive
enough. The measurements were then performed with a SQUID magnetometer in the University of Santiago de Compostela (Department of Applied Physics).

In order to get specific information from the nanodots, we have been looking for a Magneto-Optic Kerr Effect (MOKE) equipment with a focusing system. The additional challenge regarding the Fe$_{50}$Pt$_{50}$ alloys was to find a device equipped with an electromagnet/cryostat capable of reaching high field values, which remains relatively rare in this area of research. We performed first tests in the Paris Nanoscience Institute (Team “Nanostructures and Quantum Systems” - Dr Catherine Gourdon).

The Co samples were measured in the University of York (Department of Physics - Dr Jing Wu).

Besides those quantitative analyses, we studied the magnetic domain structures by MFM. As the tip was magnetized along its axis, the force gradient normal to the film plane is detected in all cases.

Each material will now be discussed following this guideline.

3.3.1 FePt

Quantitative study (SQUID)

As-deposited Fe$_{50}$Pt$_{50}$ thin films (Figure IV - 26) and nanodots (Figure IV - 27) revealed a soft magnetic behavior. The in-plane and out-of-plane hysteresis loops correspond to configurations in which the magnetic field is applied respectively parallel or perpendicular to the plane of the sample.

![Figure IV - 26](image1)

![Figure IV - 27](image2)

In-plane & Out-of-plane hysteresis loops of as-deposited Fe$_{50}$Pt$_{50}$ 35 nm thin film. M is the magnetization.

In-plane & Out-of-plane hysteresis loops of as-deposited Fe$_{50}$Pt$_{50}$ nanodots obtained through the PS 490 nm mask. M is the magnetization.

The slope in the out-of-plane hysteresis loop is due to shape anisotropy (Appendix D). The saturation magnetization (M$_s$) in the case of the nanodots reached higher values but it is only because they were obtained by deposition of 345 nm of FePt. Indeed, as we
already mentioned the samples are composed of thin films areas (345 nm in this case), which are separated by nanodots areas (35 nm height).

On the other hand, the higher out-of-plane $M_s$ value compared with the in-plane value for the plain thin film could be due the beginning of an out-of-plane texturing of the material and will be further discussed with the annealed plain thin films.\[51]\n
After the annealing, a sharp increase of the coercivity is observed. The in-plane hysteresis loops of the nanodots obtained through the PS 490 nm masks for the four previously discussed (section 3.1.1) deposition thicknesses are presented in Figure IV - 28. All samples were annealed at 700 °C during 2h.

As expected, the saturation magnetization increased linearly with the deposition thickness. Although no other phase was detected by XRD analysis, the apparent shoulders observed at low fields could originate from the coexistence of soft (with a rather low nucleation field) and hard magnetic phases.\[51,52]\n
![Figure IV - 28](image)

**Influence of deposited thickness**

In-plane hysteresis loops of Fe$_{50}$Pt$_{50}$ nanodots obtained through the PS 490 nm mask. The different colors refer to the different deposited total thickness as follows 75 nm, $135 \text{ nm}$, $223 \text{ nm}$ and $345 \text{ nm}$. $M$ is the magnetization.

It has been reported that FePt films deposited at room temperature, and subsequently post annealed proceed via an inhomogeneous, or first order, process.\[53,54]\n
In an inhomogeneous situation, annealed FePt films contain ordered, partially ordered, and disordered regions. As no impurities were found in XRD or EDX analysis, we concluded that residual A1 phase in the samples was the origin of the shoulder, as already pointed out by Kuo et al.\[55] and Liu et al.\[56]\n
Figure IV - 29 highlights the decrease of in-plane coercivity in the Fe$_{50}$Pt$_{50}$ nanodots as the deposited thickness increased. As observed from the hysteresis loops before and after annealing, the coercivity is strongly dependent on the chemical ordering, since the magnetic anisotropy also depends on the chemical ordering. This gradual drop could be attributed to a short loss of chemical ordering with thickness.\[57]\n
![Figure IV - 29](image)
The impact of annealing temperature on the magnetic properties of the Fe\textsubscript{50}Pt\textsubscript{50} nanodots is evidenced with the normalized in-plane (Figure IV - 30) and out-of-plane (Figure IV - 31) hysteresis loops.

The large magnetocrystalline anisotropy of the L\textsubscript{10} phase took over the shape anisotropy. In-plane and out-of-plane coercivities present an isotropic behavior, which is in accordance with the random orientation shown in the XRD patterns.

