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Electrochemical preparation of Co-Ag nanostructured materials for GMR applications

Memòria que presenta JOSÉ MANUEL GARCÍA TORRES per optar al títol de Doctor per la Universitat de Barcelona

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CHAPTER 1

INTRODUCTION

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INTRODUCTION

1.1. A future of nanoscience and nanotechnology

Probably, the importance of materials in our cultures is higher than what it is normally believed. Practically, our daily lives are influenced and surrounded by materials, such as transportation, housing, clothing, communication, diversion/fun and food. This fact confers great value to science and engineering of materials, as well as other related disciplines as chemistry, physics or other engineerings to follow the task to make our lives easier. Materials science has undergone a great evolution during the last decades, however and in spite of the spectacular progress made on both the material's knowledge and development, the continuous technological challenge requires more sophisticated and specialized materials. In this sense, nanoscience and nanotechnology seems to represent a new channel to achieve this objective as true progress is being made in this field.

In the framework of the rapid development of this new branch of science, the domain of nanostructured materials is attracting more and more interest [1-10]. The question which one immediately raises oneself is: Why nanostructured materials are being so important? But first we should give answer to the question: What is a nanostructured material? Nanostructured materials may be defined as those materials whose structural features are in between those of atoms and bulk materials, with at least one dimension in the nanometer range. Table 1.1 is a list of typical nanomaterials of different dimensions. The explosion for the interest in these nanometer-scale structures arises from remarkable variations in fundamental properties i.e. electrical, optical or magnetic that occurs as one progresses from an "infinitely extended" solid to a particle of material consisting of a countable number of atoms [11-20]. Suitable control of the properties of these materials can lead to new nanoscience as well as new devices and technologies [21-25].

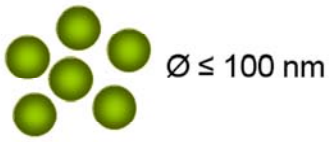
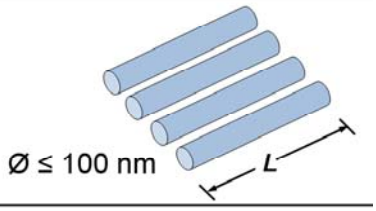
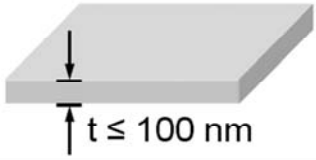
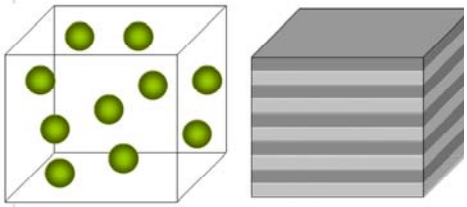
Classification	Examples	Scheme
0-D: All dimensions at nanoscale	Nanoparticles, nanocrystals and clusters (quantum dots)	
1-D: Two dimensions at nanoscale, while other (L) is not	Nanowires, nanorods, nanotubes	
2-D: One dimension (t) at nanoscale	Surfaces and thin films	
3-D: No dimensions at nanoscale but these materials posses a nanocrystalline structure or involve the presence of features at the nanoscale	Nanocrystalline and nanocomposite materials (granular films, multinanolayers,...)	

Table 1.1. Classification of nanomaterials according to their dimensions in the nanometer scale.

A clear example of the breakthrough in nanoscience and nanotechnology was the discovery of the Giant Magnetoresistance (GMR) effect in 1988 [26,27]. Giant magnetoresistance can be considered one of the most fascinating discoveries in the last decades as it combines both tremendous technological potential and deep fundamental physics. Just to know the importance of the discovery, within a decade of GMR being discovered commercial devices based on this phenomenon, such as hard-disks read-heads, magnetic field sensors or magnetic memory chips, had become available in the market [28-30]. Moreover, this scientific finding made the fathers of the discovery to earn the Nobel Prize in Physics in 2007.

1.2. Nanostructured materials growth

1.2.1. Electrodeposition: A real tool to prepare nanostructured materials

The discovery of the GMR phenomenon was to a great extent due to the significant progress in thin-film deposition techniques, which made it possible to fabricate layers of various materials with nearly a monolayer precision. Most of the thin film growth processes used so far to prepare nanostructured magnetic materials, i.e. molecular beam epitaxy (MBE) or sputtering [31-35], require high or ultrahigh vacuum conditions. However, since a few decades ago electrodeposition is considered as a real alternative to the physical deposition methods to grow high quality nanostructured materials, i.e. films, multilayers, nanowires, among others [36-45]. The considerable increase on scientific papers related to the electrodeposition of these nanostructures since the last twenty years is a proof, as it is shown in figure 1.1. Day by day electrodeposition is gaining positions among those techniques which are the mainly employed to grow the GMR materials.

The reason is that electrodeposition technique shows some advantages that make this technique to be the choice in a lot of circumstances. One of these advantages is its low cost. The equipment used is cheap and maintenance is hardly required. Moreover, a high quantity of the precursor material used in vacuum techniques is deposited on the chamber's walls, situation that does not occur in electrodeposition.

On the other hand, room temperature is usual to grow the material or, at least, temperatures lower than 100 °C. This characteristic avoids mechanical stress, problems induced during substrate cooling.

Another advantage is the higher deposition rate achieved regarding vacuum techniques, allowing obtaining thicker films. This makes electroplating irreplaceable on certain applications like magnetic read-heads fabrication and magnetic nucleus for inductive systems [46,47] as well as in the piezoelectric-magnetostrictive sensors response improvement [48].

But maybe one of the most important advantages of the electrodeposition and surely the characteristic that has greatly contributed to its incorporation in the microelectronic industry is the capacity to deposit the material over the conducting part of the substrate leaving free the insulating zones. In this sense, this technique allows achieving the designed pattern growing the material by electrodeposition over a lithographic substrate without any subsequent treatment like chemical etching or lift-off.