A coercivity of 9 kOe was obtained after annealing at 600 °C, while the samples annealed at 700°C showed a coercivity of 12 kOe, indicating an increase in chemical ordering.\textsuperscript{[26]} No influence of the annealing time was evidenced.
The samples annealed for 1h at 600 °C presented a strong shoulder at low fields as already reported previously, which could be the sign of the presence of the soft magnetic phase A1.

Fe\textsubscript{50}Pt\textsubscript{50} nanodots fabricated through the PS 250 nm masks were annealed 2h at 700°C and the obtained in-plane and out-of-plane are presented in Figure IV - 32. As for the dots prepared with the PS 490 nm masks, the samples present an isotropic behavior (H\textsubscript{C} = 9 kOe), which is due to a random orientation of the material.

Finally, Figure IV - 33 presents the in-plane and out-plane hysteresis loops of the Fe\textsubscript{50}Pt\textsubscript{50} thin films (35 nm) annealed 2h at 700 °C. The samples show a distinct anisotropic behavior with higher out-of-plane saturation, which was already observed in the not-annealed sample. However, the in-plane and out-of-plane coercivities reach equivalent values (H\textsubscript{C} = 12 kOe).
The thickness effects on perpendicular magnetic properties were seldom discussed in the past. Hence, it is important to understand how film thickness affects the magnetic properties and microstructures in perpendicular magnetic recording media.

Breitling et al.\[^{51}\] studied hard magnetic L1\(_0\) FePt plain thin films and nanopatterns prepared by electron beam lithography. The composition of their alloy was found to be Fe\(_{54}\)Pt\(_{46}\) and the thin films (50 nm thick) displayed lower coercive field (7 kOe) for almost same annealing conditions. From a general point of view, they reported that the films with a thickness < 20 nm displayed an out-of-plane texture, whereas thicker films (d > 50 nm) exhibited an isotropic behavior.

In our thin films (35 nm), the anisotropic behavior is only present in the magnetization but does not affect the coercive field, which would mean that we are in the limit between these two regimes.

These results agree with recent studies made by Sun et al.\[^{58}\] in which the upper limit of the magnetic FePt layer thickness with good perpendicular anisotropic behavior was determined to be about 30 nm.

In view of these results, it appeared obvious to make use of a technique, which could give us specific information of the nanodots instead of a global analysis.

We performed first tests on the Fe\(_{50}\)Pt\(_{50}\) nanodots samples prepared through the PS 490 nm masks using a MOKE equipment (polar mode) with a 60 kOe. The set up is presented in appendix E.

In high fields, most optical components cause a substantial Faraday rotation\[^{59}\] of the polarization.\[^{60}\] We therefore acquired calibration curves by replacing the samples with a mirror to evaluate the Faraday rotation (1.12 deg/kOe) of the whole set-up, assuming that there is no magnetic signal.

Regarding the analysis of the magnetic samples, we evidenced a significant displacement (\(\approx\) 30 \(\mu\)m) of the analyzed areas following a parabolic behavior under magnetic field. Thanks to image analysis, the displacement was precisely fitted and used to match the extracted Kerr signal with the corresponding magnetic field.

To maximize signal-to-noise ratio, we acquired data from eight different areas both in nanodots and plain thin film areas (with higher signal in the thin films). The global shape of the signal (Figure IV - 34) is due to Faraday rotation in the objective lens. However, we can observe hysteresis in the measurement, which is a sign of the magnetic behavior of the samples.

---

\[^{51}\] Breitling et al.

\[^{58}\] Sun et al.

\[^{59}\] Faraday Rotation is a magneto-optical phenomenon that rotates the polarization of light when passing through transparent dielectric materials.
The hysteresis behavior is highlighted by plotting the difference curves between the ascending and descending branches of the hysteresis cycle (Figure IV - 35 & Figure IV - 36). A great similarity between the thin film and the nanodots areas is observed which let us suppose that the nanodots still present a ferromagnetic behavior.

![Graph showing hysteresis loops for thin film and nanodots areas](image)

**Figure IV - 34**
As-acquired MOKE signal acquired from thin film and nanodots areas.

However, the fitting of the curves to extract the exact parameters of the hysteresis loops is not so easy as the expected Kerr signal is expected to be more or less 0.5 deg. The curves were fitted with various parameters on the basis of one (Figure IV - 35) or two major cycles (Figure IV - 36).