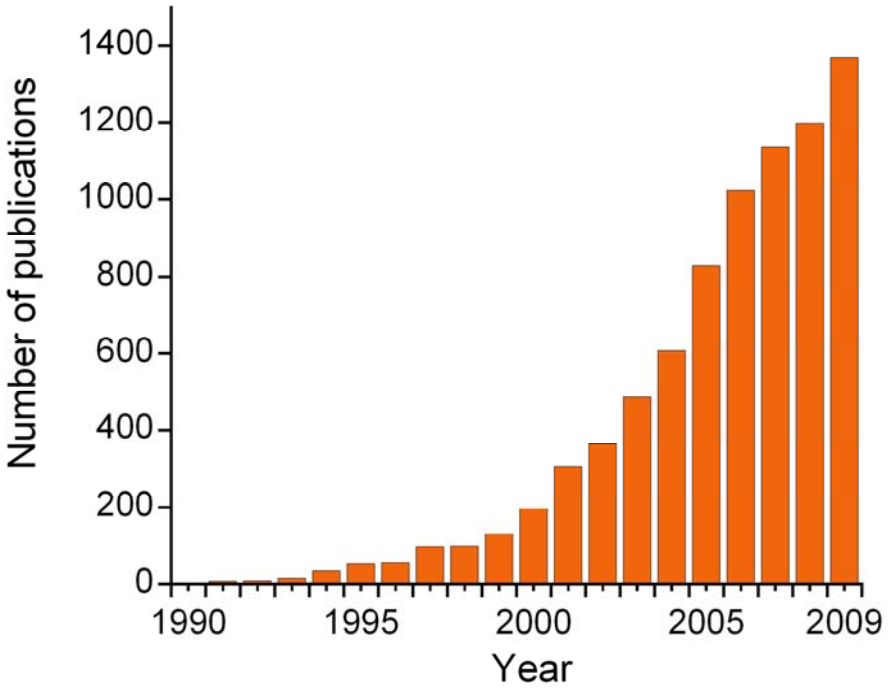


Figure 1.1. Evolution on the number of publications related to the electrodeposition of nanostructured materials. Information obtained from *Scifinder Scholar* (*Chemical Abstracts*).

On the contrary, electrodeposition also presents some drawbacks. On one hand, the uniformity of the electrodeposited films (thickness and chemical composition) depends on not only the cell geometry [49] but also the hydrodynamic of the process [50], factors which are sometimes difficult to control. On the other hand, the electrolyte composition depletion is also important to consider in such processes in which the concentration is a critical parameter.

We could conclude saying that weighing up the pros and cons of electrodeposition, this method is a real alternative to physical techniques to fabricate nanostructured materials with GMR. In this sense, electrodeposition has been selected as the preparation technique for some of the nanostructured materials this thesis deals with: granular films, multilayers and nanowires.

1.2.2. Electrodeposition technique

Electrodeposition is a process in which metal.lic ions present in a solution are incorporated in a conductive substrate by means of a chemical reaction of the kind:

$$M^{n+} + ne^{-} \longrightarrow M$$

leading to the formation of a film on the substrate. This process involves the application of an electric current through the solution containing the ions to reduce them on the substrate. This reaction is characterized by a potential known as equilibrium potential and is characteristic of each species. At potential values more negative than the equilibrium potential the reduction reaction could take place, but the exact potential at which deposition occurs depends on nucleation overpotential or growth overpotential. This fact forces to perform a basic electrochemical study in order to establish the potentials at which each process takes place.

The basic elements necessary to perform the electrodeposition are the electrolyte and the electrolytic cell, the electrodes and the potentiostat/galvanostat. The electrolyte is a solution, generally an aqueous solution, containing the ions of the metal/s to be deposited and usually known as electroactive ions. Moreover, other species are added to the electrolyte to control the pH, to increase the conductivity of the solution or to improve the characteristic of the deposits. The receptacle that contains the electrolyte is the electrolytic cell. In order to perform the electrodeposition, at least two electrodes are necessary: a conductive substrate (the working electrode where the reduction of the electroactive ions will take place) and the counter or auxiliary which will act as the anode of the process. A third electrode can be used to have a better control of the process, the reference electrode which will allow controlling the potential of the working electrode. Finally, the potentiostat/galvanostat is the equipment responsible to apply and measure the signal during the electrodeposition.

Although electrodeposition technique seems an easy method to prepare materials, a lot of processing parameters such as electrolyte composition, pH, temperature and agitation, applied potential and current are important to be controlled. The importance for such control lies in that the variation of these parameters may affect the characteristics of the films such as thickness, composition, grain size or crystalline structure, among others, which in turn will affect the properties of the material, i.e. magnetic, electric or optic properties.

1.3. What is magnetoresistance? Definition and different magnetoresistance effects

The magnetoresistance effect (MR) could be defined as the change in the electrical resistance of the material under study upon the application of an external magnetic field H: $\Delta R = R_H - R_0$ where R_H and R_0 are the resistances measured under the presence and absence of a magnetic field, respectively. However, it is customary to define a magnetoresistance ratio, which is usually expressed in percentage, in the following form:

(1.a) $$MR(H) = \Delta R/R_0 = (R_H - R_0)*100/R_0$$

For convenience, the resistance R is used in this definition but it is evident that by using the resistivity ρ, the MR ratio will be the same.

Although magnetoresistance seems to be a unique phenomenon in accordance with its definition, different effects are known up to now under the term magnetoresistance: ordinary magnetoresistance, anisotropic magnetoresistance, giant magnetoresistance, tunneling magnetoresistance and colossal magnetoresistance. Although all of them have in common the defining property, their intrinsic mechanisms are completely different. A brief overview of MR effects is given below.