![Graph showing difference curves and extracted hysteresis loops](image)

**Figure IV - 35**
Difference curves and extracted hysteresis loops (insets) corresponding to the fitting (red curve) with one cycle on (a) plain thin area and (b) nanodots area.
domains, which with an out domain structure changes from an in domain structure. The MFM analysis of the as-deposited Fe₅₀Pt₅₀ revealed a strip-like pattern, which agrees with recent studies over FePt thin films.

Indeed, it was recently reported that sputter deposited FePt films in the soft magnetic phase (A1) present a critical thickness (35 nm) above which the magnetic domain structure changes from an in-plane planar structure to a periodic stripe array with an out-of-plane component. This kind of magnetic domain structure is observed in films in which there is a component of the magnetic anisotropy perpendicular to the film plane.

Drastic change is observed in the annealed samples, revealing smaller magnetic domains, which are the reason of the high coercivity.

Figure IV - 36
Difference curves and extracted hysteresis loops (insets) corresponding to the fitting (red curve) with two cycles on (a) plain thin area and (b) nanodots area.

However, the fittings are far from perfect and the choice between them is pretty difficult. More work has to be performed to refine the fitting.

Nevertheless, although we cannot yet affirm the shape of the hysteresis loops, we can conclude that the nanodots do present a stable ferromagnetic character at room temperature, which is of major importance for further use in magnetic storage applications.

Qualitative study (MFM)
We studied the Fe₅₀Pt₅₀ thin films (35 nm thick) by AFM & MFM before (Figure IV - 37(a)) and after annealing (Figure IV - 37(b)). Both AFM micrographs are presented at the same z-scale, highlighting a net difference between the two samples. The root-mean-square (RMS) roughness, measured over a 5 μm square area, increased from 0.4 nm to 3.9 nm after the annealing (2h - 700°C).

The MFM analysis of the as-deposited Fe₅₀Pt₅₀ revealed a strip-like pattern, which agrees with recent studies over FePt thin films.
Figure IV - 37
AFM & MFM micrographs of Fe_{50}Pt_{50} thin films (35 nm): (a) Before annealing and (b) After annealing 2h at 700 °C.

Figure IV - 38 shows the AFM morphology and the corresponding MFM image of as-deposited Fe_{50}Pt_{50} nanodots. Some dots present a symmetrical black-white dipole contrast, characteristic of a single domain state with magnetization lying in (red circle) or out (light blue circle) of the plane of the dot. This phase contrast is due to the fact that the tip is being attracted or repelled by the magnetic stray fields pointing into or out of the surface of the magnetic element, respectively (Figure IV - 39).

The other nanodots show a more complex phase contrast, as a result of a specific magnetic fine structure. An attempt to interpret such phase contrast is to proceed to micromagnetic simulations.
AFM & MFM micrographs of Fe\textsubscript{50}Pt\textsubscript{50} nanodots manufactured with PS 490 nm mask and annealed 2h at 700 °C. The samples were not previously magnetized before imaging. The red circle and blue circles delimitate single-domain particles with in-plane and out-of-plane magnetization, respectively.

Figure IV - 38

Expected MFM phase contrast in single domain nanodots (section view) with in-plane or out-of-plane magnetizations. The MFM contrast has been represented in a circular shape. The black (white) contrast indicates that the magnetic tip is being attracted (repelled) due to interaction with the magnetic stray fields (red arrows).

We magnetized the samples in a magnetic field of 10 kOe, applied in the sample plane. Most of the nanodots exhibited a bipolar contrast, with in-plane magnetization (Figure IV - 40).

However, due to the low value of the applied magnetic field, magnetic moments were not yet all pointing towards the same direction (Figure IV - 41). Further studies with magnetization at higher field values could therefore be performed to saturate the samples.
AFM & MFM micrographs of as-deposited Fe$_{50}$Pt$_{50}$ nanodots manufactured with PS 490 nm mask annealed 2h at 700 °C. The samples were magnetized in a 10 kOe magnetic field, applied in the sample plane.

Some dots still exhibited more complex phase contrast. We attributed those complex structures to the existence of double or multi-domain nanodots.

According to Table IV - 1, the transition from multi-domain to single-domain states should appear around 340 nm for spherical particles. The observation of those more complex domains should suggest that the transition between these domain regimes appears at a lower critical value in this case of nanostructures. However, the transition is of course not expected to be clear-cut, given the fluctuation of the shape and size of the dots.

However, one way to understand or to corroborate these observations would be to proceed to micromagnetic simulations. Zhong et al.[63] calculated simulations on FePt
nanodots prepared by NSL. They observed that regardless single or double domain nanodots, the magnetizations tend to be parallel to one edge of triangular shape.