1.3.1. Ordinary magnetoresistance

Ordinary magnetoresistance (OMR) is the increase in the electrical resistivity of metallic materials under an external magnetic field. OMR arises from the effect of the Lorentz force on the electron trajectories due to the applied magnetic field. The interaction leads to an increase of the current path length, thus increasing the electrical resistance of the material. In non-magnetic metals the change is typically smaller than 1 % in fields of the order of 10 kOe. Moreover, the change in resistivity ($\Delta\rho$) is positive for both magnetic field parallel ($\Delta\rho_{//}$) and transverse ($\Delta\rho_{\perp}$) to the current direction with $\rho_{\perp} > \rho_{//}$.

1.3.2. Anisotropic magnetoresistance

In an opposite way than non-magnetic metallic materials, the electrical resistivity of ferromagnetic metals and their alloys depends on the relative orientation between the external magnetic field and the flow direction of the measuring current. This phenomenon called anisotropic magnetoresistance (AMR) results from the spin-orbit interaction and is the responsible for the resistance to depend on the relative orientations of the magnetization and the electric current. In contrast to OMR, the AMR effect is anisotropic. The reason for such anisotropy lies on the physical origin of AMR, the spin-orbit coupling. The electronic orbits about each nucleus deforms slightly as the direction of the magnetization rotates, and this deformation changes the amount of scattering undergone by the conduction electrons when traversing the lattice (Figure 1.2). Whereas a wide cross-section for scattering is available when the magnetic field and the magnetization are parallel to the current direction, giving a high resistance state ($\Delta\rho_{//}$ increases with field) (Figure 1.2A); a small cross-section is obtained when both the field and the magnetization are perpendicular to the current, leading to a low resistance state ($\Delta\rho_{\perp}$ decreases with field) (Figure 1.2B).

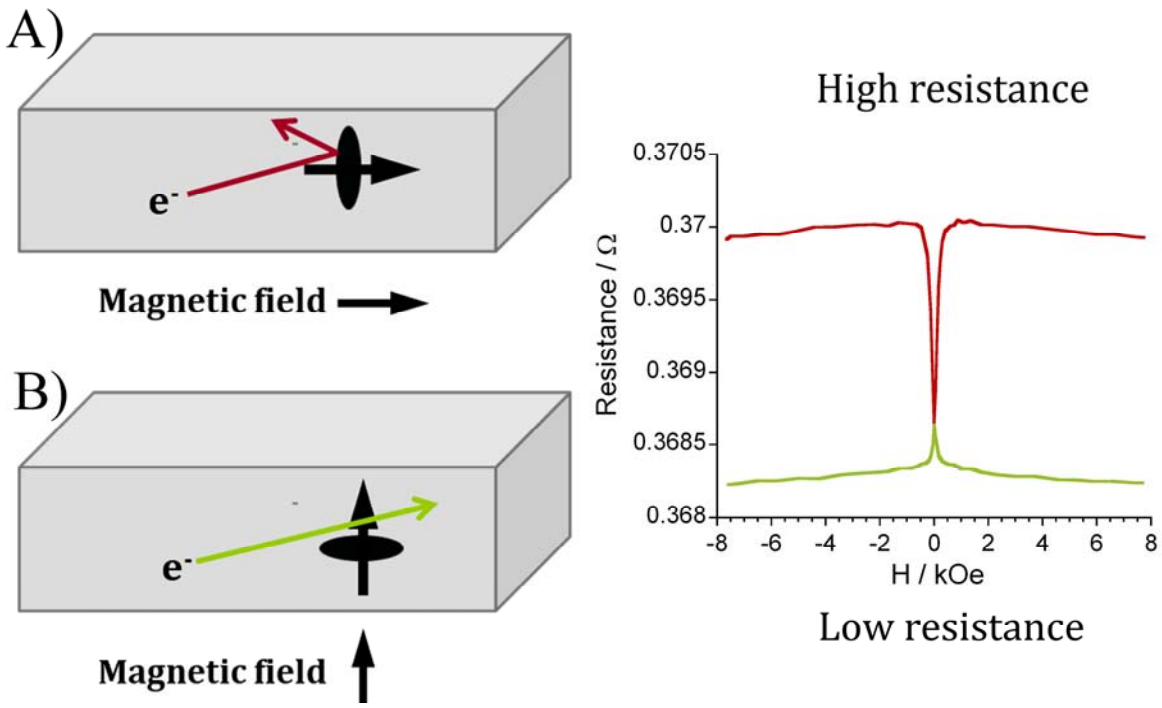


Figure 1.2. Scheme demonstrating the physical origin of AMR. Shaded ovals represent the scattering cross-sections of the bound electronic orbits. A) When the applied magnetic field is parallel to the current direction, a wide cross-section for electron scattering exists, giving a high resistance state. B) When applied field and current direction are transverse, there is a small cross-section for electron scattering, giving a low resistance state

Although the AMR effect is not too high, the importance of it lies in that the resistance change takes place in a few hundreds of Oersteds. That is why in the beginning of the 90's, inductive read heads in hard disk drives were replaced by AMR read heads.

1.3.3. Giant magnetoresistance

Giant magnetoresistance (GMR) effect was independently discovered by Peter Grünberg of the Jülich Research Centre (Germany) [27] and Albert Fert of the University of Paris-Sud (France) in Fe/Cr multilayers [26]. A pronounced change in the electrical resistance was observed when the magnetization configuration changed from antiferromagnetism (AF) to ferromagnetism (F) between neighbouring magnetic layers as is illustrated schematically in figure 1.3. In the absence of the magnetic field the magnetizations of the ferromagnetic layers are antiparallel (or AF). The application of the magnetic field, which aligns the magnetic moments and saturates the magnetization of the multilayer, leads to a drop in the electrical resistance of the multilayer. This effect was found to be much larger than either ordinary or anisotropic magnetoresistance and was, therefore, called "Giant" magnetoresistance or GMR. A huge scientific interest was focused on the GMR effect immediately after the first reports and was arisen by the considerable industrial interest in the area of magnetoelectronic devices such as the introduction of the GMR read heads, which increased the data storage density within a decade by orders of magnitudes. Due to both tremendous technological potential and great scientific interest, the GMR investigation remains still nowadays one of the most active areas in the solid state- and materials physics [51-55]. The GMR effect will be seen in more detail in the next section.

1.3.4. Tunneling magnetoresistance

A related phenomenon to GMR was tunnelling magnetoresistance. When nanoscale ferromagnetic materials are separated by thin insulating layers, i.e. Al_2O_3 or MgO, there is a significant probability that electrons can quantum mechanically tunnel from one ferromagnet to the other and through the insulating barrier leading to the tunnelling magnetoresistance effect [56-59]. The same effect was observed when nanoscale magnetic particles were dispersed in an insulating matrix [60,61]. As these kinds of systems can not be prepared by electrodeposition, they are out of our interest.

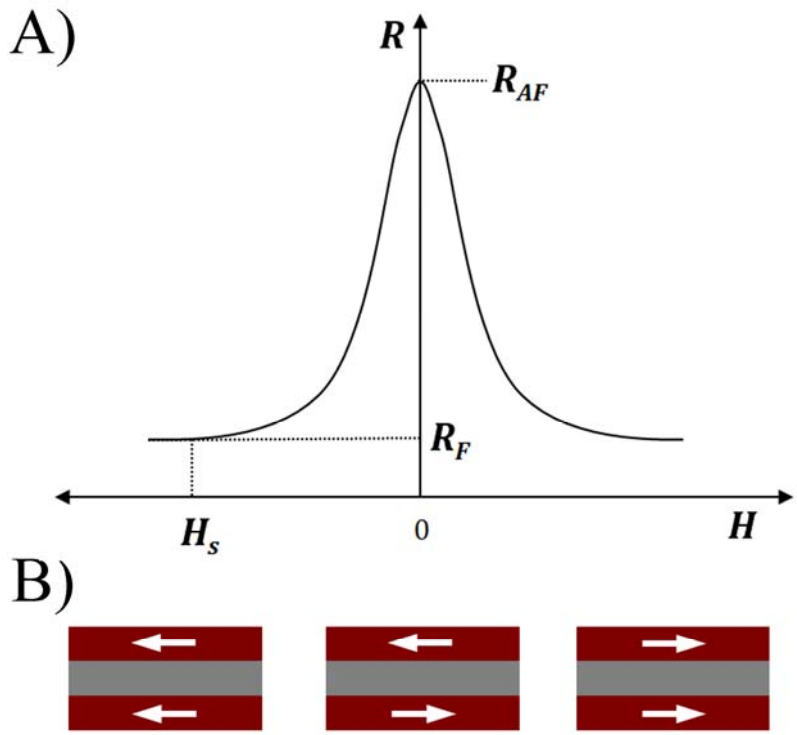


Figure 1.3. Schematic representation of the GMR effect in multilayers. A) Change in the resistance of the magnetic multilayer as a function of the applied magnetic field (H). B) Change in the magnetization orientations of two adjacent ferromagnetic layers with the applied magnetic field. The magnetizations are antiparallel at zero applied magnetic field, whereas they are parallel when the applied magnetic field is larger than saturating field (H_s).

1.3.5. Colossal magnetoresistance

In addition to ordinary, anisotropic, giant and tunnelling magnetoresistance, a different magnetoresistance effect (named colossal magnetoresistance (CMR)) was found in doped manganite perovskites such as $La_{3-x}Ca_xMnO_3$ [62]. The CMR effect can be extremely large resulting in a resistance change of a few orders in magnitude (up to 125 %), owing the term "colossal" to this high value. The mechanism for magnetoresistance in these materials is distinctly different than that in the GMR multilayer systems. Just to have an idea, in the CMR materials conduction occurs by hopping (i.e. in manganite perovskites basically by exchanging a Mn^{3+}-Mn^{4+} pair to a Mn^{4+}-Mn^{3+} pair) instead of metallic conduction as in GMR materials.

As our interest lies on the preparation of magnetic metallic nanostructured materials by means of electrodeposition with magnetoresistive applications we will focus on aspects related with the GMR phenomenon.

1.4. Giant magnetoresistance in nanostructured materials

Since the discovery of giant magnetoresistance phenomenon in Fe/Cr multilayers grown by molecular beam epitaxy (MBE), great efforts have been made in this field. On one hand, Parkin *et al.* [63] demonstrated in 1990 that GMR could be obtained in sputter-deposited Fe/Cr, Co/Cr and Co/Ru multilayers and that the GMR amplitude could be even larger in sputtered multilayers than in MBE-grown samples. Since then, other multilayer systems, such as Co/Cu [64], Fe/Cu [65], CoNiFe/Cu [66] or Co/Ag [67] have been found to exhibit GMR. On the other hand and although the discovery was firstly found in layered systems, it was lately observed by Berkowitz *et al.* [68] and Xiao *et al.* [69] in the so called granular films. Moreover, some years later the GMR effect was also detected in other nanostructured materials i.e. nanowires and nanoparticles [70,71]. As it is obvious from the above lines, great efforts have been dedicated since then not only to study the origin of the magnetoresistance effect but also to improve the GMR magnitude in the different magnetic/non-magnetic configurations.

In view of the above paragraph, a great number of parameters can be changed in order to modify the magnitude of the giant magnetoresistance. But, how these parameters must be modified in order to improve the GMR effect? To give answer to this question some aspects related to the GMR phenomenon must be known.