This is consistent with Chou studies[64] on size and shape effects on the properties of patterned magnetic structures.

The magnetization direction in a single domain or multidomain patterned magnetic nanostructure can be controlled by the shape of the structure. In a single domain, the stable magnetization is always along the long axis of the structure, to reduce demagnetization field and lower the total energy. In a multi-domain patterned magnetic nanostructure, the magnetization at the edges tends to be parallel to the edge to avoid free magnetic poles for lowering the magnetostatic energy.[64]

We also performed some first measurements on the nanodots manufactured with the PS 250 nm masks. We encountered many difficulties in acquiring the data. However, we observed single domain nanodots, which would confirm the magnetic stability of the nanodots. However, we should perform some MOKE analysis on the nanodot arrays to confirm this hypothesis.

![MFM micrographs of Fe_{50}Pt_{50} nanodots manufactured with PS 250 nm mask and annealed 2h at 700°C.](image)

**Figure IV - 42**

MFM micrographs of Fe_{50}Pt_{50} nanodots manufactured with PS 250 nm mask and annealed 2h at 700°C.

In an attempt to evaluate the potentiality of using these materials as perpendicular magnetic media, the samples prepared with PS 490 nm masks were magnetized in high field in the normal direction (70 kOe). To ensure that we were imaging the magnetic contrast, we acquired the MFM images with opposite tip magnetizations (upwards and downwards).

The results are presented in Figure IV - 43. The nearly exact reversal of the magnetic contrasts in MFM micrographs confirms the stability of the magnetizations of both the magnetic tip and the sample.
3.3.2 Co

*Quantitative study (SQUID)*

The as-deposited Co thin film (Figure IV - 44) and nanodots (Figure IV - 45) present a soft magnetic behavior. As for the FePt samples before annealing (Figure IV - 26 & Figure IV - 27), the low magnetocrystalline of the Co could not counter the shape anisotropy, which is therefore responsible of the observed (≅ 45°) slope in the out-of-plane loops.

The saturation magnetization is again higher for the nanodots than for the thin film due to the fact that they were synthesized by deposition of ≅ 320 nm of Co.
In-plane & Out-of-plane hysteresis loops of as-deposited Co 25 nm thin film. M is the magnetization. The inset is a zoom in the dotted area.

Due to their soft magnetic behavior, the Co samples have the significant advantage to allow working at rather low magnetic fields.

Both thin film (Figure IV - 46) and Co nanodots (Figure IV - 47) were studied by focused-MOKE in the longitudinal mode. The patterning of the film resulted in a sharp increase of the coercive field.

Indeed, the unpatterned Co plain thin film displayed a low coercivity value of \( \approx 12 \) Oe, which agrees with reported values in literature for plain thin films.\(^{65,66}\)

The hysteresis loop acquired from focus on a nanodot area exhibited a coercive value of \( \approx 90 \) Oe.
The increased coercivity undoubtedly highlight that the patterned Co array remain magnetically stable at room temperature. This is due to the fact that in this continuous film the coercivity is controlled by the nucleation and depinning of the domain wall but in the nanoscale structures the exchange energy is too high to form a domain wall and the coercivity is controlled by magnetization rotation.\[67, 68\]

Besides those differences in terms of coercive field, the global shape of the MOKE loops from the nanodots or thin film is deeply different. While the remnant ratio ($M/M_s$) is close to 1 for the thin film area, it barely reaches 0.5 for the nanodots. This is certainly due to a shape anisotropy in the magnetization reversal.

Indeed, the group of Dr. Wu recently reported the focused MOKE study of FeNi dot arrays manufactured by NSL.\[67, 68\] They evidenced the same behavior in the hysteresis loops.

In order to identify the magnetization reversal process, they performed micromagnetic calculations. They concluded that the magnetization process in the triangular dots follow two steps (Figure IV - 48): (1) the rotation process preliminary determined by the moving of the top corner spin from state A to C, which leads to a reduced remnant ratio; (2) The switching process essentially determined by the bottom base spins from state C to D.

![Micromagnetic simulation for the hysteresis loop of Fe$_{64}$Ni$_{36}$ triangular dot arrays. The simulation clearly shows the magnetization process which follows two main steps: (1) the rotation process primarily determined by the top corner from state A to state C; (2) the switching process essentially determined by the bottom base from state C to state D.\[67\]](image_url)

A collaboration has just been started to proceed to micromagnetic simulations on our Co samples.
Qualitative study (MFM)

We first studied the Co thin films (25 nm thick) by AFM & MFM (Figure IV - 49). The measured surface roughness was of 0.494 nm.