1.4.1. Basic physics of the GMR phenomenon

Why the electrical resistance of such magnetic/non-magnetic nanostructured materials varies with the applied magnetic field? In order to comprehend it, first one has to understand some physical aspects about the electrical conduction in ferromagnetic transition metals. In this sense, the model proposed by Mott as early as in 1936 [72] will be examined.

There are two main points that Mott's model rises. The first point is that the electrical resistivity in 3*d* ferromagnetic metals can be described in terms of two largely independent conducting channels, corresponding to the spin-up and spin-down electrons. So the electrical conduction occurs in parallel for the two spin channels. The second one is that in ferromagnetic metals the scattering rates of the spin-up and spin-down electrons are quite different, whatever the nature of the scattering centre is.

The valence electrons from the *s*-band (*s*-electrons) are thought to be, according to Mott's model, mainly responsible for the conductivity in 3*d* transition metals in comparison to the *d*-electrons because of the higher velocity, the delocalized nature of the *s*-electrons, the low density of states and consequently the long mean free

path (MFP)[1] of the formers. Moreover, the scattering probability of conduction electrons depends not only on the scattering potential but also on the number of final states at the Fermi level into which the electrons can be scattered during the scattering process. On the other hand, the number of these states is determined by the electronic density of states at the Fermi level ($N(E_F)$). Since the electrical resistivity is actually proportional to the total scattering probability, according to Mott's suggestion, the resistivity ρ_s of the current carried by the *s*-electrons will be proportional to the density of states of the *s*- and *d*-bands $N(E_F) = N_s(E_F) + N_d(E_F)$. However, the *d*-band in transition metals is localized in a relatively narrow energy window and is characterized by a high density of states (Figure 1.4), therefore the relation $N_d(E_F) >> N_s(E_F)$ is usually fulfilled, thus the electrical resistivity of the *s*-electrons is mainly proportional to the $N_d(E_F)$

(1.b) $\rho_s \propto N_d(E_F)$

Figure 1.4 is a schematic illustration of the electronic band diagrams for the 3*d* magnetic and nonmagnetic transition metals. The density of states for such metals is divided into two components depending on the spin direction; on one hand, the $4s_\uparrow$ and $3d_\uparrow$ bands and on the other hand, the $4s_\downarrow$ and $3d_\downarrow$ bands. Moreover, for a non-magnetic 3*d* transition metal the density of states within each band are identical for the two spins ($N_{d\uparrow}(E_F) = N_{d\downarrow}(E_F)$ and $N_{s\uparrow}(E_F) = N_{s\downarrow}(E_F)$) (Figure 1.4A). However, in ferromagnetic metals the two 3*d* subbands are shifted in energy with respect to each other (the *d*-band becomes split) (Figure 1.4B) because of the exchange interaction[2], which is the basis of the Stoner model of itinerant ferromagnetism [73]. The result is that the majority spin $3d_\uparrow$ subband is completely filled and, at the Fermi level, there are $3d_\downarrow$ states only, so $N_{d\uparrow}(E_F) = 0$ and $N_{d\downarrow}(E_F) > 0$.

(1) Average distance covered by an electron between successive collisions.

(2) Quantum mechanical phenomenon in which the coupling among neighbouring magnetic moments forms magnetically ordered states.

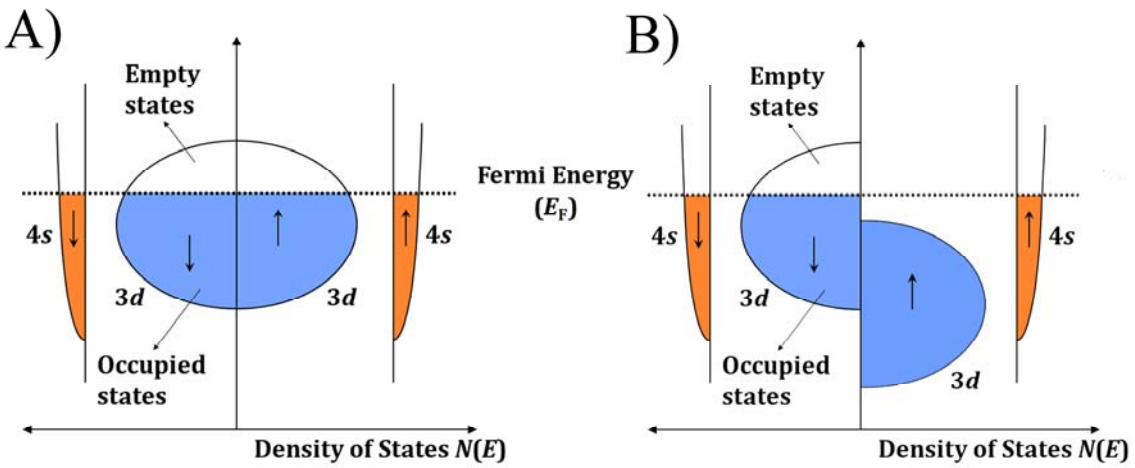


Figure 1.4. Schematic energy band structure for A) non-magnetic and B) ferromagnetic *d* transition metals. The electronic subbands corresponding to the two possible spin states (↑ and ↓) are separately indicated for both the *s*- and *d*- electrons.

As it has been previously said the *s*-electrons are the responsible for the conduction in 3*d* transition metals which have also been differentiate between $s_\uparrow$-electrons and $s_\downarrow$-electrons. This enables one to write

(1.c) $$\rho_{s\uparrow} \propto [N_{s\uparrow}(E_F) + N_{d\uparrow}(E_F)] = N_{s\uparrow}(E_F)$$

and

(1.d) $$\rho_{s\downarrow} \propto [N_{s\downarrow}(E_F) + N_{d\downarrow}(E_F)] \sim N_{d\downarrow}(E_F)$$

The previously relation $N_{d\downarrow}(E_F) >> N_{s\downarrow}(E_F) = N_{s\uparrow}(E_F)$ has been applied in deriving the expressions (1.c) and (1.d). Finally, the following expression for the resistivity of ferromagnetic transition metals is obtained:

(1.e) $$\rho_{s\uparrow} << \rho_{s\downarrow}$$

The last result allows pointing out that the electrical transport in ferromagnetic metals takes place through a two parallel channels ($s_\uparrow$ and $s_\downarrow$ channels)

characterized by having very different resistivities. The fact to differentiate between ↑ and ↓ channels allows speaking about spin-dependent electron scattering processes. This is the so-called two-current model the elaboration of which was carried out mainly by Fert and Campbell [74,75] and which allowed the explanation of the GMR effect.

1.4.2 Mechanism of the GMR phenomenon in multilayers

Giant magnetoresistance phenomenon in magnetic/non-magnetic multilayers can be successfully explained by considering the preceding observation in the context of Mott's model and the two-current model. Assume that scattering is more likely for electrons with spin antiparallel to the magnetization direction than for electrons with spin parallel to it. At zero magnetic field an antiparallel magnetization configuration due to the interlayer antiferromagnetic coupling exists (Figure 1.5A). For this antiparallel configuration, both the spin-up and spin-down electrons are alternately strongly and weakly scattered as they cross the successive ferromagnetic layers or interfaces. The resistance of the multlilayer in such an antiparallel magnetization configuration is maximum. However, if an external magnetic field is applied (Figure 1.5B) a parallel magnetization of consecutive magnetic layers is achieved. At these conditions, the spin-up electrons pass through the structure almost without scattering, because their spin is parallel to the magnetization of the layers. Therefore, they have low resistivity. On the contrary, the spin-down electrons are scattered strongly in every layer experiencing high resistivity. Since conduction occurs in parallel for the two spin channels, the total resistivity of the multilayer is determined mainly by the highly-conductive spin-up electrons and appears to be minimum.

This scheme holds only when the mean free path of the conduction electrons is larger than the layers thicknesses. When the MFP/layer thickness ratio decreases (that is thickness increases) below one, there is a progressive decoupling of the scattering processes in successive layers and the GMR progressively vanishes.

However, the ideal change from antiparallel to parallel alignment in adjacent magnetic layers is not always obeyed for real multilayers fabricated by any technique [76]. Although no AF coupling is obtained in multilayers prepared by certain methods showing magnetoresistance all that is necessary is that the adjacent layer magnetizations must have non-negligible antiparallel component in order to show magnetoresistance effect.

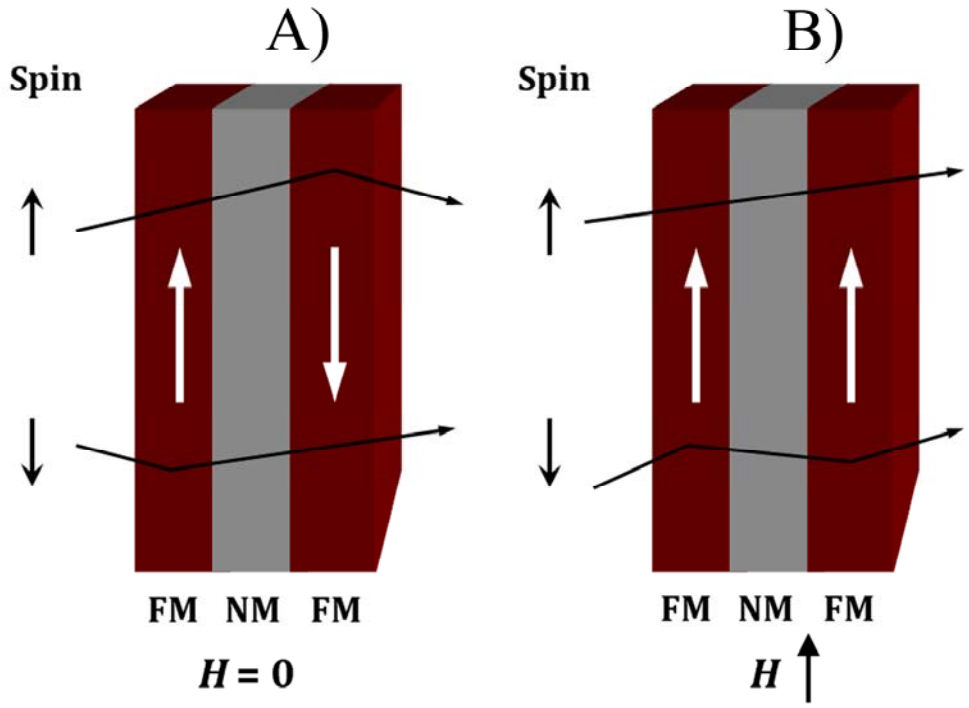


Figure 1.5. Scheme of the spin-dependent scattering for the explanation of the GMR in multilayer systems. A) In the case of AF alignment, conduction electrons in both majority and minority spin channels experience the same resistivity when passing through the multilayer structure. B) In the case of the parallel magnetization configuration, the conduction electrons aligned parallel to the magnetization can pass with low resistivity through both ferromagnetic layers whereas the conduction electrons antiparallel to the magnetization direction experience a large resistivity in both ferromagnetic layers.

But, what parameters do influence the GMR in multilayers? The first and the most evident parameter is the thickness of each individual layer. As the exchange coupling changes from antiferromangetic to ferromagnetic, MR also changes. The MR ratio is maximum when the AF coupling is maximum and zero when the coupling is ferromagnetic. On the other hand, other parameters that can affect GMR are layer composition, undulation of the layers, and interface roughness.