The MFM analysis revealed no clear correlation between the edges of magnetic domains and physical features in the AFM image. The MFM image show widespread irregularly shaped domains, which according to Chioncel et al.[69] can be attributed to in-plane magnetization.

MFM analysis on the patterned samples revealed that although the Co nanodots seemed to be very close to each other, most of them exhibited highly ordered remanent states whose symmetry and configuration are governed by shape anisotropy.

First, we applied a magnetic field in the plane of the samples. The MFM image in Figure IV - 50 (a) displays a purely dipole character in which almost no other contrast was observed. All dipoles were almost pointing towards the same direction. This type of behavior is consistent with hysteresis loops obtained by focused-Moke (Figure IV - 47).

On the opposite, when the dots were magnetized in a perpendicular way, they relaxed into a single-vortex (Figure IV - 50 (b)).

This perpendicular magnetization of the vortex core is verified experimentally through MFM images that show light dots at the center of the dots, arising from the uncompensated magnetic poles.
AFM & MFM micrographs of as-deposited Co nanodots. The samples were (a) in-plane and (b) out-of-plane magnetized.
The existence of this $z$ component is due to the fact that the cost, in terms of exchange energy, of keeping the magnetic moments turning in a small circle in the plane near the center of the dot is locally very high, and the only form of lowering this energy is to tend towards parallelism of the atomic moments, pointing them out of the disk plane in the vortex core (Figure IV - 51).

![Diagram](image1)

**Figure IV - 51**

**Vortex type domain**

(a) Vortex arrangement of magnetic moments in a nanodot of soft magnetic material. The tips of the moments point out of the plane near the center – this is the vortex core, a region that has a net magnetization perpendicular to the plane of the dot.[3]

(b) Experimental MFM 3D view of a vortex domain, clearly highlighting the vortex core region.

A focused-MOKE experiment in the polar mode should reveal a specific hysteresis loop with a sudden loss of magnetization close to zero field (Figure IV - 52). This behavior is highly dependent on the aspect ratio of the dots.[66,70]

![Diagram](image2)

**Figure IV - 52**

Hysteresis loops measured from nanomagnets of diameter $d=300$ nm and thickness $t = 10$ nm, highlighting vortex domain formation.[71]
4. Conclusions

We successfully synthesized Fe$_{50}$Pt$_{50}$ nanodots through PS 490 nm and PS 250 nm masks. The as-deposited alloys were crystallized in the soft-magnetic A1 phase. We annealed the samples in order to induce the transition to the hard-magnetic L1$_0$ phase (confirmed by XRD analysis).

Morphological studies on nanodots prepared with both masks highlighted that the annealing not only modified the edges of the particles but also increased their height.

In an attempt to modify the size of the dots, we deposited four different thicknesses (from 75 nm to 345 nm) on the PS 490 nm masks. However, we did not observe drastic variation between the samples and the maximum height of the annealed nanoparticles was $\approx$ 35 nm.

We concluded that at this evaporation layer thickness the mask became closed and that no more material reached the substrate. Another hypothesis could be a heating of the samples during the deposition, which would have resulted in the decrease of the aperture size.

Due to the high magnetocrystalline constant of the L1$_0$ phase and the random texturing of the material, both in-plane and out-of-plane hysteresis loops revealed almost equivalent coercive fields. However, due to the coexistence of thin film and nanodot areas in the samples, we did not evidence any difference ($H_c$) with the hysteresis loops of thin film (35 nm).

We therefore tried to study the structures by MOKE (polar mode). So far, we are only able to say that the detected signal from the nanodots is very close to the one from a thin film, which is nevertheless a significant result to prove the magnetic stability of these small nanodots. More work will be necessary to extract the exact shape of the hysteresis loops.

The MFM results on the structures prepared with the PS 490 nm masks revealed that most of the nanodots were single-domain, which indicated that the critical single domain size is not so far from 100 nm (in-plane height). We also evidenced single domain states in the samples manufactured with the PS 250 nm masks but further work has to be done to confirm these results.

Co soft magnetic nanodots were manufactured through the PS 490 nm masks. The focused-MOKE analysis (longitudinal mode) on the nanodots revealed a large increase of the coercive field (90 Oe) in comparison with thin films where the measured coercive field is equal to 12 Oe. This has never been reported for Co nanodots synthesized through so small PS nanopsheres.

The MFM results revealed in-plane single domain states when the dots were in-plane magnetized and vortex domain states when perpendicular magnetized.
5. References