1.4.2 Mechanism of the GMR phenomenon in granular films

This mechanism can also be successfully applied to granular films. Granular film refers to a composite material consisting of nanoscale magnetic granules embedded in an immiscible metallic matrix. Again in this case, one must assume that scattering is more likely for electrons with spin not parallel to the magnetization direction

than for electrons with spin parallel to it. In the absence of a magnetic field, the magnetic moments of the ferromagnetic granules are randomly-oriented (Figure 1.6A). At these conditions, a conduction electron just leaving a magnetic particle is polarized by its magnetic moment. When the electron reaches a second magnetic region within its mean free path (i.e. it arrives with its original spin orientation) the electron will undergo a spin-dependent scattering since the orientations of the two magnetic moments are uncorrelated. The resistance in this case will be larger. On the contrary, when a saturating magnetic field is applied the magnetic moments are aligned and hence the resistance will be lower (Figure 1.6B).

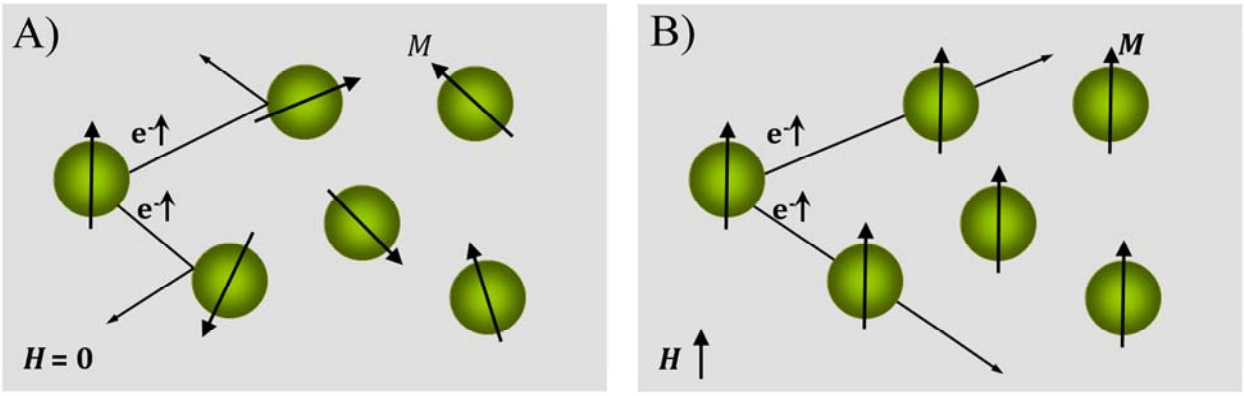


Figure 1.6. Scheme of the spin-dependent scattering for the explanation of the GMR in granular systems. The arrows attached to each particle represent the magnetic moment (*M*) of each particle. The arrow connecting two particles indicates the path of a conduction electron travelling between the particles. A) Due to the rapid and uncorrelated fluctuation of the particle magnetic moments at zero magnetic field, an electron polarized by a first particle will encounter a second particle with a different orientation of the magnetic moment and, therefore, will experience a spin-dependent scattering. B) When all the magnetic moments are aligned in the direction of an external magnetic field, the electrons whose spin is parallel to *M* will not experience such scattering.

In granular films, the parameters which are important to be optimize for the improvement of the GMR are the size and size distribution of the magnetic granules, their volume fraction, the surface area to volume ratio, the intergranular separation and the density of particles, parameters which are all interrelated to each other, as well as the effective magnetization.

1.5. Choice of the material under study: The Co-Ag system

Since the discovery of GMR, a large number of nanostructured materials which display the magnetoresistance effect have been discovered. Moreover, it was also observed that for each nanostructure the magnitude of the GMR was highly dependent on the chemical constituents of the materials. Table 1.2 shows the GMR values obtained for different multilayered systems. The question that one rises oneself in view of the table is: Why are some of the nanostructures highly magnetoresistive, whereas the others are not? All the above materials contain ferromagnetic 3*d* metals, which should have a pronounced spin asymmetry in their conductivity due to the presence of exchange split *d*-bands. It appears that the spin asymmetry in the band structure is required but not sufficient condition for high GMR values. However, GMR to a great extent is determined by the ferromagnetic metal/non-magnetic metal pair, rather than by individual materials considered separately. For example, and in view of table 1.2 GMR was found to be much lower in the Co/Cr and Fe/Cu pairs than in the Co/Cu and Fe/Cr exchanged pairs. To explain it, there are two factors which are crucial for obtaining high values of GMR. Theses are the band matching and the lattice matching between the ferromagnetic and non-magnetic metals. For example, these two conditions are almost perfectly satisfied in Co/Cu and Fe/Cr multilayers, which display the highest GMR values.

Multilayer system	GMR / %
Fe/Cr [77]	150
Co/Cu [64]	115
CoFe/Ag [79]	100
NiFe/Ag [80]	50
Ni/Ag [81]	28
Ni/Cu [82]	9
Fe/Cu [78]	5.5
Co/Cr [63]	3

Table 1.2. GMR values measured at 4.2 K for different multilayered systems prepared by sputtering.

On the other hand, it is interesting to note that the systems with the highest GMR values, such as Fe/Cr, Co/Cu, Co/Ag, $Ni_{80}Fe_{20}$/Au and $Ni_{80}Fe_{20}$/Ag, are all immiscible. This fact indicates that intermixing at the interfaces is detrimental to GMR.

In this thesis the selected system to study the magnetotransport properties is the Co-Ag system. The Co-Ag system, which is one of the systems with the highest GMR values reported [83,84], is very interesting as the phase diagram indicates practically total immiscibility [85]. Thus, sharp magnetic/non-magnetic interfaces are expected to be obtained, characteristic required to have high GMR values.

On the other hand, the preparation of the Co-Ag system is a challenge because of real progress regarding the magnetoresistance effect can be made, as the electrodeposition of this system in either of the forms that this thesis deals with (granular films, multilayers and nanowires) as well as the preparation of Co-Ag nanoparticles by the chemical synthesis have been very little studied issues.

1.6. Literature review

The electrodeposition of Co-Ag granular films was firstly reported by Zaman and coworkers [86,87] who studied the preparation of Co-Ag granular films by galvanostatic deposition. The granular deposits were prepared from alkaline solutions containing, apart from the metal salts, sodium citrate as complexing agent. The structural analysis revealed that both cobalt and silver were in the fcc structure. Moreover, no solid solution formation was detected at any condition. The only structural difference was the smaller grain size detected as the current density increased. From the zero-field cooled (ZFC) magnetization curves they estimated a mean particle size of 10 nm at 10 mA cm^{-2}. GMR values up to 5 % at an applied magnetic field of 21 kOe were measured at room temperature for samples prepared at the highest current density applied (10 mA cm^{-2}).

Later, Kenane *et al*.[88,89] also reported on the electrodeposition of Co-Ag granular films but by means of pulse deposition. They employed an electrolyte containing the metal salts and sodium chloride at a pH = 2 to grow the films. The structural characterization also revealed in this case the fcc nature of both metals. An increase in the cobalt granule size with cobalt content into the films was observed, it ranging from 3 to 9 nm at 5 at.% and 40 at.%, respectively. The maximum GMR value of 4 % measured at 20 kOe and at room temperature was obtained for the sample $Co_{0.20}Ag_{0.80}$.

A few more efforts were dedicated to the preparation of the Co-Ag system in the form of multilayers. Ueda and coworkers [90,91], who were the first dealing with the multilayer preparation, reported on the preparation of magnetic/non-magnetic stacks of the Co-Ag system by means of current control of both layers. A sulphate-based electrolyte with sodium citrate addition was employed to grow the multilayers. $Co_{70}Ag_{30}/Co_8Ag_{92}$ was the composition for the magnetic/non-magnetic layers. A clear GMR dependence on the cobalt and silver layer thickness were detected, and a maximum GMR of 8.7 % was found at d_{Ag} = 1.2 nm and d_{Co} = 1.6 nm for an applied field of 21 kOe. No structural characterization was presented.

Later, Ueda *et al.* [92] reported again on the preparation of Co-Ag multilayers by current control but from a bath containing $CoSO_4$ and AgI. Although the magnetic layer was richer in cobalt ($Co_{92}Ag_8$), the GMR values were slightly smaller, the maximum being around 7 % for H = 21 kOe. As in their previous works, GMR values were dependent on the individual layer thickness. Structural characterization was neither presented in this work.

Valizadeh *et al.* [93] also attempted to fabricate Co-Ag multilayers by current control of the magnetic and non-magnetic layers. They employed a less friendly electrolyte from an environmental point of view as they used cyanide to prepare the electrolyte. From this bath, they succeed in preparing Co-Ag (5nm)/Ag (5nm) multilayers, as the TEM studies revealed, with the magnetic layers containing only a few percent of Ag only. However, no magnetic and magnetotransport properties were measured.

Finally, Fedosyuk *et al.* [94] also reported on the preparation of Co-Ag multilayers by current control and from a bath containing $CoSO_4$ and $AgNO_3$. The compositional analysis revealed that silver incorporation into the cobalt layer amounted up to 15 at.%. The structural characterization indicated the presence of fcc for both cobalt and silver. The maximum GMR value measured in these multilayers was 0.7 % at room temperature in a magnetic field of 8 kOe. No specification of the individual layer thickness was given.

On the other hand, the literature in the GMR of Co-Ag electrodeposited nanowires is restricted to one paper [95]. They prepared Co-Ag heterogeneous alloy nanowires at a constant current density of 3.75 mA cm^{-2}. The maximum GMR value measured at room temperature in a magnetic field of 8 kOe was 0.2 %. Neither structural analysis nor chemical composition of the nanowires was reported.

Other two works [96,97] were related with the electrodeposition of Co-Ag granular nanowires, but no magnetoresistance measurements were reported. In both cases, nanowires were prepared by galvanostatic deposition at 1.5 mA cm^{-2}. The structural characterization revealed a solid solution in the as-deposited state, which disappeared after annealing the sample. Magnetization-applied magnetic field (*M-H*) loops indicated a great difference in the coercivity depending on the magnetic field-nanowire axis orientation (either parallel or perpendicular).

Finally, Valizadeh *et al.* [98] reported on the preparation of Co-Ag/Ag multilayered nanowires by pulse deposition. The chemical composition was $Co_{92}Ag_8$ and Co_0Ag_{100} for the magnetic and non-mangnetic layers, respectively. TEM analyses were necessary to reveal the multilayered structure of the nanowires. Again in this case, a great difference in the coercivity depending on the magnetic field-nanowire axis orientation was observed. No magnetotranport properties measurements were made.

The preparation of $Co_{Core}Ag_{Shell}$ nanoparticles was attempted in some cases. Different chemical methods have been employed, i.e. thermal decomposition and wet chemical methods combined with transmetallation reaction [99,100]. However, few are the works dealing with the preparation of these core-shell nanoparticles by means of the microemulsion method [101]. In all these works, the particles were deeply characterized but in some cases, the core-shell structure was not clearly justified. None of the works dealt with the measurement of the magnetoresistance. Just one work reported on the GMR properties of Co-Ag nanoparticles but not in the form of core-shell [71]. They reported GMR values of 3 % at 2 K in the as-prepared samples. This value increases up to 38 % at 2 K after annealing the sample at 600 K during 2 h.